

# Environmental

Science & Technology

AUGUST 1977

**Recovering  
metals from  
process industries  
wastewaters**

752

Designed for indoor or outdoor use, these precision instruments sample gases in ambient air . . . accurately

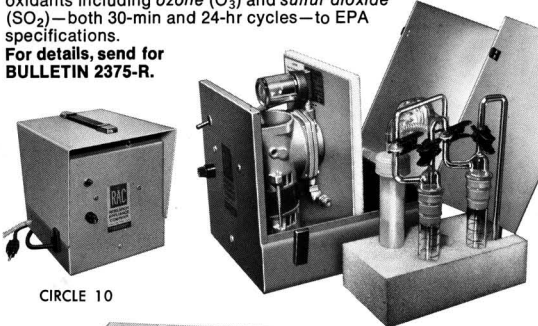
# RAC Gas Samplers

*RAC wet-chemical instruments can sample any gas for which accepted sampling/analyzing procedures have been developed. Each design offers specific features that adapt it to a range of sampling operations.*

## RAC AMBIENT AIR SAMPLER

This single-gas system uses modular, interchangeable bubbler trains to collect *acrolein* ( $C_3H_4O$ ) and *aliphatic aldehydes* (CHO) to HEW specifications as well as *nitrogen dioxide* ( $NO_2$ ), oxidants including *ozone* ( $O_3$ ) and *sulfur dioxide* ( $SO_2$ )—both 30-min and 24-hr cycles—to EPA specifications.

For details, send for BULLETIN 2375-R.



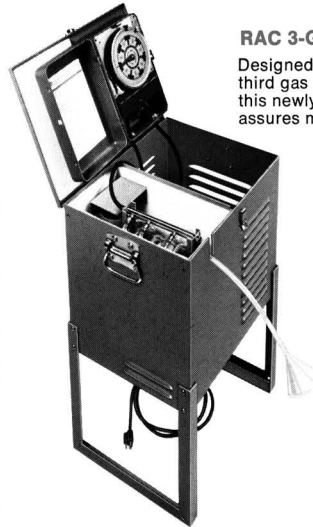
CIRCLE 10

## RAC 3-GAS SAMPLER

Designed to sample  $SO_2$ ,  $NO_2$  and a third gas (optional) simultaneously, this newly-developed instrument assures maximum accuracy for  $SO_2$  sampling at ambient temperatures ranging from  $-25$  to  $50^\circ C$ . It features a unique solid-state thermoelectric cooling-heating system (patent pending) that maintains the  $SO_2$  reagent between  $7$  and  $17^\circ C$ , thereby preventing the loss of sample that occurs when the ambient temperature reaches/exceeds  $20^\circ C$ .

For details, send for BULLETIN 2441.

CIRCLE 11

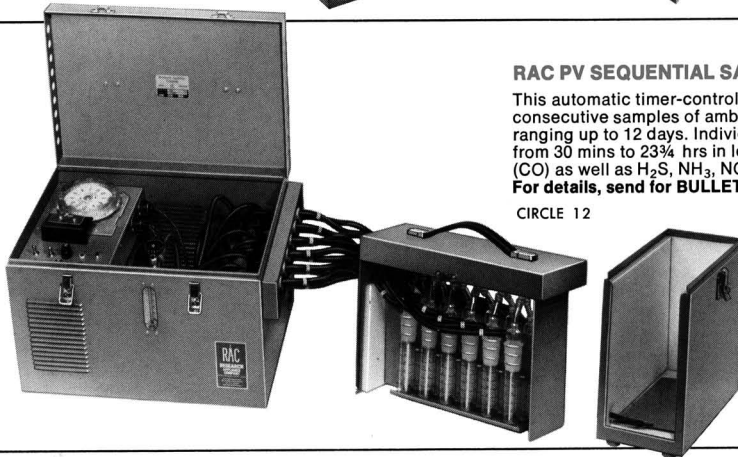


## RAC PV SEQUENTIAL SAMPLER

This automatic timer-controlled instrument collects 12 consecutive samples of ambient gases over time periods ranging up to 12 days. Individual sampling cycles can range from 30 mins to  $23\frac{3}{4}$  hrs in length. It samples *carbon monoxide* (CO) as well as  $H_2S$ ,  $NH_3$ ,  $NO_2$ ,  $SO_2$  and other gases.

For details, send for BULLETIN 2340-A.

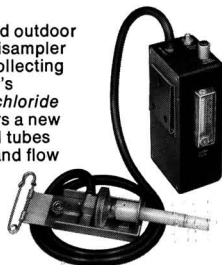
CIRCLE 12



## RAC PERSONAL SAMPLER

Suitable for underground, indoor and outdoor sampling, this battery-powered minisampler is NIOSH and MESA approved for collecting respirable particles from the wearer's breathing zone. For sampling *vinyl chloride* and other organic vapors, RAC offers a new sampling head that utilizes charcoal tubes and features an integral flowmeter and flow adjusting valve. This organic vapor accessory also can be used with other existing personal particulate or gas samplers. For details, send for BULLETIN 2392-A.

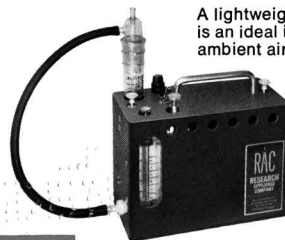
CIRCLE 13



## RAC MIDGET SAMPLER

A lightweight dual-purpose design, this is an ideal instrument for spot checking ambient air to comply with OSHA requirements. It can sample airborne particulate matter in addition to  $CHO$ ,  $H_2S$ ,  $NH_3$  and  $NO_2$ . An optional battery-powered model also is available. For details, send for BULLETIN 2312AB-R.

CIRCLE 14



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# Environmental Science & Technology

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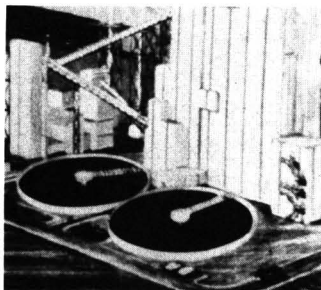
## CONTENTS

### PAT report

- 742 Aerial photos are used to show the cleanup of a eutrophic lake

### Outlook

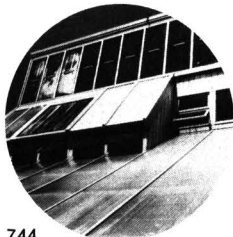
- 744 Soft technology: The Canadian sunhouse, the Ark, is a humane habitat
- 748 Water and wastewater treatment—highlights from Montreal ACS meeting
- 750 Coal conference: EPA takes a new look at cleaning before burning



750

### Features

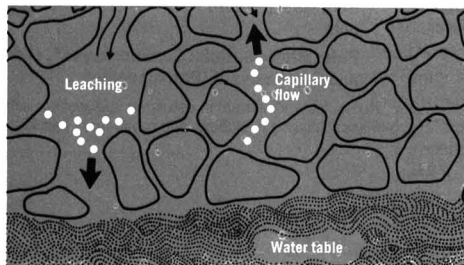
- 752 Recovering metals from wastewater—Corning Glass Works' Bhatia & Jump
- 756 Rating scheme for old and new pesticides—Jerome Weber, N.C. State University
- 762 Hazardous wastes are inventoried in Massachusetts—Mass. team of 6
- 767 Drinking water surveillance—U.S. Army Environmental Health Agency team



744

### Departments

- 737 Editorial
- 738 Letters
- 739 Currents
- 822 Industry trends
- 823 New products
- 824 New literature
- 825 Books
- 826 Meeting guide
- 828 Consulting services
- 830 Classified section



756

### Current research

- 735 Contents
- 773 Papers



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Volume 11, Number 8, August 1977 735

# CURRENT RESEARCH

## **Environmental trace metal contamination in Kellogg, Idaho, near a lead smelting complex** 773

**R. C. Ragaini\*, H. R. Ralston, and N. Roberts**

Soil, grasses, and ambient air aerosols are sampled in the vicinity of a Pb smelting complex in Kellogg, Idaho. Toxic elements are discussed.

## **Fractionator for size classification of aerosolized solid particulate matter** 781

**Andrew R. McFarland\*, Russell W. Bertch, Gerald L. Fisher, and Bruce A. Prentice**

A system is developed for collecting kilogram quantities of size-fractionated particulate matter from an air pollution emission source. The system can be used for biologic testing programs.

## **Reduction of aqueous free chlorine with granular activated carbon—pH and temperature effects** 785

**Makram T. Suidan\*, Vernon L. Snoeyink, and Roger A. Schmitz**

A mathematical model is used to analyze the effect of pH and temperature on the reaction between free chlorine and activated carbon in batch and packed bed reactors. Kinetic constants are determined.

## **Evaluation of particulate trace species in southwest desert atmosphere** 789

**J. L. Moyers\*, L. E. Ranweiler, S. B. Hopf, and N. E. Korte**

A particulate sampling program is established to characterize the chemical composition of atmospheric particulate constituents in the southern Arizona atmosphere.

## **Application of pattern recognition and factor analysis for characterization of atmospheric particulate composition in southwest desert atmosphere** 795

**Phillip D. Gaarenstroom, Sam P. Perone\*, and Jarvis L. Moyers**

The composition of atmospheric particulate matter collected in the greater Tucson, Ariz., area is examined by use of pattern recognition and factor analysis.

## **Modeling study of seasonal effect on air pollution at 60°N latitude** 801

**Jan W. Bottenheim, Silvia E. Braslavsky, and Otto P. Strausz\***

The effect of temperature and solar altitude variation on a photochemical air pollution system at 60°N latitude is studied with a computer model. The temporal behaviors of the major pollutants are discussed.

## **Stability constants of copper-organic chelates in aquatic samples** 809

**Mark S. Shuman\* and George P. Woodward, Jr.**

A procedure similar to an amperometric titration of a ligand with copper is used to determine the conditional formation constants of copper-organic chelates in fresh water samples.

## **Fractionation and concentration from water of volatiles and organics on high vacuum system: Examination of sanitary landfill leachate** 814

**Mohan Khare\* and Norman C. Dondero**

Sanitary landfill leachate and other waters are examined by a high vacuum system developed to isolate, fractionate, and concentrate trace components from aquatic environments.

## NOTES

## **Copper and other heavy metal contamination in sediments from New Bedford Harbor, Massachusetts: A preliminary note** 819

**Peter Stoffers, Colin Summerhayes\*, Ulrich Förstner, and Sambasiva R. Patchineelam**

Heavy metal dispersal in estuarine sediments on the coastal zone of Massachusetts is studied, and preliminary results are discussed.

\* To whom correspondence should be addressed.

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

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The adequacy of research programs conducted by the Environmental Protection Agency has been the subject of review by various groups, including the National Academy of Sciences and the House Subcommittee on the Environment and Atmosphere. The latter in particular found "... serious problems with the quality and management of EPA research programs in the past." Similar conclusions were reached by an independent review of EPA's 1976 Five-Year Research Plan conducted by the Office of Technology Assessment.

Congress has interpreted this criticism of a single agency as a general deficiency in our national commitment to long-term environmental research and has responded (H.R. 6379) with a proposal for a creation of a new National Center for Long-Term Environmental Research to be funded at \$50 million/annum. This unfortunate plan could seriously interfere with the development of sound environmental research.

What exactly are the problems? First, there is a serious lack of coordination among the current leading agencies; the National Institute for Environmental Health Sciences (HEW), the National Institute of Occupational Safety and Health (NIOSH), the National Center for Toxicological Research (FDA/HEW), Environmental Protection Agency, the Energy Research and Development Administration. The combined health-related research expenditures of these institutions currently exceed \$200 million. Each is competing for research personnel from the same talent pool, justifying expansion of its stake in environmental research, and none has emerged as a source of enlightenment for protecting the environmental heritage of future generations.

It could be argued that we need fewer national institutions, not more, as present management problems preclude the possibility that any incremental change will be successful. Second, the separation of personnel and facilities into short-term problem-solving units and longer-term basic-research units will lead to scientific sterility in both groups, even if the role ambiguities between competing agencies were to be clarified.

Innovation, utility, and scientific creditability do not automatically result from the artificial manipulation of scientists within their organizations. Congress should demand the delineation of objectives, require the coordination of efforts among existing agencies, and not add obstacles to the research delivery system.



# LETTERS

## California smog

Dear Sir: Dr. Pitts points out in a May feature article (*ES&T*, May 1977, p 456) that there is inadequate data for tighter controls on  $\text{NO}_x$  and low reactivity hydrocarbons, but appears to favor their imposition on the basis of speculative harmful effects even though the cost is extremely high. He justifies  $\text{NO}_x$  controls on the following bases:

- Downwind  $\text{O}_3$  may be increased by increased overall  $\text{NO}_x$  emissions.
- Nitrosamines are "suspected" carcinogens.
- Control of  $\text{NO}_x$  decreases  $\text{NO}_2$  levels.
- Reduction of  $\text{NO}_x$  lowers secondary nitrate aerosols, nitric acid and PAN.
- The only known source of ozone is the photolysis of  $\text{NO}_2$ .

There appears to be no clear-cut evidence that downwind ozone was increased by higher  $\text{NO}_x$  emissions. Such increases could be attributed to a combination of meteorology, limited and unreliable ozone data, and growth in reactive hydrocarbon (RHC) emissions in nearby Orange County.

As Dr. Pitts points out, there is no evidence for the presence of nitrosamines in the Los Angeles atmosphere or, if they were present, that they would contribute to human cancer. Also, it is questionable that if they did form, whether realistic tighter  $\text{NO}_x$  controls would decrease their level.

The statement that decreases in  $\text{NO}_x$  emissions would result in decreased  $\text{NO}_2$  must consider the trade off involved in the rapid reaction ( $\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2$ ). Ozone is 10–50 times as toxic as  $\text{NO}_2$  (*Federal Register*, Vol. 36, No. 105). The benefits derived from this reaction in the major population areas far outweigh the effects of  $\text{NO}_2$ . The toxicity of  $\text{NO}_2$  at current levels is extremely questionable. If reactive hydrocarbons are reduced by about 50% and present peak  $\text{NO}_x$  values applied (0.2–0.3 ppm), only a minor part of the NO would be oxidized in the basin below the inversion layer.

Also, ozone would be below present ambient standards according to Dr. Pitts' isopleths. This decrease in RHC should be achieved by measures now in place such as old car phaseout and evaporative controls. Increased downwind NO emissions from future growth in the eastern end of the basin would also decrease local ozone levels because of reaction with ozone. If  $\text{NO}_x$  is more tightly controlled to its practical limit (0.1 ppm), it would appear that a level of 0.15 ppm ozone would never be achieved.

Regarding secondary nitrogen products (aerosols, PAN, nitric acid), these do not form significantly until NO is depleted. For fixed HC level and radiation, NO depletion

time is proportional to initial NO level. A lower level of  $\text{NO}_x$  to its practical limit (0.1 ppm) would increase the time available for secondary reactions and, thereby, be expected to increase secondary products. Dr. Pitts presents no evidence to support his view that realistic stricter  $\text{NO}_x$  controls would produce lower levels of secondary nitrogen products.

The argument is made that the photolysis of  $\text{NO}_2$  is the only known source of ozone. While this may be true, it is a misleading statement. The photolysis generates NO, which rapidly reacts with ozone, so that there is negligible net effect in producing ozone, which is proportional to the radiation level and the ratio of  $\text{NO}_2/\text{NO}$ . NO emissions serve to decrease this ratio. In the absence of HC's this quasi-equilibrium gives a very low ozone level. SAPRC's chamber work with zero added  $\text{NO}_x$  and 0.6 ppm NMHC produced an ozone level of 0.16 ppm in 6 h, showing that if  $\text{NO}_2$  is required, only the amounts present in unpolluted atmospheres are necessary for ozone formation.

Certainly the reactivity of all organics is of concern and there is no doubt that low reactivity hydrocarbons make a minor contribution to NO oxidation and resultant ozone formation. However, Dr. Pitts appears to condone the current policy of regulatory agencies that regard all organics as equivalent on a weight basis, since they eventually will contribute to ozone formation somewhere.

**W. B. Innes**  
Upland, Calif. 91786

## California smog (cont.)

Dear Sir: The excerpts selected by Dr. Innes from the feature (*ES&T*, May 1977, p 456) in many cases do not reflect what I actually wrote, nor do they necessarily reflect what I really believe. For example, statements such as:

- "appears to favor their imposition on the basis of speculative harmful effects even though the cost is extremely high" and

- "However, Dr. Pitts appears to condone the current policy of regulatory agencies that regard all organics as equivalent on a weight basis, since they eventually will contribute to ozone formation somewhere," are straw men, contrary to the thrust of my article, and not worth discussing in this forum.

Turning to matters of science, Dr. Innes' statement that "There appears to be no clear cut evidence that downwind ozone was increased by higher  $\text{NO}_x$  emissions" is clearly contradicted by the vast amount of information presently available on simulated and real polluted atmospheres. With respect to southern California, Dr. John Trijonis et al. recently carried out a detailed analysis of air quality

and emission data and concluded that "the historical trends in ambient oxidant over the past decade represent, in effect, a test of an oxidant control strategy in which hydrocarbon emissions are reduced while increasing  $\text{NO}_x$  emissions, thus reducing the hydrocarbon to  $\text{NO}_x$  ratio. The net result has been a decrease in oxidant levels in western and central Los Angeles County and an increase in oxidant levels in the eastern South Coast Air Basin." Furthermore, as I noted, the complex nature of the chemical and physical transformations during transport of polluted air parcels and the associated "downwind  $\text{O}_3$  effect" are not unique to southern California.

Considering nitrosamines, my point clearly was that we need to know far more about the atmospheric reactions of their possible precursors,  $\text{NO}_x$  and amines. Dr. Innes has only to consult the recent EPA Star Series document "Scientific and Technical Assessment Report on Nitrosamines" to appreciate my concern and that of the scientific community.

As far as  $\text{NO}_2$  being the only known photochemical source of ozone, as well as a host of toxic nitrogenous compounds (e.g., PAN), Dr. Innes' arguments fail to take into account the well-established fact that severe smog episodes can last for days, providing ample time for complete photooxidation of HC and  $\text{NO}_x$ , if not in the central city areas, then certainly in downwind suburbs miles away. Thus, the air quality of someone (or something), somewhere, will be further degraded by increased  $\text{NO}_x$  emissions. Whether or not this is significant depends on the situation.

Space limitations preclude a detailed discussion of several other of Dr. Innes' arguments; I can only restate my belief that different strategies for  $\text{NO}_x$  and hydrocarbon control may be required for different basins. These will depend upon the present ambient levels of HC and  $\text{NO}_x$  in a given urban atmosphere, as well as, of course, on meteorological and topological conditions, projected growth, etc. Smog chamber isopleths provide one basis for assessing the relative merits of HC and  $\text{NO}_x$  controls in reducing ozone in the central city and downwind.

In conclusion, rather than relying on Dr. Innes' interpretation of my views, and of our SAPRC chamber data, I would encourage readers to consult our original technical articles as well as my testimony to legislative bodies and control agencies. As are all scientists, we will be pleased to furnish reprints!

**James N. Pitts, Jr.**  
Statewide Air Pollution Research Center  
University of California  
Riverside, Calif. 92521

# CURRENTS

## INTERNATIONAL

**A joint U.S./Canadian effort is studying pollution from non-point sources** and its effect on the water quality of the Great Lakes. The Pollution From Land Use Activities Reference Group was created in 1972 by the International Joint Commission. This group is intensely looking at urban areas, transportation corridors, mining, agriculture, recreational and forested areas, waste disposal areas, shoreline landfill activities and lakeshore and riverbank erosion. These studies should be able to answer the questions: Are the Great Lakes being polluted from land-use sources? What land use and other activities are contributing what pollutants? And how can these pollutants be controlled and at what cost? The reference group's final report is scheduled for publication July 1978.

**\$5.7 million will be spent over the next year on renewable energy** and conservation projects by the Ministry of Energy of Ontario (Canada). Of that sum, \$600 000 will go for "renewables", with emphasis on solar heating and water heaters, improved heat pumps, monitoring of alternate energy resource developments, and energy from waste. Other ministries/agencies and Ontario Hydro will contribute an additional \$300 000 for "renewables".

## WASHINGTON

**EPA scientists report that sulfuric acid emissions from catalyst-equipped vehicles** are lower than predicted last year in the first annual report of the agency's catalyst research program. Further, EPA reports that these emissions appear to decrease with increasing vehicle mileage, while controls for hydrocarbons and carbon monoxide do not appear to deteriorate with increased mileage. The three-way catalyst appears to present no major sulfuric acid emissions problem. In a cooperative EPA/General Motors sulfate dispersion experiment on a Los Angeles freeway, sulfate aerosol size was found to be in the range of 0.01-0.1  $\mu\text{g}$  in diameter, much smaller than size range (0.3  $\mu\text{g}$  in diameter) focused on in previous studies. This size disparity "may significantly affect the direction of EPA's health effects research on sulfates," the EPA report stated.

**NRC's Safe Drinking Water Committee's** 18-month study concluded that hard evidence doesn't yet exist to link current levels of compounds found in drinking water with cancer. But the committee cautioned that the uncertainties about their toxic and carcinogenic effects warranted a "cautious approach." This study, mandated under the Safe Drinking Water Act of 1974, was delivered to Congress and the EPA. Chaired by Gerald A. Rohlich, the committee was able to identify 22 organic compounds in drinking water that are known or suspected carcinogens; risk assessments were calculated for these.



*NRC committee chairman Rohlich*

Recognizing the risks associated with chlorine use, the committee nevertheless stated that "much more research is required before [an alternative] can be recommended as a sole substitute for chlorine in water treatment."

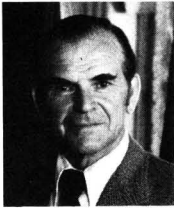
**Under the Clean Air Act, the EPA has the authority to list violating facilities,** which then cannot receive federal contracts. The U.S. District Court for the Northern District of Illinois ruled in *U.S. v. Interlake, Inc.* that the EPA is authorized under Section 306(c) of the Clean Air Act and under Section 1 of Executive Order 11738 to establish regulations for the listing of facilities violating air laws. The EPA has listed benzene as a hazardous air pollutant under Section 112 of the Clean Air Act. The agency cited studies by the NAS and NIOSH that linked exposure to benzene to leukemia. OSHA had issued an emergency standard that lowered worker exposure to 1 ppm over an 8-h day. The Fifth Circuit Court of Appeals stayed the emergency standard. The case has now been transferred to the U.S. Court of Appeals for the District of Columbia.

**OSHA has a draft document for regulating carcinogens** in the works that offers an alternative approach to the Delaney clause. The National Advisory Committee on Occupational Safety and Health (NACOSH) recommended that the draft be published in the *Federal Register* for the purpose of information gathering, but not for rulemaking at this time. NACOSH also listed five issues that need elaboration, such as the carcinogenicity of impurities and mixtures, and other testing routes besides animal testing. The notice of "Regulation of Certain Toxic Materials" will probably be published in the *Federal Register* in September. Nevertheless, word knowledge of its existence has spread by word of mouth and interested parties are submitting comments that will be incorporated in a reworked draft.

**The Dept. of the Interior is conducting an inventory of wetlands in the U.S.,** its territories and possessions. This is the first complete census of these lands to be performed. The National Wetlands Inventory program within the Office of Biological Services of the U.S. Fish and Wildlife Service will develop a data base in map and computer form. Data will be collected, interpreted, stored and reproduced, and will be made available to agencies responsible for the management of these lands. Initially 17 continental states and Alaska will be surveyed using high-altitude color IR aerial photography. The inventory will be completed by 1979. Besides their biological importance, two studies sponsored by the NAS indicate that wetlands can be substituted for conventional tertiary wastewater treatment.

## STATES

**N.D. Governor Arthur Link signed into law safe drinking water legislation** that meets primacy provisions under the federal Safe Drinking Water Act. The state law authorizes the state Dept. of Health to establish regulations to enforce and administer the federal act. Once developed, the regulations will be submitted to EPA Region VIII for approval. Among its provisions, the state law requires that the health department maintain an inventory of public water systems, set maximum contaminant levels and monitor groundwater. Procedures for certifying



N.D. governor Link

laboratories for water sampling analysis are also to be established by the health department. Colorado is also gearing up to meet the new regulations under the Safe Drinking Water Act that went into effect last month; the state is now revising its regulations so as to be able to assume enforcement of the federal program.

**The Pa. Dept. of Environmental Resources issued air quality control permits to Volkswagen Manufacturing Corp. of America for construction of the company's new car assembly plant at New Stanton (Westmoreland County), Pa.** The permits are for those assembling and painting operations that emit hydrocarbons to the air. To assure that total hydrocarbon levels do not rise, the Pa. Dept. of Transportation will begin using a different road-paving material on road surfacing work in southwestern Pa. This change in procedure from a petroleum-based product to a water-based product is estimated to reduce hydrocarbon emissions by 1025 tpy in that part of the state. Economic and energy savings are also envisioned. The U.S. EPA approved construction of this plant in this non-attainment area under the agency's emission offset policy.

**Milwaukee, Wis., now has a \$18 million, 400 000-tpy waste recycling center.** The center was built and will be operated by American Can's Americology Division. Milwaukee will pay Americology \$10/t to separate and recycle its solid waste, now estimated at 250 000 tpy. Ninety percent of the solid waste is expected to be recycled. As much as 65% of the recycled materials are combustibles that can be used by the Wisconsin Electric Power Co. as supplemental fuel for its coal-fired boilers.

**The Jackson Hole (Wyoming) Airport in Grand Teton National Park should remain in use** concludes a study conducted by consulting engineers for the Jackson Hole Airport Board. Not only did the report recommend continued use of the only airport to be located in a national park, but it recommended runway and taxiway extension of 1700 ft to the north at an estimated cost of \$1-2 million. The consulting engineers also made

recommendations to reduce noise intrusions that included the installation of an air traffic control tower, the establishment of a special flight restricted area below 3000 AGL over the park and a requirement that all aircraft meet federal noise regulations.

**Fugitive asbestos emissions from an inactive refuse pile in Ambler, Pa.,** appear to be insignificant and infrequent according to the findings of a recent monitoring study performed by a contractor for the Pa. Dept. of Environmental Resources. The results of this study are comparable to findings of a U.S. EPA survey conducted in 1974, according to the consultants. The study design consisted of 13 air monitoring stations from which 123 air samples were collected last November. Of these 123 samples, 73 were analyzed and only 4 were found to have detectable levels of asbestos; only 2 of the 4 could be traced to the inactive refuse pile. The study concludes that "the lack of measurable asbestos levels in the vicinity of the pile may indicate that the pile is sufficiently stabilized so that fugitive emissions are negligible or infrequent."

**The Pitkin (Aspen, Colo.) Board of County Commissioners adopted a new air quality resolution** that incorporates state air quality standards, and creates an advisory/caution/alert procedure to be followed during high pollution episodes. The resolution also provides for fines of up to \$300 and sets up a 5-member variance board empowered to grant variances under certain conditions. To restrict automobile usage during air pollution alerts, the resolution calls for the establishment of auto-free areas and intercept parking lots, and for the imposition of parking fees. Fireplaces per dwelling are limited by the resolution to one; and one per lobby in hotels, motels, and inns.

## MONITORING

**An ambient air ozone analyzer,** the only one designated to be equivalent from 0-1 ppm, is also the only one that operates by ultraviolet absorption. Made by Dasibi Environmental Corp. (Glendale, Calif.), and known as Model 1003-AH, it has been granted equivalency by the U.S. EPA. Its equivalency designation appears in the *Federal Register*, June 3, 1977, p 28571.

**A more "painless" means to measure many sewage variables,** such as pH, toxicity, organics, and dissolved oxygen, uses tubular electrodes, according to AG Brown, Boveri & Cie (Baden, Switzerland). Sewage flows through them without hindrance; less

dirt is deposited; fouling is less significant; and easy cleaning without removing them becomes possible. Reliability is high, according to the company.

## TECHNOLOGY

**The atomic age comes to sewage treatment:** sewage sludge is disinfected by high-energy electrons. John Trump, head of the High Voltage Research Laboratory of Mass. Inst. of Technology (MIT), said that the high-energy electrons destroy pathogens in the sludge. That, in turn, would allow land disposal of the material, which is significant, since river and ocean dumping must be phased out. Trump also said that the electron acceleration approach, tried on a pilot basis at Deer Island, Mass., Boston's wastewater plant site, is "energy-sparing" and has economic merit. The accelerator for the 100 000-gpd sludge facility was leased to MIT by High Voltage Engineering Corp. (Burlington, Mass.).

**Recovery of hydrocarbons from shale gets a "boost" from a hydrotreating process** developed by the Institute of Gas Technology (IGT, Chicago, Ill.). Not only does the IGT process increase Colorado shale yield by up to 35% over "conventional" means, "but it can also be tailored to yield mostly oil or gas, as desired." IGT says that the process also opens Eastern shales—previously considered unsuitable—to exploitation. The institute found that this Eastern shale had up to 2.5 times more kerogen (hydrocarbon source) than original assays indicated, and that by hydrotreating, this kerogen can be benefited as well as Colorado kerogens. Eastern shale reserves alone could be as great as 1 trillion bbl, according to IGT, with far less of a solid waste problem.

**Water cleanup on wheels: to test and optimize technology, mobile vans** will study textile plant effluents from Maine to Georgia over the next 2 years. Engineers will determine the test technology needed to meet stringent 1983 water quality guidelines. The work is being done under a cooperative program between EPA, textile industry trade associations, and companies. Engineering-Science, Inc. is the contractor for the first phase. For the second phase, Dynamic Associates, Inc. (Cambridge, Mass.) will compute and project the cost for the entire industry to meet the 1983 "best available" guidelines.

**One way to remove almost all of the inorganic sulfur from coal** could be by "high gradient magnetic separation", developed at a unit of Mass. Inst. of



Technology, under a National Science Foundation grant. Basically, crushed coal is dissolved in an organic solvent, and heated to about 800 °F in the presence of hydrogen (H<sub>2</sub>). The H<sub>2</sub> removes about half of the sulfur, including a small amount of organic S. Then, a magnetic field generated by a water-cooled solenoid surrounding a canister of steel wool removes the pyritic S, which has been converted to more magnetically susceptible pyrrhotite. Also, about 40% of the ash-forming material is removed.

**Modern, cost-effective technology is easily applied to wastewater collection system design**, according to a patent held by Sterling Smith, an engineer from Hyattsville, Md. Groundwater infiltration and line surging are controlled; diurnal peak-load cycles are absorbed; and 24-h transport capacity of the pipes is increased. "Steady-state" operation of the treatment plant is assured by the functioning of strategically placed flow-management stations that constrict or accelerate flow in response to control elements. Full use of pipe volume provides a slight hydraulic imbalance that stops groundwater intrusion. "Steady-state" flow ensures economical plant operation. The design can be applied to retrofitting existing plants, as well as to new construction.

**Paper pulp is made with few or no chemicals when mechanical pulping is done**; with heat and steam pressure in the system, the technique is known as Thermo-Mechanical Pulping (TMP). According to C-E Bauer, developer of TMP, the technique provides about twice as much fiber yield as does a chemical system. Basically, TMP is a modification of the old "stone-ground" pulp method by which wood chips were fed between two oppositely rotating grooved metal discs. With the addition of heat and steam pressure, and subsequent improvements, TMP is especially adaptable to newsprint,

specialty stock, and paperboard making, although other papers are made equally well. There are 22 TMP systems on stream or planned, worldwide.

## INDUSTRY

### Environmental control has proved very lucrative for Titan Group, Inc.

(Paramus, N.J.), especially with regard to water, wastewater, and soil treatment plants. About \$183 million worth of construction is underway, and bidding and negotiation for construction or operation of solid waste/resource recovery facilities are proceeding. Titan has begun work on a huge, new \$23.5 million wastewater treatment plant at Lowell, Mass., for example, and that is one of 13 environmental projects now in progress in 7 states. The company's 1976 gross revenue was over \$181 million, with net income of \$2.4 million, or \$0.46/share. Environmental control comprised 23% of Titan's total revenues.

### The largest civil fine ever assessed in a water pollution case—\$4 million—

was imposed on U.S. Steel for dumping wastes into Lake Michigan and the Grand Calumet River at Gary, Ind. "Big Steel" will also pay a \$250 000 fine to settle a criminal contempt case arising from alleged Clean Air Act violations. Also, the company will have up to August 1, 1980 to complete a \$70 million water pollution control plant designed to recycle 65 mgd of wastewater. The fine levy order also affirmed a 1974 EPA order mandating reductions of 60% in ammonia; 90% in phenol; and 95% in cyanide. Fine proceeds will be shared by the federal government, Indiana's Environmental Management Fund, the University of Michigan, and U.S. Steel's own environmental R&D establishment.

**Borg-Warner announced the formation of Kemron Environmental Services** (Parkersburg, W. Va.) at the Air



*Kemron general manager Lyles*

Pollution Control Association's June meeting. George Lyles is general manager. Among other services, Kemron will sell to industry a continuous, on-site computerized air quality monitoring service called "Kempueter". A single Kempueter, a field computer, can be connected to several analyzers within the range of one field installation house. The computer collects, stores and preprocesses data that it delivers via voice-quality telephone lines to a central computer located in Baton Rouge, La. The cost of a Kempueter is estimated at \$1000–2000/month/installation; a large plant may have more than one installation.

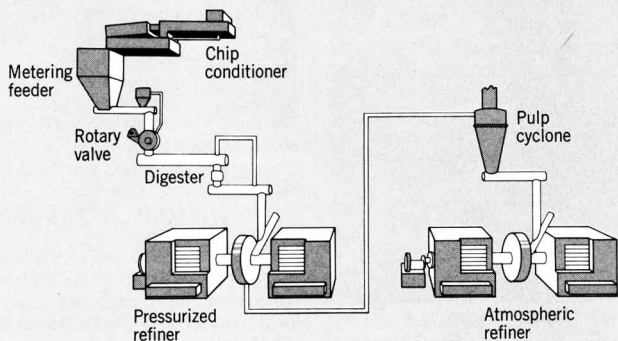
### UOP Inc., has dedicated the world's largest reverse osmosis (RO) water treatment facility to process 5 mgd.

The whole plant, of which the RO facility is a part, will produce 20 mgd of blended water to inject into ground water in the Orange County Water District (Calif.), to prevent seawater intrusion. The plant is known as Water Factory 21. R. E. Seaton, vice president/general manager of UOP's Fluid Systems Division, said that RO is an energy-efficient process, needing only 7.5 kWh/1000 gal, while 10 kWh/1000 gal were needed to pump northern California water to Orange County. He noted that by this year's end, 200 mgd of RO capacity will be purchased.

### Costs of further reductions of SO<sub>2</sub> emissions and water effluent quality improvement at refineries were

estimated in a recent study (Report No. 5/77) by Stichting CONCAWE (The Hague, Holland), an industrial/environmental group. To recover 95% of S in feed, an oil refinery must plan on a capital investment of \$500 000–800 000/t/h of SO<sub>2</sub> reduction, and operating costs of \$13–29/t SO<sub>2</sub> removed. For 99% SO<sub>2</sub> recovery, capital costs are \$9.5–12.7 million, and operating costs, \$530–590, in 1975 dollar values. A \$1.8–2.5 million investment is needed to cut oil content in effluent to less than 50 ppm. To reach a 50% improvement over that, the investment rises by 14–20%; for a 90% improvement, 120–128%, the latter with a 227–250% operating cost jump.

## Typical TMP system



# The aerial photo— eutrophication link

Cornell University scientists show that a lake is revitalized after wastewater effluent treatment

Since 1968, scientists have been collecting data at Canadarago Lake in central New York State for what may prove to be a classic study of the revitalization of a eutrophic body of water. The lake is relatively small (6 km by 1.5 km, with depths of 13.4 m), and isolated from pollutants except for effluent from a sewage treatment plant at nearby Richfield Springs (pop. 1600).

In January 1973, a new tertiary sewage treatment plant for the village went into operation as a Federal and New York State demonstration project. It replaced a plant built in the late 1800s. The old plant, virtually inoperable in its final years, had been discharging almost raw sewage into the lake. This caused a high phosphorus enrichment in the lake with consequent growth of algae.

The new treatment plant has reduced the lake's phosphorus input by about 40%. With a definite discharge cutoff date, the lake provided an ideal site to study the before-and-after effects of the cleanup on both plant and fish life. It was theorized that a change in sewage treatment would cause a change in the lake's ecology, and this seems to be the case.

Although many components of the lake's ecosystem have been monitored since 1968, little emphasis had been placed on recording changes in aquatic vegetation accompanying the decrease in nutrient loading. The lake had been highly productive of algae, which reduced light penetration through the water and apparently inhibited the growth of rooted plants.

The question was whether the lower nutrient level would reduce the algae population, thus encouraging the growth of higher forms of vegetation. Given that aerial photographs of the lake had been taken both before and after the treatment plant start-up, a project to develop

evaluative techniques was undertaken in the Remote Sensing Program of the School of Civil and Environmental Engineering, Cornell University.

## The evidence

"Aerial photos have been used in the past to map weed beds," says Brian L. Markham who, with botanist Ann E. Russell, conducted the analysis under the direction of Dr. Warren R. Philipson and Prof. Ta Liang. "Our objective was to demonstrate that aquatic vegetation could be identified reliably from aerial photographs with little or no concurrent ground data. This was also part of a larger project, now under way, to assess what changes have taken place in the lake."

Markham's study was begun under the school's grant from the National Aeronautics and Space Administration, and continued under a grant from the United States Department of the Interior, Office of Water Research and Technology. Photographs were provided by Eastman Kodak Company, the U.S. Environmental Protection Agency, NASA, and the State

University of New York College of Environmental Science and Forestry.

Aerial photographs of the lake had been taken in 1968, 1969, 1973, and 1974. Fortunately, most of the photography had been done both with Kodak Aerochrome MS film 2448 (Estar base) and with Kodak Aerochrome infrared film 2443 (Estar base) to provide a comparison between normal color and infrared color images.

## The interpretation

By studying the aerial images at a scale of 1:6000 with a zoom stereoscope, Markham was able to compare weed beds and note changes over a 6-y period. From these data, he developed three predictive classifications to be used in field studies during last summer. It was predicted that areas having vegetation during the 6-y period and those in which vegetation had developed between 1968 and 1974 would have vegetation at the time of the field survey. Areas revealing no vegetation over the period were expected to still be barren. "We found excellent agreement between the predictions and the ground-truth study," Markham states.

The other part of the study was aimed at identifying major types of vegetation from the photographs. Viewing the photographs, Markham found that he could identify five types of floating or emergent vegetation through location, shape, color, and texture of the patch, and its height above the water surface. Working with the stereoscope, Markham examined plant heights as low as 0.5 meters.

Using prints of the 1974 photography for reference, Markham and Russell identified and mapped the various stands of weeds during the summer's field study. Concurrently, new photography was flown in July and August, and later correlated with field identifications.



**Cornell's Markham**

*"differentiating between green plants"*

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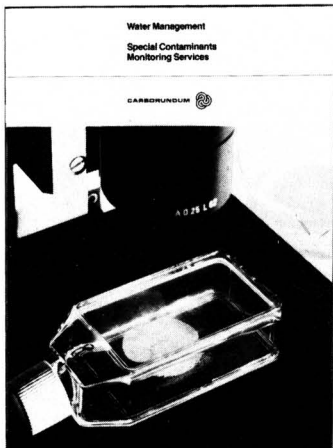
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## What the lake surveillance project showed

- Different species of floating and emergent vegetation can be identified from aerial photographs with little or no ground data. Given sufficient water transparency, submersed vegetation can be recognized and differentiated from other bottom features, such as rocks. However, the different submersed types were generally not separable in the aerial photography.

- Smaller format photography is adequate for species identification, but the coverage afforded by larger format photography is preferable for mapping. Film used for earlier photography was 9½ inches wide, while the 1976 photography was done with 70 mm film.

- Larger scale photography is preferable for detailed vegetation surveys. Generally, scales larger than 1:10 000 are recommended.

Overexposure of the film by about one-half stop aided water penetration. Markham reports that he also saw some stereo effect underwater. He could thus differentiate between low-lying bottom plants and those growing up from the bottom to near the surface. All told, Markham characterized five types of floating (lillies) or emergent vegetation (pickerelweed, bulrush, burreed, and cattail), and five species of submergent vegetation (water milfoil, mud plantain, elodea, curly-leaved pondweed, and muskgrasses).

The August 1976 photographs also were analyzed densitometrically to determine whether spectral characterization would aid in identification of emergent and floating species. "We found that, for our purposes, densitometric analysis did not add to the information we could extract visually with a stereoscope," Markham comments. "We did not attempt to characterize the submergent species in this manner because of the complicating effects of the water. In general, the tones of the submergent vegetation seemed to vary more with the water depth than with the vegetative type.

"We saw changes in the lake over the period of the study," Markham says, "and the major changes involved the submergent vegetation. The changes may have occurred because of the change in water transparency, but we don't know for certain. So, we have the effect but not the cause.

"What we have done is to develop a relatively simple, inexpensive way to assess changes of this sort through aerial photography," he concludes. "Historically, this is important. If past photography of a body of water exists, we can reach back in time and gauge years of change in the short time it takes to analyze the photos."

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CIRCLE 2 ON READER SERVICE CARD

Spry Point, Prince Edward Island. In the midst of this remote Canadian community of neat 100-acre farms, facing the sea, sits a unique structure. From one facade it looks like nothing more than a contemporary dwelling, but from its other face it appears to be an overgrown greenhouse with an array of solar collectors. Its designers call it a bioshelter and have dubbed it the Ark. Noah would not object. As the name implies, the Ark is a lifeboat, a miniature world, designed to sustain a family against the ravages of Nature.

The Ark, however, does more than coexist with Nature; insinuating itself into the whole, it actively becomes a part of Nature. For instance, Prince Edward Island (PEI), Canada's smallest province, is exposed to an extreme coastal climate and is buffeted by strong, steady winds. The power of these winds will be captured by one of the Ark's two windmills, which hydraulically will convert this natural force to electricity for use in the Ark.

By actively becoming a part of the whole, the Ark may offer communities in northern climates an option for the future. With the specter of dwindling food and fossil fuels forecasting a grim future, the Ark's basic concept—structured as it is on small, low energy, low-capital cost, decentralized ("soft") technologies—offers an alternative to the centralized energy- and capital-intensive technologies now driving industrialized societies.

#### A concept aborning

The Ark, warmed by the sun and powered by the wind, consists of a greenhouse, aquaculture ponds, living quarters and a research laboratory, all harmoniously integrated into a unique "ecosystem" whose basic architecture is solar. This integration feature makes symbiotic relationships possible; sub-components such as food culture and nourishment, energy production and use, shelter, waste treatment, and water and land use then become reinforcing functions of a self-sustaining whole.

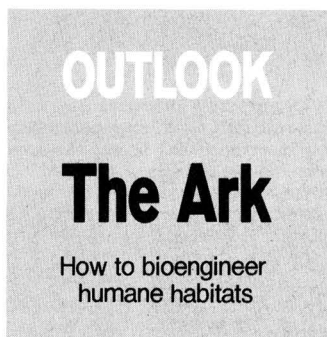
This wholistic design was the concept of future-looking scientists of the New Alchemy Institute (Falmouth, Mass.). This institute, an independent, nonprofit organization, was founded in 1969 by John Todd, its present director, William O. McLarney and Robert Angevine; there are now two additional centers, one on PEI and another in Costa Rica.

Initially established to develop methods of protein production that used indigenous food chains and renewable sources of energy—suitable for developing countries—the Institute by 1972-3 had set up several small food-producing systems that were self-sustaining. As the next natural step, the new alchemists decided to upgrade the size of these biological systems and integrate them with housing and power generation—an evolutionary step that produced the Ark.

Unable to obtain funds from the U.S.

government, and hearing of the formation of the Advanced Concepts Center within Environment Canada, the Institute's Canadian center sought funding from the Canadian government. A proposal was submitted in 1974, approved and funded by June 1975, and construction began in the fall of 1975. On September 21, 1976, Prime Minister Pierre E. Trudeau formally dedicated the Ark.

The cost of construction, from 1975 through March 1977, totaled \$354 000. These monies were federally funded from the Advanced Concepts Center within the Department of Fisheries and the Environment. The provincial government (PEI), under a 21-year leasing agreement, "donated" the land on which the Ark sits, evaluated at approximately \$80 000, and provided access roads and snow-clearing services to the project.



Under a joint federal/provincial agreement, the Department of Energy, Mines and Resources and PEI will supply matching funds totaling \$140 000/y for the next three years. This money will support on-going research at the Ark directed, for instance, to the optimization of food production. In one experiment, fish raising is being coupled to leafy crop hydroponics on the pond surfaces.

The full significance of the Canadian support becomes evident when it is realized that this project is the first attempt in northern climates to assembly within a single structure the diverse elements—energy, heat, food-growing capacity—that sustain humans at the household level, and to do so in an environmentally acceptable and renewable fashion. But the Ark concept goes one step further, beyond mere self-sustenance. After considerably more research, the Ark could develop into a small economic unit that could pay for itself through the sale of excess produce and power.

Food production comes from the intensive aquaculture of food fishes—Tilapia, salmonids, mirror carp and white amur—and the greenhouse culture of vegetables, fruits and rice. Heat for the fish ponds and greenhouse comes from the sun, with primary storage in the fish ponds. Additional heat to the greenhouse is provided by an electricity-generating

windmill designed by Institute scientists and contractors, and a water-pumping windmill that circulates warmed water throughout. The residential area, hovering above the ponds and greenhouse, receives some of its heat from these solar-heated food-producing areas.

#### "Spaceship" food production

The new alchemists term the food-producing areas of the Ark an early experiment in "spaceship" or intensive closed-system aqua- and agriculture. These biological areas are small, interconnected ecosystems that "assist and regulate" each other. The components of these ecosystems are ponds, fish, microorganisms, soils, compost, plants, and soil animals and insects that, through recycling, provide nutrients and disease (integrated pest) control.

Through continued experimentation it is expected that productivity will be optimized, but not at the expense of self-regulation.

The fish ponds were designed to culture fish and to function simultaneously as low-temperature solar-powered "furnaces" that can radiate heat to the greenhouse and adjacent laboratory and residential areas when temperatures fall. But, in addition to the integration of food production and heating, the ponds are also a source of irrigation and fertilization for the plants growing within the greenhouse.

The aquaculture facility consists of 40 light-transmitting fiberglass (sheets imported from the Kalwall Co., Manchester, N.H.) cylindrical solar-algae ponds. In this innovative closed system, biohardware—sunlight and microorganisms—substitute for the heavily fertilized and fed, highly engineered, fuel-consuming elements (aeration and filtration, for example) usually found in closed fish-culture systems.

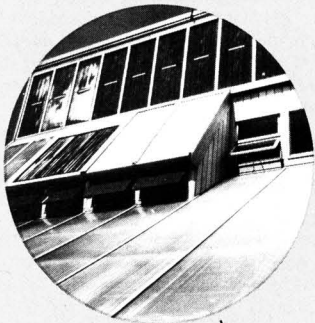
The ponds' translucent walls collect almost all available sunlight, which stimulates dense blooms of green algae. The algae act as effective solar collectors, provide the basic feedstock for herbivorous fish and zooplankton, purify the water by feeding directly on toxic fish wastes, and produce oxygen while consuming carbon dioxide.

Initial yields in a prototype system have been high (have out-yielded the South China polyculture, the standard against which fresh-water cultures are compared), and this closed system has been rapidly adopted by fresh and marine aquaculturists throughout North America. PEI's Department of Fisheries, for instance, has used the solar-algae ponds to culture oyster feeds, with a resulting nine-fold increase in feedstock production.

#### Architectural layout

Although the Ark has the potential for becoming a year-round food-producing

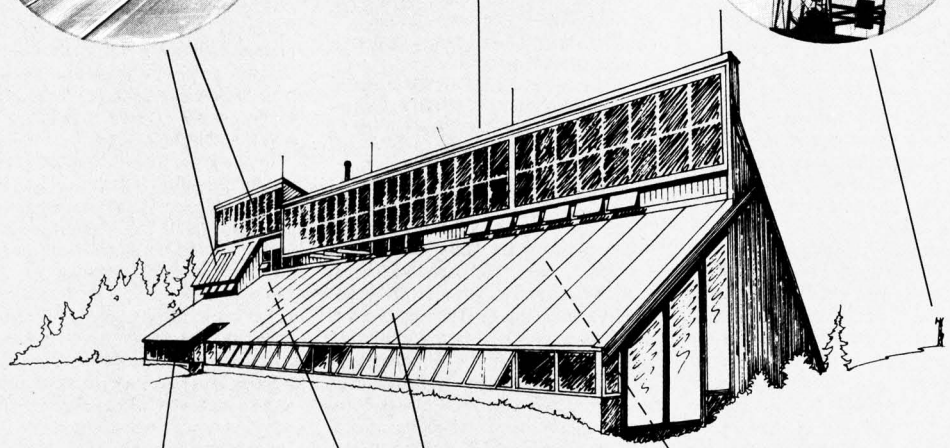
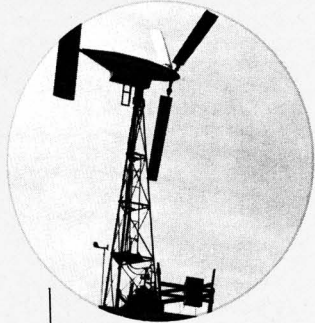
**Solar collectors.** Three flat plate types (Sunworks, Solatherm, Hoflar) are used. The heating system is all Sunworks' collectors installed vertically; sloped collectors heat the domestic hot water tanks under the living room floor



**North face.** Despite its resemblance to a modern dwelling, this windward face contains no windows except for the unheated entranceway



**Windmill.** This wind-driven power plant, 1000 ft north of the Ark, hydraulically transmits power from the blades to a ground-level electric generating plant



**South facade.** This face is entirely devoted to sun collection—passively through windows and greenhouse roof, actively in collectors



**Kitchen garden.** One level below the residential area, but opened to it, is the domestic food-producing area



**Residential area.** A view of the living room shows the domestic auxiliary heating system—the wood-burning stove



**Solar-algae ponds.** Eventually 40 light-transmitting fiberglass cylindrical tanks will constitute the aquaculture facility. Only fresh water fish are presently being cultured, but experiments are being designed to culture marine species

system, from its north face it resembles a modern home. But appearances are deceptive.

Unlike a modern dwelling, the Ark uses primary, renewable energy sources: the sun and wind. The windward, north facade contains few windows, while the south face is entirely devoted to solar collection—passively through windows and the greenhouse roof and actively via 42 solar collectors. This conservative design, plus tight construction and extra layers of insulation, allows the bioshelter to store heat at various temperatures in a variety of ways.

Still another dissimilarity: the Ark treats and uses its own wastes. Instead of flushing away the wastes to a sewage system, the bioshelter decomposes human, fish and agricultural wastes microbially. By using the Swedish Clivus Multrum dry toilet-composting system, organic wastes become fertilizer for produce growing.

The bioshelter is designed to conserve and efficiently use trapped solar heat. For example, the greenhouse, on the eastern end of the structure, comprises the largest area of the Ark. At this end, fish culture, tree propagation, and vegetable and fruit produce research also take place. Sunlight is collected by the acrylic glazing of the greenhouse.

The resultant heat is drawn from the greenhouse gable and forced through the rock storage area (90 m<sup>2</sup>) below the greenhouse. Heat absorbed by the rocks by day is passively released to the greenhouse during the cool evening hours. However, a forced air/hot rock circulation system can be used to augment the passive heating system. Heat is also stored in the solar-algae ponds and in the deep bed soils.

On the western end of the shelter are the living quarters and a domestic food-producing area. This section is warmed during the day by heat trapped by the domestic greenhouse, and in the evening or during cold or overcast days by a fan coil hot water system connected to solar-heated [Sunworks (Guilford, Conn.) collectors] water storage tanks. Hot water drawn from these storage tanks is passed through a fan coil, which heats the air in the duct. Hot air is then distributed throughout the building, including the greenhouse.

Auxiliary heating to the residential section can be provided by the combination wood-burning stove/fireplace. But, by placing the domestic garden under the residential area, a heating bonus was achieved. Moisture from this "kitchen garden" rises to the living quarters and permits the residents to be comfortable at cooler temperatures.

Control systems for both heating the water storage tanks and for distributing and circulating heat throughout the shelter are complex and, in some cases, components have been especially designed

for the Ark. Controls are both manual and automatic.

### A glowing performance

Despite the fact that the Ark's solar heating system was not completed by the September 21, 1976, opening date and complete heating characteristics cannot be documented for 1976, the shelter's early performance was more than satisfactory. With outdoor temperatures often as much as 35 °C cooler, the biological environments within the Ark remained relatively stable.

Except for solar heating controls, the greenhouse became operational by mid-October, just as Spry Point was hit by severe winter weather. With essentially no supplemental source of heat, the greenhouse performed, according to John Todd, "beyond all expectations."

Air temperatures in the lower plant growing zones were usually above 10 °C (50 °F). The forced air/hot rock storage heating system maintained air temperatures below 25 °C (77 °F). Soil temperatures stabilized at 12 °C (53.5 °F), and the solar-algae ponds remained at 21 °C (70 °F) until early December.

### Capturing the winds

The Ark will be powered by two windmill systems. One, a water-pumping unit, will ensure that heat exchange, water purification and filtration occur in the fish culture ponds. The second, a wind-driven power plant, will catch the abundant island winds (frequently 15–25 mph) and, through special design, will hydraulically transmit power from the blades to the electric generating plant on the ground.

A prototype of this wind machine—HYDROWIND—produces 7.5 kW (10 hp) of electricity in 25 mph winds. Four such mills will provide more than enough power for the Ark and the excess could make the bioshelter a net exporter of energy to the island.

In fact, as an alternative energy strategy for PEI, the new alchemists envision larger windmills of this type coupled to the island's electricity grid that could initially augment the fossil fuel plant. Later, when enough windmills are on-line, the power plant could act as a storage site for excess wind-generated electricity.

In the Ark, wind-derived electricity is needed to:

- operate the control elements of the solar heating systems
- provide lighting for the residential portion as well as ancillary lighting in the greenhouse
- operate a computer and sensors for monitoring the performance of the Ark
- drive water exchangers and heat pumps
- operate the instruments used in research experiments. At present, because HYDROWIND is still under development, the Ark receives most of its electricity

from the island's grid system, although HYDROWIND supplies power intermittently.

The bioshelter is monitored for energy dynamics and climatological and biological processes. Data from more than 30 sensors are recorded in analog form onto recorders. Later this year, however, a computer-based system for modeling and simulations is to be installed. Computer models of the Ark's "dynamic system of interacting components" will be used to improve on the design of bioshelters, to make them more applicable to environments that differ from PEI.

### Criticism and accolades

The bioshelter, comprised as it is of engineered interacting ecosystems, is a complex "organism." Its very complexity has fostered the major criticism of the concept: it is "too esoteric and beyond the average person to operate and maintain." Although it is true that the Ark is the product of an array of highly-trained specialists, Todd maintains that there has been "a conscious effort to design the Ark for lay people." Research to further simplify the design continues.

Prince Edward Islanders have generally accepted the Ark. Being practical people, keenly aware of their dependency on imported fuels, the islanders are "intrigued" by the potentials of solar heating and find windmill electricity generation "exciting."

But no islander has lived in the Ark; Todd has and he describes the experience in these seductive words: "Living and working in a place where the sun, wind, architecture and ecosystems operate in beautiful concert has affected most of us. The Ark as a humanly-derived microcosm creates a sense of wholeness and self-worth engendered by a high degree of self-sufficiency. There are no barriers, only external 'membranes' separating the innermost living and laboratory spaces from the biological communities where one works and the out-of-doors . . . the world outside appears less hostile, more familiar and even an ally since it is the source of ones fuel and power needs."

The Ark shares many characteristics with natural ecosystems. Among these are redundancy and diversity, integration, homeostasis, self-regulation, and a dependency on renewable energy sources. Further, the Ark interphases and contributes to its surrounding environment. Because it captures the sun's energy to provide a controlled environment for plant and fish growth, the Ark may free energy-hamstrung societies from their fossil fuel dependencies and, in the process, offer high-quality food the year round. The bioshelter concept for amenable societies may provide the way to a saner lifestyle. At any rate, the first Ark, according to Todd, "is in no way an end point, but an early investigation of a viable new direction." LRE



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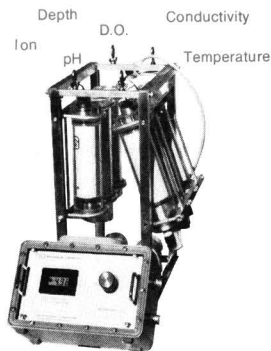
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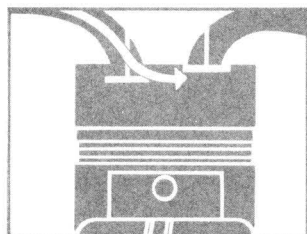
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# Wanted: better ways to clean water

Stiff anti-pollution regulations and possible water shortages are coming. U.S. and Canadian chemists talked about ways of meeting those challenges

When American and Canadian chemists meet, as they did for the 2nd Joint Conference of the Chemical Institute of Canada and American Chemical Society (Montreal), they:

- greet friends and colleagues
- attend social functions
- hold press conferences
- take part in many other activities associated with such a meeting. Some of them also discuss advanced water and wastewater treatment.

Up to now, one differentiated between water and wastewater treatment. However, perhaps this differentiation will be more hazy in the future. As water resources could become increasingly scarce, wastewater may have to be processed enough to be adequate for industry, agriculture, or perhaps even human consumption.

Indeed, in a rudimentary way, this processing may have been going on for many years, through a combination of water treatment and natural dilution of pollution. For example, more than two years ago, one water expert from Philadelphia, Pa., told *ES&T* that his city's water, taken from the Schuylkill River, probably goes through 17 cycles of uptake, use, and discharge before it ever gets to Philadelphia's water system.

## A "pore" way of doing things

Now, water/wastewater treatment is faced with increasing challenges in handling bacteria, viruses, heavy metals, organics, and other contaminants, in order to meet effluent guidelines or drinking water standards, as the case may be.

One approach to a very severe problem—that of toxic organics removal—involves combinations of granular activated carbon (GAC) and synthetic resins. The organics in question might include 1,4-dioxane, nitromethane, *n*-butanol, and methylethyl ketone, for example. Among others could be trihalomethanes (THM) from industrial wastes, or from the reactions of halogens, such as chlorine used for drinking water disinfection, with naturally occurring humic acids, perhaps.

The GAC used experimentally to attack the organics problem was generally Filtrasorb 400, made by Calgon Corp. The synthetic resin was mostly Ambersorb XE-340 made by Rohm & Haas. This

combination showed considerable effectiveness in adsorbing numerous organic compounds, including THM's or their precursors. However, as M. McGuire of Drexel University (Philadelphia) warned, care must be taken so that the "chromatographic" effect of one pollutant does not cause desorption of another pollutant. Also, with respect to adsorption, Paul Wood of Florida International University (Miami) noted that adsorbability of a halogenated organic might vary according to molecular structure. For example, the isomer *cis*-dichloroethene is not very well adsorbed by the GAC/resin, but the *trans* isomer is!

Other approaches to water/wastewater treatment can include changing the site of prechlorination, in the case of drinking water. They might also call for use of powdered carbon; substitution of ozone (O<sub>3</sub>) or chlorine dioxide (ClO<sub>2</sub>) for Cl<sub>2</sub> prechlorination; aeration; or other means. Indeed, for wastewater, O<sub>3</sub> and ClO<sub>2</sub> appear to show great promise. Other techniques could include multimedia filtration after clarification (textile industry), or acid destruct, as at a plant where organophosphorus pesticides are manufactured.

## Ozone

One of the "hottest" items discussed at the environmental symposium by Union

Carbide's Harvey Rosen was water/wastewater treatment with O<sub>3</sub>. While O<sub>3</sub> has been in use in Europe and Canada for many years for water disinfection—Montreal will have the world's largest O<sub>3</sub> drinking water plant (*ES&T*, July 1975, p 618)—its use in the U.S. is increasing. For instance, near Youngstown, Ohio, O<sub>3</sub> produced by a W. R. Grace LG-90 system (currently licensed to Union Carbide) at the rate of 200 lbs/d will treat municipal wastewater by means of positive pressure injection contacting.

Rosen also spoke of virtually complete bacteria and virus kill; color, odor, and bad taste removal; and lack of sludge, except where iron and manganese precipitation was concerned, when ozone is used for water treatment. New approaches to O<sub>3</sub> production, devised by Union Carbide engineer Frank Lowther, make its use considerably more economical and practical than has previously been the case. Not only is up to 15 times more O<sub>3</sub>/unit area of electrode made, but waste heat can be used profitably, he said. For improving O<sub>3</sub> production and system economy, including the potential for recovering waste heat, Lowther finished second in a national inventors' competition, and was named 1977 Niagara Frontier "Inventor of the Year."

Other municipal sites where O<sub>3</sub> is used, planned, or is being considered for

Application	Stage of development	User or Investigator
Chemical manufacture (cyanide)	Commercial	Du Pont (France)
Dye plant (color, COD)	Commercial	Several Japanese installations
Metal working (cyanide, phenol)	Commercial	Boeing Corp. (Wichita, Kans.)
Photographic bleach regeneration	Commercial	Berkey Photo (Fitchburg, Mass.)
Plating (cyanide)	Commercial	Seallectro Corp. (Mamaroneck, N.Y.)
Coke oven (phenol)	Start-up	Allen Wood Steel (Conshohocken, Pa.)
Wood products (phenol)	Start-up	Blandon F.P. (Grand Rapids, Mich.)

Source: Presentation by Union Carbide's Harvey Rosen

wastewater treatment, include Concord, N.C., Estes Park, Colo., Indianapolis, Ind., Indiantown, Fla., and Springfield, Mo. Industry, too, is getting on the bandwagon. For instance, the plating, refinery, dye, and pulp/paper industries are running pilot studies. Indeed, use of ozone at 15 different industrial locations ranges from the treatability study stage to the commercial stage, Rosen pointed out. A partial list of applications of O<sub>3</sub> wastewater treatment entails reuse, cyanide and phenol removal, odor control, color reduction, and processes.

#### Adding a spark

Another approach for smaller-scale water treatment might be electrolysis. Here, saline well water or dissolved sodium chloride (NaCl) is used as an electrolyte. I. J. Wilk of Stanford, Calif., described an electrolysis test at Glendale, Colo., involving a 3-g/L NaCl concentration subjected to a current of 50 amps, which led to destruction of bacterial growth, and bad odor and taste in a 90 800-L drinking water holding tank. He also said that at Neo Pendeli and Zakynthos (Greece) coliform was eliminated, and BOD reduced, sometimes to less than 1 mg/L. Operating since March 1970, the Zakynthos installation processes water for a 378 000-L reservoir. Twice-a-week electrode cleaning is necessary; however, full servicing was not needed until the system had been operating for 3.5 years.

At Zakynthos, a 7-kg solution of NaCl in 757 L of water is circulated in a cell past two 10.16 X 5.08 cm electrodes for 7 hours. Electrolysis is at 40 amps. The electrolyzed solution is then quickly dumped into the spring-filled reservoir, whose NaCl content is increased by only 19 mg/L. Test results showed that with Zakynthos' raw sewage waste containing 155 mg/L of NaCl, on electrolysis, coliform was virtually eliminated, and BOD decreased from 140 to 25 mg/L. Dissolved oxygen (DO), previously zero, became 2-4 mg/L, and chlorine, in hypochlorite form, increased from zero to 1 mg/L. "Further treatment brought BOD to less than 1 mg/L," Wilk said.

#### No discharge

With future water regulations to increase in stringency, perhaps one way to solve effluent problems is not to discharge any effluent in the first place. With this concept in mind, the managers of the 15-tpd Robertson Paper Mill at Hinsdale (N.H.) decided to install a closed wastewater treatment system made by Krofta Engineering Corp. (Lenox, Mass.). The system has been working since 1975, Milos Krofta, president of Krofta Engineering, told *ES&T*. The Krofta closed system has also operated as much as five years straight without discharging any water, at the 150-tpd Papierfabrik Harzer

paper mill, (Rhumspringe, W. Germany). The Harzer installation is a pioneering effort dating back to 1971.

This closed system uses what Krofta calls a "Supercell," which clarifies water in 2-3 min; "conventional" clarifiers need 2-3 h. This fast clarification eliminates odor, biofouling, and temperature loss, as long as the clarifier remains aerobic, which the Supercell does. Clarified water generally contains 3.2-5.5 mg/L of DO, and is adequate for meeting a paper mill's fresh-water replacement requirements. Also, for certain parts of the paper-making or recycling process, white water can be used in place of fresh water, and this enhances water conservation. White water is water separated from the pulp as the pulp goes through the paper-making process.

Any raw material for paper manufacturing is first slushed in water. Approximately 1-2% dissolves in the water. The dissolved material content builds up in the recycled water to approximately 1%. Approximately 1.7 t of water are evaporated per ton of paper produced in the dryer section and such evaporated water is replaced by fresh water addition.

During the evaporation, the dissolved material remains in the paper. Conservatively 0.5-2% of dissolved solids remains there. That may not sound like much, until one considers that at a 200-tpd paper mill, for example, a 0.5-2.5% DS loss can represent a 1-4-tpd potential product loss. Krofta said that with his company's closed system, that loss does not occur.

#### Groundwater protection

Another advantage that Krofta listed was that with the closed system, the need for secondary and tertiary predischARGE treatment is "short-circuited", since there is no discharge, except possibly for uncontaminated cooling water. By contrast, in an open system, water from the processed waste paper raw material carries away the dissolved solids, as well as bacteria and viruses that end up in groundwater and drinking water.

In a closed system, the dissolved solids, toxic materials, viruses, and bacteria are deposited in the paper. However, through a multiple high-temperature drying process that is part of the system, the paper is fully sterilized.

Krofta estimated that, based on this year's dollar values and energy costs, his company's closed system can save about \$233 000/year for a 200-tpd paper mill in the U.S., on heat, fiber, and sewer charges alone. He also estimated a payback on his company's equipment in 2.2 years.

These savings do not include the capital conserved through obviation of the need for a secondary and tertiary treatment system. They also do not include another cost that the closed system might

save a paper mill in the U.S. in the future, and would save in Europe. That cost is the "polluter pays" levy.

European countries such as West Germany, for example, are adopting the "polluter pays" principle. Payments will be based on the P.U. ("population unit"); that is, the amount of BOD, suspended solids (SS), and wastewater one person discharges per day. The yearly charge per P.U. in W. Germany will be \$4.90 starting in 1981 and will rise to \$14.70 by 1986. It is not inconceivable that a similar scheme might one day be adopted in the U.S.



**Krofta Engineering's Krofta**  
*"The closed system is the way"*

A 200-tpd paper mill in W. Germany, with primary treatment and clarification only, could incur a levy for discharging 47 310 P.U./day, according to Krofta's estimate. Given biological secondary treatment, the mill could still discharge 6210 P.U./day.

If by 1986, the annual "polluter pays" levy were \$14.70/P.U./year, the 200-tpd paper mill without secondary treatment would have to pay \$695 000/year. With secondary treatment, it could still incur a yearly charge of \$92 000/year, plus the operational and installation expenses for the secondary treatment plant. This is quite an incentive to go to zero pollution discharge!

Nevertheless, whether or not specific "polluter pays" fees are ever instituted in the U.S., water recycling is a worthy goal for which to strive; after all, water, like most other resources, is finite. Also, as one industrialist put it, "Don't discharge, and you'll keep the EPA off your back." Actually, if one thinks in those terms, in any industry, the closed loop, if it can be made economical, might be said to be the most advanced means of wastewater processing. JJ

# Coal use: which of three choices?

Until recently, few considered coal cleaning to be a viable option. However, new technology is causing that view to be reconsidered

Remember the good old days? You could see those factory or power plant chimneys belching out thick, black smoke. Your heart would swell with pride at this tangible expression of the nation's industrial prowess. In those times, much of the industrial might was powered by the burning of raw, or minimally cleaned coal. Then, pollution became a national issue; legislation was passed. Black smoke and sulfur fumes became a "no-no", and cheap oil and gas came to the rescue, for they were abundant.

The trauma of the 1973-1974 oil embargo rudely brought home the knowledge that petroleum products' abundance and inexpensiveness were things of the past. Suddenly, coal looked good again. But the problem was, and still is, how does one use coal without generating that no-longer-desired black smoke, and other products that people are better off without?

## Three ways to go

There are three basic ways to go. These comprise cleaning coal before burning; combustion methods that reduce pollution (fluidized-bed, for example); or "scrubbing" stack gas before discharge.

The first alternative was discussed at the conference, "Coal Cleaning: An Option for Increased Coal Utilization?" (Arlington, Va). Cosponsored by the U.S. EPA and Battelle's Columbus (Ohio) Laboratories, the conference attracted 200 people.

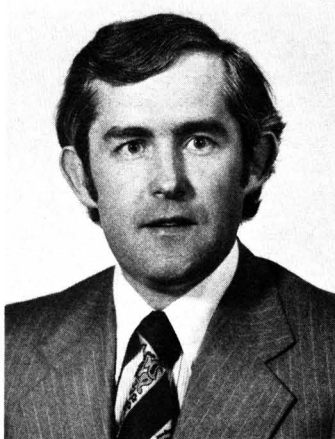
About two years ago, top EPA spokesmen, including former administrator Russell Train, maintained that scrubbers were generally the most immediate, realistic approach to air pollution control necessitated by the burning of coal. At the conference, however, EPA's acting assistant administrator for research and development, Stephen Gage, noted that his agency is taking a second look at coal cleaning possibilities. Now EPA is helping to surmount the non-technical and technical barriers that have inhibited coal cleaning to date.

Gage also noted President Carter's goal of increasing coal production to 1 billion tons by 1985, from 660 million tons last year. He said, however, "There can be no compromise on the environment. Energy production and use must be controlled to minimize the cost to property and public health. In these matters, the environment-energy dichotomy is to be swept aside." Thus, stringent cleanup measures

must be taken, and in this regard, Gage observed that coal cleaning, for instance, could be an advantageous, economic approach, instead of scrubbing.

## Physical approaches

At present, the most economical methods of cleaning coal are physical, according to EPA's Frank Princiotta. By "physical" is meant breaking or crushing coal, and removing pyritic sulfur, ash-producing material, and certain other non-combustibles by non-chemical techniques. Often, the physical techniques comprise washing, and its cost and the amount of undesirable matter removed will vary with the amount of crushing, screening, separation from waste, and actual washing done. What might the cost be? Battelle's Joseph Oxley provided an estimate. For example, for coal ground to "top size"—about 1½ in.—costs could be \$1.20/t. On the other hand, if the coal is pulverized ("deep cleaning"), and all coarse and fine material is processed, costs could be as much as \$11.80/t. However, the degree of cleaning is then greatly enhanced.



**EPA's Gage**  
*taking a second look*

Princiotta indicated that coal cleaning alone can now be considered an effective control approach for certain coals. He also suggested that coal cleaning/gas scrubbing mixes could be considered as possible low-cost alternatives to scrubbers alone, for many future applications.

## Some chemical routes

How simple life would be if all of the world's coal were of identical composition! One general coal cleaning process could then be optimized, and would suffice. Unfortunately, as James Kilgrove, manager of the EPA's coal cleaning programs (Research Triangle Park, N.C.), reminded the meeting, coals and their "cleanability" vary not only from region

to region but from bed to bed, and even within a given bed.

One salient example of this variability is found in a coal with a sulfur content that ranged from 0.2–7%. It may be pyritic or organic; proportions of these can vary widely. To remove this sulfur, or part of it, the task is eased when the sulfur is inorganic in the form of pyritic sulfur. But when the sulfur is organic, and bound up in the molecular structure of the coal itself, chemical means must be employed, and the job becomes more expensive. Indeed, Richard Balzhiser of the Electric Power Research Institute (EPRI, Palo Alto, Calif.) estimated that removing the organic sulfur from coals can more than double, or even triple coal cleaning costs, in some cases.

For coals, the bulk of whose sulfur is pyritic, the Meyers Chemical process (TRW, Inc.), which uses iron (III) sulfate as a chemical leaching agent, may be in the most advanced development stage, at present, of the approaches discussed at the conference. With EPA support, TRW has constructed a 667-lb/h desulfurization reactor test unit to prove the process out. It has removed up to 95% of pyritic sulfur in laboratory tests.

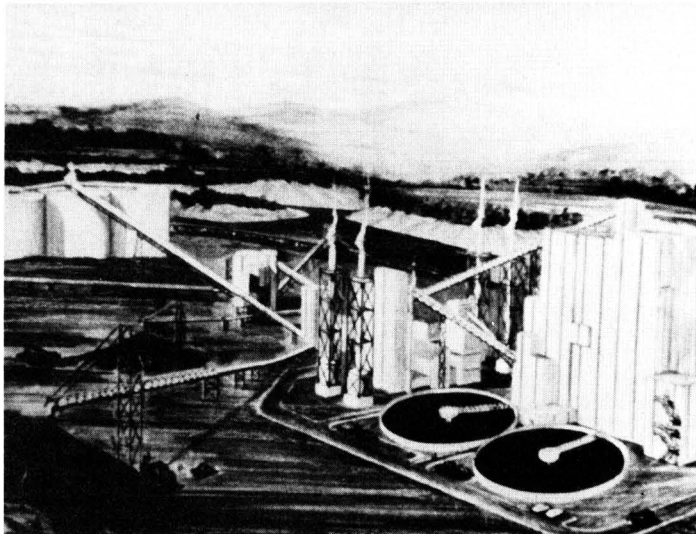
Another approach to getting the sulfur out before burning is Arco's catalytic method, now in laboratory stage. EPA's Kilgrove said that this method is slated to remove up to 95% of pyritic sulfur, and 40% of organic sulfur. Also, Battelle is testing a caustic leach process in a 0.25-tpd miniplant. That process, like that of Arco, is expected to remove 95% of the pyritic, and 40% of the organic sulfur.

On the other hand, ERDA is seeking designs for continuous units for an "oxid-desulfurization" air-steam system. Now in the laboratory stage, it should take care of 99% of the pyritic, and 40% of the organic sulfur.

Kilgrove said that 23 chemical coal cleaning processes have been documented as of late May. Of these, 7 or 8 are considered to be feasible, he pointed out. He also mentioned that in most cases, Appalachian coals are more "cleanable" than are Midwestern coals. Illinois coals, for example, not only have a high sulfur content, but much of that sulfur is organic.

#### **SRC on the horizon?**

For a yet newer generation of coal cleaning or conversion techniques—gasification, liquefaction—EPRI's Balzhiser saw solvent-refined coal (SRC) as a possibly viable option coming "down the pike". SRC removes pyritic, and a large portion of organic sulfur (ES&T, June 1974, p 510), as well as mineral matter from coal. The coal is essentially "dissolved" in its own organic solvents under conditions of hydrogenation, temperature, and pressure that are mild in comparison to those of gasification or liquefaction.



**Coal cleaning.** This is how facility at Homer City, Pa., will appear

The refined coal, with enhanced Btu value, is recovered in either solid (SRC I) or liquid (SRC II) form.

Balzhiser said that his organization plans to find out if the product from the SRC II process can be used in place of oil, even though it will still have some sulfur, and about 10% more mineral matter than would oil. He also said that EPRI is participating in a project to generate 20 MW of electricity at Georgia Power, by use of SRC. This use of SRC is not expected to worsen the NO<sub>x</sub> problem. He also noted, however, that SRC from most coals could generally meet the existing new source performance standard, 12 lbs of SO<sub>2</sub>/10<sup>6</sup> Btu.

Much of the coal cleaning and SRC talk one hears concerns sulfur and SO<sub>2</sub> standards. But, as EPA's Kilgrove reminded the conference, mineral matter or ash content must not be overlooked, and that matter could comprise 5–40% of a given coal. The larger amount will almost certainly be a problem, especially if and when a fine particulate emission standard comes into effect. Indeed, one might do well to anticipate a particulate standard of 0.05 lb/10<sup>6</sup> Btu by no later than 1985, according to this EPA spokesman. Also, coal cleaning should reduce air emissions and solid waste from combustion, as well as eliminate scrubber sludge production. On the other hand, it could lead to a disposal problem for liquid and solid wastes from coal preparation.

#### **Dollar estimates**

Still, coal cleaning may have cost advantages. To illustrate this point, Lawrence Hoffman, president of Hoffman-Muntner Corp. (Silver Spring, Md.), compared figures of deep coal cleaning by physical means with scrubbing and found the latter more expensive. He assumed

that a Pennsylvania coal (2–3% S) would be used at Tonawanda, N.Y., with a 15-year plant payoff, 2% for insurance and taxes, unfavorable interest rates, and grinding costs at 50¢/ton. His "bottom line" figures for cleaning coal came to \$3.55/t; comparative scrubbing costs were \$5.56/t. In terms of 10<sup>6</sup> Btu, Hoffman estimated coal cleaning/use to run 10–12¢, while flue gas scrubbing might be 22¢. He listed other advantages for coal cleaning, such as less need for land space, no need to reheat flue gas, and more net power to sell.

One prediction was that coal cleaning might take place at the mine mouth. However, as Joseph Mullan, a vice-president of the National Coal Association said, such coal cleaning, there or elsewhere, could virtually call for development of a new industry with needs for new personnel skills. He added, "How many people know how to run a coal-cleaning plant? Or, for that matter, how to design one?" He also said that if some proposed more strict air standards come into force, coal cleaning or cleaning/scrubbing combinations may not meet these standards. "How do you tell that to potential investors in plants that would clean or burn coal?" he asked.

Perhaps, with the right incentives and technological advances, coal cleaning will advance to the stage at which coal refinery complexes, analogous to today's oil refinery complexes, will be developed. These complexes would not only provide clean coal but perhaps marketable sulfur and other chemicals, as well. However, there is a long way to go. Numerous technical, economic, and regulatory uncertainties will have to be resolved before coal cleaning becomes a factor in providing an environmentally acceptable fossil-fueled energy supply. JJ

# FEATURE

## Metal recovery makes good sense!

In a plating shop, material recycling is not all; water, energy, and labor can also be saved. Often, existing equipment can be modified. Here's how

**Salim Bhatia and Robert Jump**

*Corning Glass Works  
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Process industries—including the electroplating and metal and plastics finishing industries—are constantly considering the question of what to do with their waste products, particularly waste fluids. Usually, the answer is found in one of two alternatives or a combination of both: destroy the contaminating or toxic elements of the waste, or recover them for reuse.

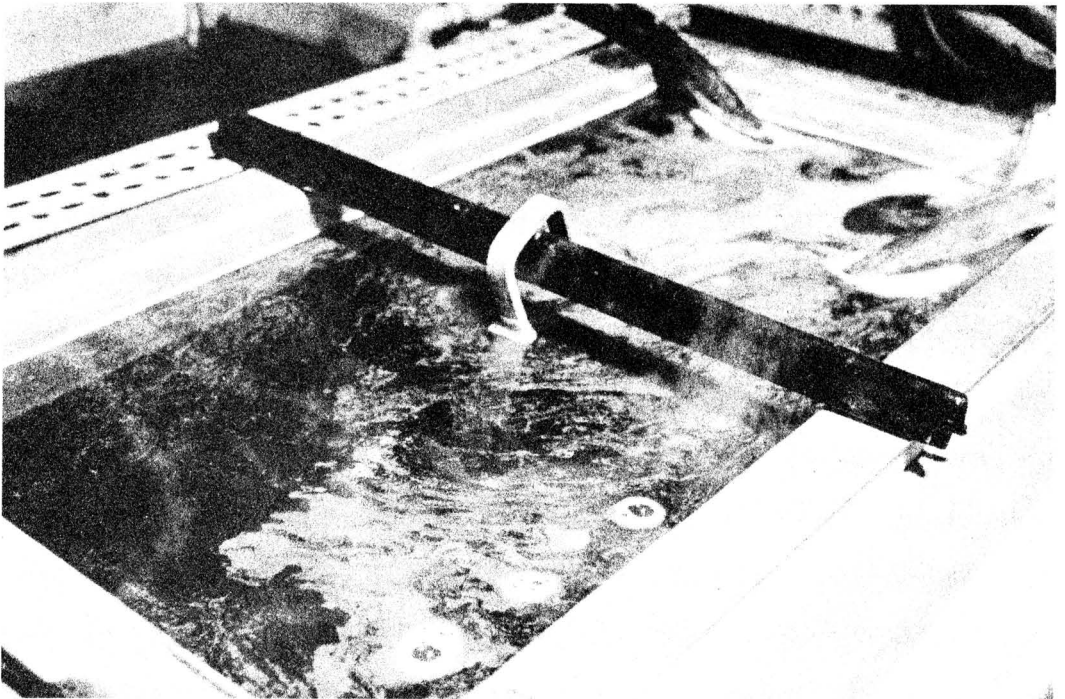
Certainly, the idea of recovering and reusing materials would seem the most attractive answer. However, recovery is seldom the first approach seriously considered as a solution to total waste problems. A principal reason is that industrial waste frequently takes several forms, and available recovery processes are usually limited to particular materials, to certain processes, or to steps within a process.

The most common—and apparently most practical—approach has been the construction of total waste “destruct” systems in which all of an industry's waste is pooled and treated, and the resulting sludge is appropriately discarded. Once such “destruct” systems were installed, often at considerable ex-

pense, there was understandable reluctance to consider further investment in recovery systems.

Even so, time and a growing concern for the total environment have given increasingly stronger indications that destruct-oriented approaches fall far short of the mark. Usually chemical in nature, destruct systems simply convert a water pollution problem into a solid waste (sludge) pollution problem. This is particularly true in the metal plating industry—especially chrome and nickel plating—where the waste treatment approach, usually by precipitation, produces toxic sludges. The net result is that possibilities of eventual surface water contamination is not really eliminated, and disposal becomes more complicated. The destruct approach is also much more costly in the long run, because the expenses of treatment and disposal, including hauling and dumping fees, are added to the cost of the recoverable plating chemicals lost in the process.

Nevertheless, as recently as five years ago, destruct systems and the proper disposal of the resulting sludges appeared to be



the best solution. But for certain types of plating done in significant volume, a number of new factors strongly indicate that recovery makes sense—even for companies that have already invested in expensive destruct systems. These factors include improved recovery equipment (particularly, climbing-film evaporators), and the development of recovery systems capable of handling smaller volumes of waste streams, which make them more affordable to more users. And broader financial incentives from government agencies "sweeten the pot."

### The plating process

In typical plating operations, conveyor racks carrying parts to be plated are dipped into various solutions long enough to allow the desired extent of etching or plating to occur. From the plating tank, the racks move to several rinse tanks to remove excess plating solution.

To conserve water, rinse water is usually added to the system in a continuous flow that is counter to the progress of the workpiece. As a result, the workpiece is dipped into cleaner water with each successive rinse. The number of rinse tanks varies from one plating process to another, and from plant to plant. For instance, the use of three rinse tanks is fairly common for chrome plating operations.

However, since the flow of rinse water is from back to front in the work progression, the water leaving the system from the first rinse tank contains the greatest concentration of excess chrome or nickel plating solution. This concentration can sometimes be considerable. Experience has shown that as much as 90% of the chrome plating metals put into a plating bath ends up in the rinse water leaving the system at this point.

### The climbing-film evaporator

Of several recovery methods suitable for use in the plating industries, the climbing-film evaporator (CFE) is the most recent development. It is proving to be the most flexible in terms of installation and operation ease, minimal disruptive impact on existing production lines, and efficiency in plating chemicals

recovery. Moreover, its rinse water is purified by distillation and returned to the rinse tanks.

Plating rinse water is continuously fed to a CFE. Low-pressure steam provides the energy by which the rinse water vaporizes and drives the climbing film of concentrate up the tube and into the vapor-liquid separator. In the separator, the heavier chrome or nickel materials settle out, while the water vapor continues through a filter to a condenser. When the recovered solution reaches the desired concentration, it is drained into a storage tank and held for reuse. The recovered distilled water returns to the rinse water system to complete the closed-loop rinse water process.

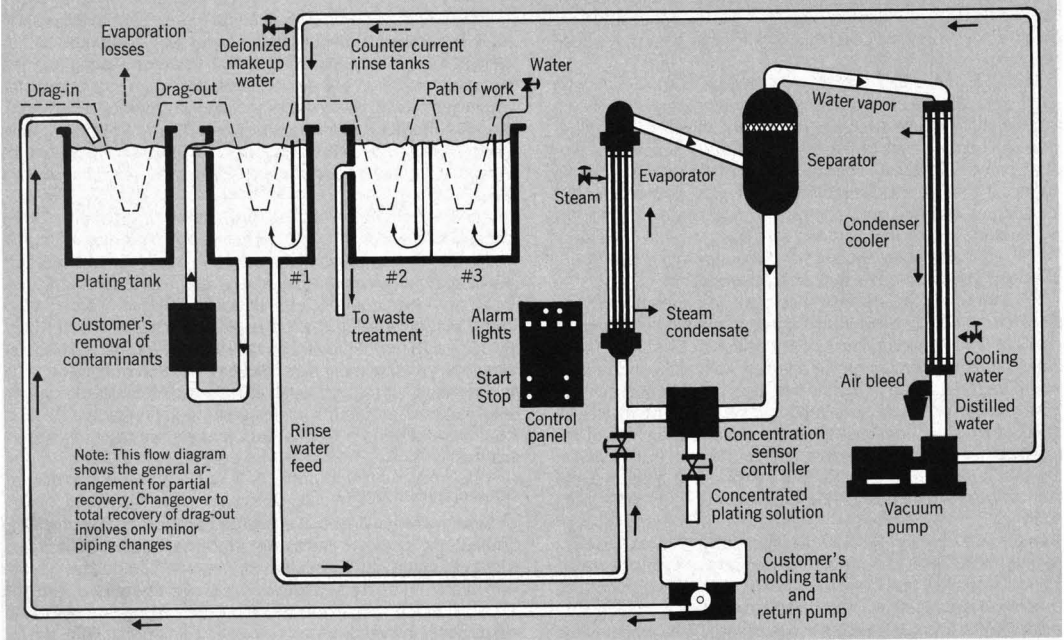
Figure 1 shows such a recovery system connected only to the first rinse tank, usually called the drag-out rinse tank. The bulk of the excess plating solution is captured in that drag-out rinse tank. Connected as shown, the system provides partial but highly efficient and economical recovery. Now in most operations, rinse water leaving the system from subsequent rinse tanks usually has a contamination level that poses no serious problem for in-house waste treatment systems. However, when warranted, linking more rinse tanks to the evaporator provides even more effective plating materials recovery.

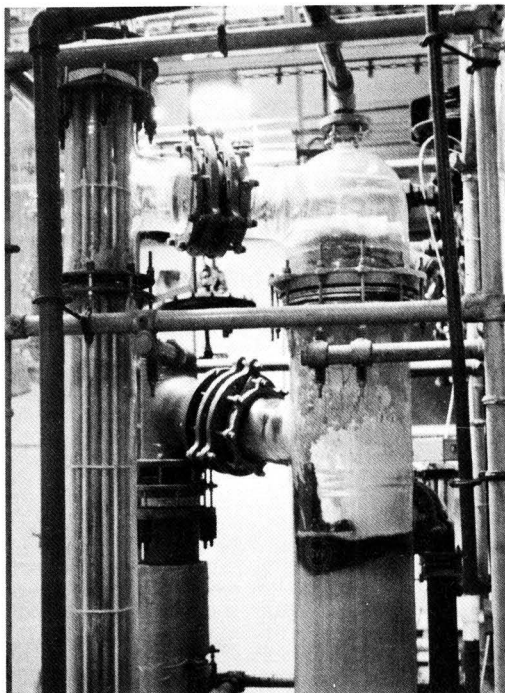
Besides recovering valuable plating chemicals and reducing rinse water demands, CFE systems provide other cost savings. For example, because the level of contamination from the plating line is reduced or eliminated, the plater's treatment chemicals cost (purchase, storage, handling, consumption) are reduced.

Recovering plating solution in the desired high concentration also reduces labor costs in preparing makeup plating solution to replace that lost in the process. Table 1 shows some typical cost/performance parameters that illustrate the economic potential that CFE's offer to typical chrome and nickel plating operations.

From the increasingly important standpoint of labor, CFE systems have proved readily insertable into existing plating process lines with minimal additional attention. An Environmental Protection Agency demonstration project (EPA Project S803781-01) proved that existing maintenance personnel were

FIGURE 1  
Climbing-film evaporator (CFE)





**Recycling.** *The system at work*

quick to learn how a CFE unit operates, and that maintenance was simple and required no additional personnel.

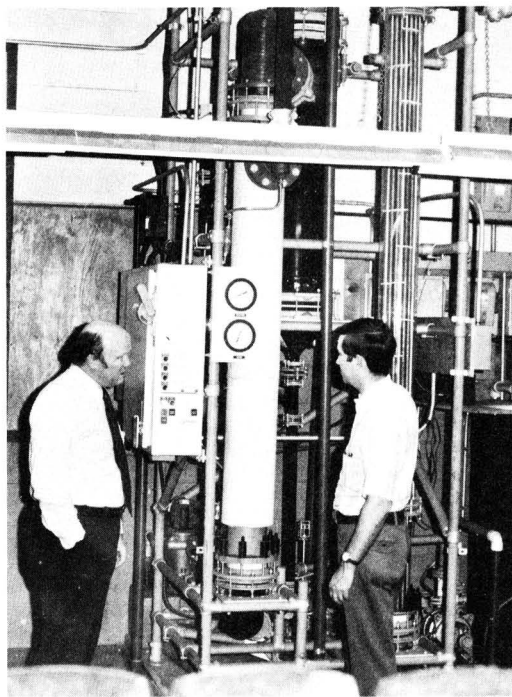
#### **Demonstrated effectiveness**

General Plating (Detroit, Mich.) installed one of the country's first CFE units in early 1975. A division of Indian Head, General Plating is a major supplier of chrome-plated automotive parts, such as bumpers, bumper guards, valve covers, and headlight rims. Savings of better than 70% of the company's former chromic acid costs and cost reductions in other areas have been reported.

The CFE unit at General Plating is used in combination with a cation exchange column and related treatment capability, so that the chromic acid discharge in the plant effluent is essentially zero. An added bonus of the CFE unit is that it recovers a proprietary mist suppressant used at General Plating, thereby cutting chemical costs further. In addition, at a typical cost of 50¢/lb/d to destruct chromic acid chemically, and by use of the approximately 350 lb/d of chromic acid waste typical of General Plating for calculation, the system translates into a \$30 000/y saving in treatment costs that are not needed.

Ford Motor Company's plastics plant in Saline, Mich., has installed a multiple-evaporator recovery system on a plastics preplate line containing chromic and sulfuric acid baths. These baths are extremely corrosive and hard to handle, in terms of waste treatment. The company has reported chemical savings from reduced chemical consumption in the etching bath, as well as reduced water consumption in the rinse line, and the elimination of the need for expensive destruct chemicals. In addition, there is no sludge to discard, and contaminant buildup in the etching bath is minimized, thus lengthening the life of the bath itself.

In Canada, Hudson Bay Diecastings, Ltd. of Bramalea, Ont., has had a CFE unit on its automotive parts plating line for 18 months. Recovery was the route chosen because of high chrome consumption caused by heavy drag-out of plating bath on cup-shaped parts, and in blind holes in diecastings. The company also



**Testing.** *System checkout for EPA project*

experienced high chemical costs in its waste treatment facility.

Chrome recovery is reported at 80–85%, with a corresponding decrease in chrome treatment chemicals. For Hudson Bay Diecastings, the ability of the evaporative process to recover plating solution at concentrations of greater than 70 oz/gal in a single-step operation is particularly attractive.

#### **An EPA project**

The previously cited EPA-sponsored demonstration project for the recovery of decorative chrome was conducted at Advance Plating Co. (Cleveland, Ohio). Advance Plating is a job shop that works on a wide variety of items ranging from automotive parts to appliance parts and plumbing goods to fasteners. The EPA project involved one of the company's two automatic plating lines. The line processes 20 000–25 000 racks of products per month, and operates 18 hours a day, five days a week.

Aside from noting the obvious financial advantages of reducing chrome consumption by 80%, the study's final report (publication pending) stresses that the system had minimal impact on the plant's operations. It required an average of about 10 minutes a day of routine operator attendance. Two hours a week were spent in regenerating the ion exchange system used in conjunction with the CFE unit. The entire recovery system was operated by existing manpower. Manual addition of chromic acid to the plating bath was drastically reduced, because the system was installed to dump the recovered solution at the desired concentration into a plating bath makeup storage tank automatically.

#### **Financial incentives**

Even with the financial advantages offered by using CFE technology, as evidenced by the examples cited, the purchase and installation of CFE equipment may represent large capital expenditures for some platers. This holds true particularly for the smaller job shops, which comprise a major segment of the electroplating industry.



TABLE 1

## Potential savings

	Chrome (CrO <sub>3</sub> )	Nickel (as function of B <sub>2</sub> O <sub>3</sub> )
<b>Plating Chemicals Used Per Line:</b>		
1. Lbs/shift	45	5
2. Lbs/day (2 shifts/day)	90	10
3. Lbs/y	21 600	2400
<b>Drag-Out Loss:</b>		
4. % lost in drag-out <sup>a</sup>	90%	100%
5. Loss, lbs/y (No. 3 X No. 4 ÷ 100)	19 440	2400
6. Bath concentration, oz/gal.	45	6
7. Loss, gal/y (16 X No. 5 ÷ No. 6)	6912	6400
8. Plating chemical cost, \$/lb of chrome or \$/gal nickel solution	\$0.75	\$2.50
9. Value of loss (for chrome use No. 5 X No. 8; for nickel use No. 7 X No. 8)	\$14 580 <sup>b</sup>	\$16 000 <sup>b</sup>
<b>Destruct Chemical Usage:</b>		
10. Drag-out loss (for chrome use No. 5 in lbs/y; for nickel use No. 7 in gal/y)	19 440	6400
11. Destruct chemical cost	\$0.50/lb	\$0.06/gal
12. Purchases of destruct chemical, \$/y (No. 10 X No. 11)	\$9720	\$380 <sup>c</sup>
13. Sludge removal charge, \$/y	\$12 000	\$3000
14. Total cost to destruct, \$/y (No. 12 + No. 13)	\$21 720	\$3380
<b>Total Potential Savings Per Line, \$/y:</b> (No. 9 + No. 14)	\$36 300	\$19 380

<sup>a</sup> For hard chrome, use 50%; for all other chrome, use 80–90%; for nickel, use 100% because boric acid use equals drag-out.

<sup>b</sup> Does not include cost of storing and handling extra chemicals.

<sup>c</sup> May increase as tighter requirements are placed on precipitation of nickel.

**Note:** Examples are for chrome and nickel. For chrome, use consumption of dry chromic acid flake. For nickel, use consumption of boric acid to calculate nickel recoverable from drag-out.

Calculations are simplified and assume 240 actual operating days per year, which allows for holidays and vacation shutdown.

In order to install systems in order to help them comply with EPA effluent discharge requirements, small shops can obtain funding assistance from the Small Business Administration (SBA) in the form of low-interest or guaranteed loans with up to 30 years to repay. A booklet ("Loans to Small Businesses Under The Federal Water Pollution Control Act") describes these SBA programs. It is available from the Environmental Protection Agency, State Programs Branch, Room 801-East Tower, 401 M Street, S.W., Washington, D.C. 20460.

Because the purchase and installation of plating chemicals recovery units is intended to minimize the pollution potential of such operations, most states waive sales taxes on such purchases. This, coupled with the normal investment tax credits, capital equipment write-offs and depreciations, and real property tax deductions, provides even greater financial incentive to the recovery approach. For this type of equipment, there is also a federal rapid tax amortization program administered by the states. Information about these programs is available from the Small Business Loan Section, Environmental Protection Agency, 401 M Street, S.W., Washington, D.C. 20460.

### No contamination, no sludge

Whatever the EPA decides with respect to electroplating effluent contamination levels, the several recovery applications previously discussed demonstrate the new techniques, equipment, and capabilities that are effective in practically eliminating metal contamination attributable to the plating process. Numerous evaporator systems are already in the field, and are recovering chrome, chrome etch, nickel, and various cyanide solutions. Development is well along on systems for tin-lead fluoroborate, and precious metals recovery.

More important, perhaps, these evaporative techniques have an advantage over chemical destruct approaches because recovery produces no sludge that requires disposal. In this respect, by contrast, the destruct systems really exchange one form of pollution for another.

For the plater and the user of plated products, recovery

techniques have shown that they can provide substantial operating cost savings with no detrimental effect on the quality of the finished products. As a result, platers are learning that recovery does indeed make sense—economically as well as environmentally.

### Additional reading

"Interim Report on EPA Demonstration Project Evaporative Recovery of Chromium Plating Rinse Waters (EPA Project S80371-01)", Technical paper, Roger W. Lacy, 63rd Technical Conference, American Electroplaters' Society, July 1, 1976.

"Chrome: Reclaim or Destroy," *Michigan Plant & Equipment*, June 1976, pp 12–14.

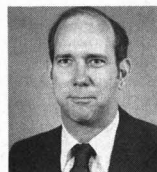
"Closed-Loop Waste Treatment System Saves Chemicals," *Industrial Finishing*, July 1976, pp 38–42.

Case History, Hudson Bay Diecasting, Ltd. (to be published).

Final Report, EPA Project S803781-01 (to be published).



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Coordinated by JJ



# The pesticide scorecard

Toxicological effects, biological distributions,  
and the fate of these chemicals can be quantified  
in a simplified, straightforward manner

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On April 7–8, 1976, A "Food-Day Dial-ogue" was sponsored by CAST (Council of Agricultural Science and Technology). Students and citizens from all over the U.S. called in questions to a panel of 28 scientists stationed in Washington, D.C. The 20 or so telephones rang constantly for two days. The callers had questions about Kepone, PBB, Red Dye No. 2, health foods, organic gardening, cholesterol, sodium nitrite, herbicides, the green revolution, overpopulation, and many other topics.

Of major concern to many, however, was the presence of chemicals in food, especially pesticides. One question that was asked repeatedly was, "Are the new pesticides any safer than the old ones?" While the callers could generally be assured that the newer pesticides were environmentally safer, they had to be told that some, such as the organophosphorus chemicals (*ES&T*, April 1975, p 308), were much more toxic to the men who applied them and to those who had to work around them. Indeed, the answers were complex, and attempts to simplify them were no more satisfying to the callers than they had been to students who had asked similar questions. Thus, a quantitative comparison was needed of the properties and behavior of some of the old versus some of the new pesticides.

To gain a better understanding of the relative safety of pesticides to man and the environment, one needs to have a general idea of:

- the kind of toxicological tests that are used to measure the safety of pesticides
- the fate of pesticides in the environment
- a scheme that allows one to compare the relative properties of one pesticide with another.

## Toxicological tests

Pesticides are subjected to many biological tests in order to obtain information on their relative toxicity to various animals, and thus, their potential toxicity to man. Some of these toxicological tests are illustrated in Figure 1. Pesticides are administered to various mammals and wildlife by putting the chemicals in their feed. These substances are also injected into the air in inhalation studies, or into the water in studies with fish and other aquatic organisms. Dermal toxicity is measured by applying the pesticides to the skin of sensitive species, and eye sensitivity is measured by applying dilute solutions of the chemicals to the eyes.

Dermal, oral, and inhalation are the routes of entry, and relative order of actual hazard of most pesticides. The most common measure of the relative mammalian oral toxicity of pesticides is the  $LD_{50}$  value for rats.  $LD_{50}$  is defined as the oral dose of toxicant necessary to kill 50% of a species being tested. It is normally expressed in mg of chemical per kg of body weight of the test species.

Toxicities of pesticides to aquatic invertebrates and fish such as rainbow trout or bluegills are often very sensitive predictors of a chemical's potential hazard in the environment. The most common measure of the relative toxicity of a pesticide to those and other aquatic species is the  $LC_{50}$  value.  $LC_{50}$  is defined as the concentration of toxicant necessary to kill 50% of a species being tested. It is generally expressed in parts per million (ppm).

Subacute toxicological studies are done by administering a pesticide to a test species over several days or weeks and then

## Types of toxicological tests of pesticides

- Acute ingestion toxicity
  - Acute oral toxicity to rats
  - Acute oral toxicity to wildlife (birds, fish)
- Acute inhalation toxicity to mammals
- Acute dermal toxicity to mammals
- Toxicity to eyes of mammals
- Subacute effects on mammals
- Chronic effects on mammals
  - Behavioral
  - Carcinogenic/oncogenic/mutagenic/teratogenic
  - Pathological

measuring the response. Chronic toxicological studies are done by administering trace amounts of a pesticide to a test species over long periods of time. These are sometimes called life-stage or egg-to-egg studies. Changes in behavioral patterns, unnatural growth (tumors), or abnormal forms, and increases in the normal mutation rate or in diseases of a test species are carefully examined.

### Fate of pesticides in the environment

The various processes and factors involved in the dissipation of pesticides in the environment are shown in Figure 2. In nature, degradation and transfer processes play a role in the ultimate fate of a pesticide in the environment. The degradation processes include biological, chemical, and photochemical decomposition, and are shown in the figure as processes whereby the pesticide (PS) molecule is split apart.

The transfer processes include absorption, retention, accumulation, and exudation (excretion) by organisms, adsorption by soil colloids and other surfaces, and movement in the vapor, liquid, and solid states through the atmosphere, soil, and water. In Figure 1, transfer processes are shown as those in which the pesticide (PS) molecules remain intact.

Innumerable different kinds of measurements and tests are required to understand the fate, behavior, and ultimate safety of a pesticide in the environment better. Measurements of the chemical, biological, and edaphic properties, and the methods of application of a particular pesticide are needed.

Cationic pesticides are readily adsorbed by soil colloids, and are therefore immobile in the soil. Pesticides with very low water solubilities (less than 1 ppm), such as the chlorinated hydrocarbon insecticides, are also very immobile in soils. Anionic and nonionic pesticides of high water solubility (greater than 500 ppm), except for arsenate and phosphate chemicals, are very mobile in soils, while those with moderate solubilities are intermediate in their movement. Pesticides with high vapor pressures (greater than  $10^{-3}$  mm Hg at 25 °C) are very volatile and mobile in the gaseous state, and special techniques, such as soil incorporation, must be used to retard their loss from the soil. Chemicals with very low vapor pressures (less than  $10^{-7}$  mm Hg, at 25 °C) are considered to be nonvolatile, while those with vapor pressures between  $10^{-4}$ – $10^{-6}$  mm Hg, at 25 °C are considered to be slightly volatile.

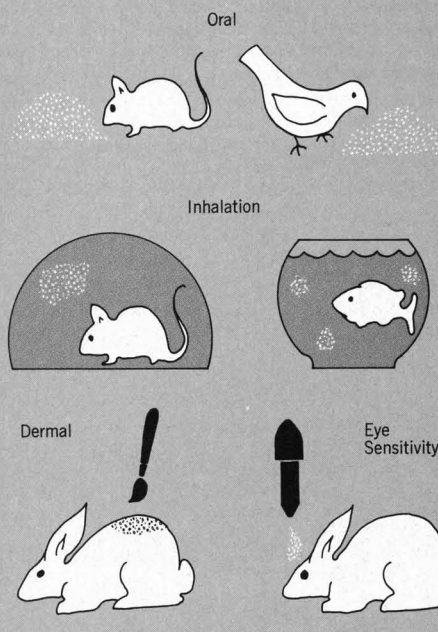
The type of formation of a pesticide also has an effect on its solubility and vaporizability. Other important chemical properties of a pesticide that must be determined are its degradability by sunlight (photodegradation) or by chemical reactions (storage stability).

Biological properties of pesticides, which must be determined, include the chemical's mechanism of action in killing a pest, and the chemical pathway by which it is degraded in the environment. Ecological effects on the other nontarget organisms, and whether or not the pesticide accumulates in a living organism, or

FIGURE 1

## Pesticide toxicity tests

Determining toxicity of pesticides (PS) =



biomagnifies from one organism to another, must also be ascertained.

Edaphic properties of a pesticide that must be determined include adsorptivity to soil colloids and mobility in soils and waters. They also encompass the longevity or length of time the chemical remains in its active form, and its biological availability when it is bound to the soil.

The two important application properties that determine a pesticide's behavior are the type of formulation and method of application. Pesticides are applied to plants, seeds, and soils in the solid, liquid, or gaseous form. They may be injected into the soil, applied directly to the plant or the soil surface, or incorporated into the soil by disking or rototilling. The chemical, biological, and edaphic properties of a pesticide determine the type of formulation and method of application that is ultimately used.

### Evaluation scheme

In order to compare the relative safety of some of the old pesticides with some of the new ones, a scheme is needed. Such a scheme should theoretically include complete data for each pesticide on toxicological tests and environmental tests relating to chemical, biological, and edaphic properties, and methods of application. However, it would be too complex for the general comparisons made in this article. Therefore, four key properties of pesticides have been selected, which, taken together, illustrate the differences among several pesticide families, and among some of the insecticides, herbicides, and fungicides. Two are taken from toxicological tests, one is taken from biological tests, and one from edaphic tests.

### Toxicity, longevity, bioaccumulation

Acute oral toxicity to rats was chosen as an indicator of a pesticide's potential hazard to mammals. LD<sub>50</sub> values for selected pesticides are given in Table 1. A rating scale is given in Table 2, and the categories that will be used are as follows:

- 1.0–1.5, Relatively nonhazardous; LD<sub>50</sub> is 4000–9000 mg/kg, or greater.
  - 1.5–2.5, Slightly hazardous; LD<sub>50</sub> is 300–4000 mg/kg.
  - 2.5–3.5, Moderately hazardous; LD<sub>50</sub> is 20–300 mg/kg.
  - 3.5–4.0, Hazardous, LD<sub>50</sub> is 6–20 mg/kg, or less.
- Acute ingestion toxicity to fish was chosen as an indicator of a pesticide's potential hazard to wildlife. LC<sub>50</sub> values for selected pesticides are given in Table 1. A rating scale is given in Table 2, and its categories are:

- 1.0–1.5, Relatively nonhazardous; LC<sub>50</sub> is 100–1000 ppm or greater.
- 1.5–2.5, Slightly hazardous; LC<sub>50</sub> is 1.0–100 ppm.
- 2.5–3.5, Moderately hazardous; LC<sub>50</sub> is 0.01–1.0 ppm.
- 3.5–4.0, Hazardous; LC<sub>50</sub> is 0.01–0.001 ppm, or less.

Pesticide longevity is dependent upon how long the parent chemical remains in the soil environment (from half-life or duration-of-toxicity data). Longevity depends on the relative susceptibility and accessibility of biological, chemical, or photochemical degradation. The longevity factor reflects on the apparent dissipation of a pesticide. Half-life or duration of activity values for selected pesticides are given in Table 1. A rating scale is given in Table 2, and the categories are:

- 1.0–1.5, Readily degradable; soil life 1–15 weeks, or less.
- 1.5–2.5, Moderately degradable; soil life 15–45 weeks.
- 2.5–3.5, Slowly degradable; soil life 45–75 weeks.
- 3.5–4.0, Persistent; soil life 75–90 weeks, or longer.

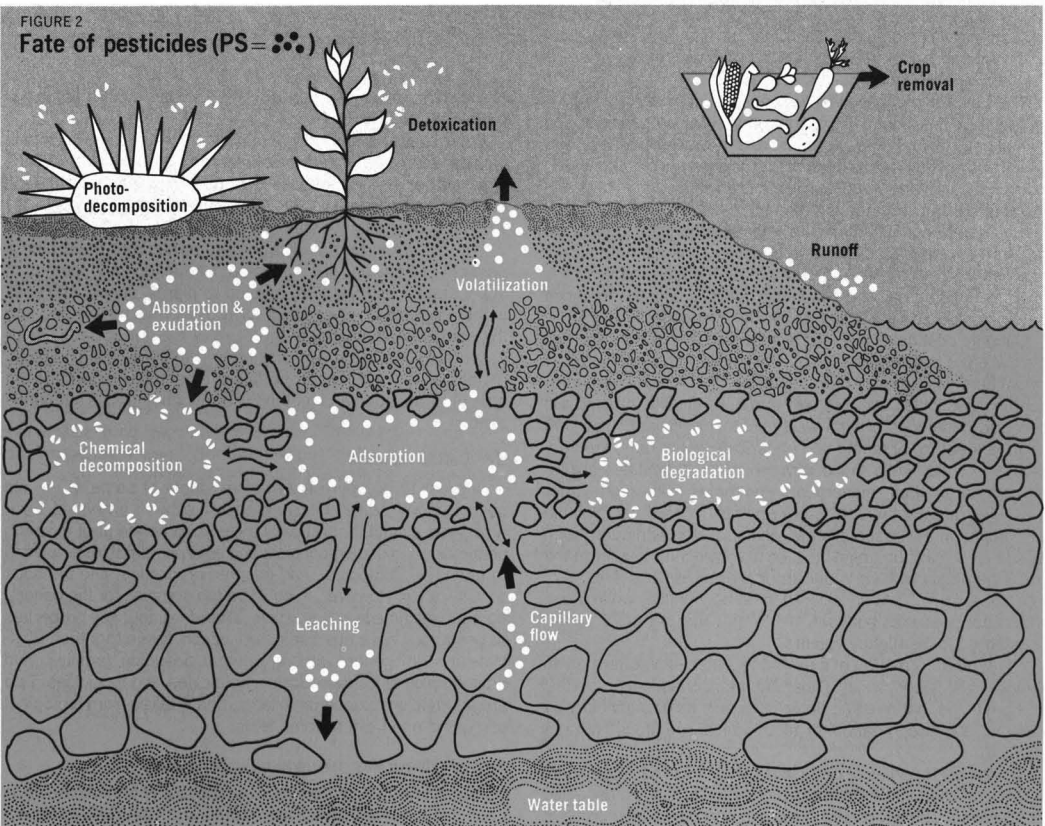
The last factor to be considered in the scheme is bioaccumulation. It is defined as the accumulation of a pesticide by an organism in amounts greater than are present in the external environment. It may lead to biomagnification in the food chain, which is defined as the total accumulation of a pesticide through a series of organisms. However, since biomagnification is even more difficult to measure than bioaccumulation, only bioaccumulation will be considered.

The presence of a pesticide in an organism may not be an actual hazard, but it is generally accepted that a potential hazard

**To determine the fate of pesticides, here are some of the properties that must be known:**

<b>Chemical</b>	Ecological effects
Ionizability	Bioaccumulation
Water solubility	<b>Edaphic</b>
Volatility	Soil adsorptivity
Formulation	Soil mobility
Photodecomposability	Longevity
Storage stability	Biological availability
<b>Biological</b>	<b>Application</b>
Mechanism of action	Formulation (solid, liquid, gas)
Degradation pathway	Method of application

**Note:** Ionizability, water solubility, volatility, and type of formulation are a pesticide's chemical properties that most greatly influence its mobility in the environment



**Note:** Degradation processes are characterized by the splitting of the pesticide molecule. Transfer processes are characterized by the pesticide molecules remaining intact.

exists. A pesticide's presence is determined as follows:

Organisms such as oysters or fish are placed in specified concentrations of a selected pesticide. After a certain period of time, generally 24, 48, or 96 hours, the organism is analyzed for pesticide content, and the ratio of that present in the organism over that present in the water is calculated. This value has been termed the bioaccumulation factor. Table 1 contains bioaccumulation factors for selected pesticides. Table 2 contains a rating scale, and the categories are:

- 1.0–1.5, Nonaccumulative; concentration in organisms is 10–60, or less, times that of the water environment, and readily decreases when the organism is placed in pure water.

- 1.5–2.5, Slightly accumulative; concentration in organisms is 60–700 times water background, and the pesticide is only gradually lost when the organism is placed in water without pesticides, or the pesticide is degraded by the organism.

- 2.5–3.5, Moderately accumulative; concentrations are 700–8000 times water background, and pesticide is only gradually lost when the organism is placed in water without pesticide, or pesticide is slowly degraded by the organism.

- 3.5–4.0, Highly accumulative; concentrations are 8000–40 000, or more, times that of the water background, and the pesticide is not lost when the organism is placed in water without pesticide, or pesticide is not degraded by the organism to any appreciable extent over a period of many weeks of sampling.

#### Relative safety of pesticides

The evaluation scheme for relative safety of a specific pesticide is simply the sum of the values of the four key factors. According to the proposed scheme, the most hazardous pesticides would have a sum of 16; i.e., toxicity to rat = 4, and 4 + 4 + 4 + 4 = 16. It would be highly toxic, very persistent, and would bioaccumulate greatly. By contrast, the safest chemical would have a sum of 4. It would be relatively nontoxic and short-lived, and would not bioaccumulate. Table 3 contains the relative toxicity values of selected pesticides, calculated according to the proposed scheme.

Using the proposed evaluation scheme, one can easily see why DDT and other chlorinated hydrocarbon insecticides re-

TABLE 1

### Toxicological and biological properties of selected pesticides<sup>a</sup>

Common name	Acute oral toxicity		Longevity in half-life or duration of activity <sup>c</sup> (wk)	Bioaccumulation factor <sup>d</sup>
	(rat) LD <sub>50</sub> values (mg/kg)	(fish) LD <sub>50</sub> values <sup>b</sup> (ppm)		
<b>Chlorinated hydrocarbons</b>				
Aldrin	55	0.003	520	4444 <sup>f</sup>
BHC	3000	0.79	208	60 <sup>g</sup>
DDT	113	0.007	546	70 000 <sup>g</sup>
Dieldrin	60	0.003	>312	3300 <sup>f</sup>
Endrin	25	0.0002	>624	1000 <sup>g</sup>
Lindane	106	0.018	>728	60 <sup>g</sup>
<b>Organophosphorus chemicals</b>				
Azinphosethyl	17.5	0.019	<4	0 <sup>g</sup>
Dichlorvos	68	0.700	8	0 <sup>h</sup>
Disulfoton	7.5	0.040	2	0 <sup>g</sup>
Malathion	1375	0.070	2	0 <sup>g</sup>
Parathion	13	0.047	8	9
Phorate	3	0.0055	2	0 <sup>i</sup>
<b>Carbamates</b>				
Carbaryl	675	2.0	2	0 <sup>g</sup>
Carbofuran	11	0.21	8–16	0
<b>Triazines</b>				
Ametryn	1100	3.4	4–12	0
Atrazine	2000	12.6	26–78	0
Cyanazine	334	>1	4–8	0
Prometon	1750	>1 <sup>e</sup>	>104	0
<b>Organic acids</b>				
Dalapon	4000	115	2–4	0 <sup>j</sup>
Dicamba	1100	35 000	8–12	0
Endothal	80	1.15	4	0
Picloram	8200	2.5	52–78	0
2,4-D	400	250	1–4	0 <sup>j</sup>
2,4,5-T	300	0.5	1–12	0
<b>Miscellaneous</b>				
Alachlor	1800	13.4	8–12	0
Bromacil	5200	75	40–48	0
Captan	9000	0.13	<1	0
Copper sulfate	2000	0.150	permanent	0
Diuron	3400	4.3	<52	0
Ethylmercury chloride	37	1.8	permanent	3000 <sup>k</sup>
Pyrazon	3300	40	4–8	0

<sup>a</sup> Values cited were those that occurred most often in documents printed by governmental agencies or in professional journals. <sup>b</sup> LC<sub>50</sub> = lethal concentration to reduce population by 50% in 24, 48, or 96 hour tests for bluegill or rainbow trout, unless specified otherwise. <sup>c</sup> All values converted to approximate full-life values. <sup>d</sup> For unknown species, unless specified otherwise. <sup>e</sup> For spot. <sup>f</sup> For fish. <sup>g</sup> For oysters. <sup>h</sup> For shrimp. <sup>i</sup> For minnow. <sup>j</sup> For goldfish. <sup>k</sup> For pike.

TABLE 2

## Fractional rating scale for toxicity, longevity, and bioaccumulation

Rating scale	I LD <sub>50</sub> rat (mg/kg)	II LC <sub>50</sub> fish (ppm)	III Longevity (wk)	IV Bioaccumulation factor
1.0	≥9000	≥1000	≤1	≤10
1.1	8000	800	3	20
1.2	7000	600	6	30
1.3	6000	400	9	40
1.4	5000	200	12	50
1.5	4000	100	15	60
1.6	3000	80	18	70
1.7	2000	60	21	80
1.8	1000	40	24	90
1.9	900	20	27	100
2.0	800	10.0	30	200
2.1	700	8.0	33	300
2.2	600	6.0	36	400
2.3	500	4.0	39	500
2.4	400	2.0	42	600
2.5	300	1.00	45	700
2.6	200	0.80	48	800
2.7	100	0.60	51	900
2.8	90	0.40	54	1000
2.9	80	0.20	57	2000
3.0	70	0.10	60	3000
3.1	60	0.080	63	4000
3.2	50	0.060	66	5000
3.3	40	0.040	69	6000
3.4	30	0.020	72	7000
3.5	20	0.010	75	8000
3.6	10	0.008	78	9000
3.7	9	0.006	81	10 000
3.8	8	0.004	84	20 000
3.9	7	0.002	87	30 000
4.0	≤6	≤0.001	≥90	≥40 000

ceived most of the attention as potentially environmentally hazardous pesticides (Table 3). These chemicals have the highest values in the table. All have values in excess of 11.6, and most are 14.0 or greater. All are moderately hazardous to hazardous in toxicity to rats and fish, long-lived, and slightly to highly accumulative. All of the chlorinated hydrocarbons are immobile in the soil, but their mobility in air varies greatly from relatively nonvolatile chemicals such as DDT and endrin to moderately volatile ones such as lindane. The mean toxicity value for the chlorinated hydrocarbons is 13.7.

Organophosphorus insecticides are generally more toxic to man, and, therefore, more hazardous to use than are the chlorinated hydrocarbons. However, their overall relative toxicity is much lower (Table 3). They are less toxic to fish than the chlorinated hydrocarbons are, and, because of their higher water solubilities, they bioaccumulate much less. Although they are much more water-soluble, they have a strong tendency to complex with soil colloids, and thus are not much more mobile than are the chlorinated hydrocarbons.

The greatest safety feature of the organophosphorus insecticides, however, is their rapid degradability. They control the pest and then dissipate readily. The relative toxicities for the organophosphorus compounds is 8.8, which is about one-half that for the chlorinated hydrocarbons.

The carbamate insecticides carbaryl and carbofuran (also a fungicide) have toxicity values of 6.6 and 8.9, respectively. Thus, they are similar to the organophosphorus insecticides in their environmental hazard potential (Table 3).

The fungicides captan and copper sulfate have toxicity values

of 6.0 and 9.7, respectively (Table 3). Because of the permanent nature of copper sulfate, however, constant and continued use would not be desirable. Ethylmercury chloride is no longer used as a fungicide seed treatment; according to this scheme, it has a toxicity value of 12.7.

Toxicity values for selected triazine, organic acid, and miscellaneous herbicides range from a low of 5.1 for dalapon and dicamba to a high of 9.2 for prometon. Most of the herbicides have toxicity values slightly lower than those of the organophosphorus and carbamate insecticides, and less than one-half of those of the chlorinated hydrocarbons. The triazine and organic acids have mean toxicity values of 7.7 and 6.7, respectively.

The evaluation scheme shows that the chlorinated hydrocarbon insecticides have a much greater potential hazard to the environment than either the organophosphorus or carbamate compounds. It also shows that ethylmercury chloride, which was once marketed as a seed treatment, also presented a relatively high potential environmental hazard.

On the other hand, toxicity values for the organic herbicides rank them on a level considerably lower than most of the insecticides. It becomes apparent from these comparisons that the new generation of pesticides are more environmentally safe than the older chemicals.

#### The rating scheme

A scheme was devised to compare the relative toxicities and environmental safety of agricultural pesticides. The scheme is based on the sum of four key factors:

TABLE 3

**Relative toxicities of selected pesticides**

Common name	Toxicity to rat	Toxicity to fish	Longevity	Bioaccumulation	Total
<b>Chlorinated hydrocarbons</b>					
Aldrin	3.2	3.9	4.0	3.1	14.2
DDT	2.7	3.7	4.0	4.0	14.2
Dieldrin	3.1	3.9	4.0	3.0	14.0
Endrin	3.5	4.0	4.0	2.8	14.3
Lindane	2.7	3.4	4.0	1.5	11.6
Mean value	3.0	3.8	4.0	2.9	13.7
<b>Organophosphorus chemicals</b>					
Azinphosethyl	3.5	3.4	1.2	1.0	9.1
Dichlorvos	3.0	2.7	1.3	1.0	8.0
Disulfoton	3.9	3.3	1.1	1.0	9.3
Malathion	1.8	3.2	1.1	1.0	7.1
Parathion	3.6	3.3	1.3	1.0	9.2
Phorate	4.0	3.7	1.1	1.0	9.8
Mean value	3.3	3.3	1.2	1.0	8.8
<b>Carbamates</b>					
Carbaryl	2.1	2.4	1.1	1.0	6.6
Carbofuran	3.6	2.9	1.4	1.0	8.9
Mean value	2.8	2.6	1.2	1.0	7.6
<b>Triazines</b>					
Ametryn	1.8	2.4	1.2	1.0	6.4
Atrazine	1.7	2.0	3.6	1.0	8.3
Cyanazine	2.5	2.5	1.2	1.0	7.2
Prometone	1.7	2.5	4.0	1.0	9.2
Mean value	1.9	2.3	2.5	1.0	7.7
<b>Organic acids</b>					
Dalapon	1.5	1.5	1.1	1.0	5.1
Dicamba	1.8	1.0	1.3	1.0	5.1
Endothall	2.9	2.5	1.1	1.0	7.5
Picloram	1.1	2.4	3.6	1.0	8.1
2,4-D	2.4	1.4	1.1	1.0	5.9
2,4,5-T	2.5	2.8	1.4	1.0	7.7
Mean value	2.0	2.1	1.6	1.0	6.7
<b>Miscellaneous</b>					
Alachlor	1.7	2.0	1.3	1.0	6.0
Bromacil	1.4	1.6	2.5	1.0	6.5
Captan	1.0	3.0	1.0	1.0	6.0
Copper sulfate	1.7	3.0	4.0	1.0	9.7
Diuron	1.6	2.3	2.7	1.0	7.6
Ethylmercury chloride	3.3	2.4	4.0	3.0	12.7
Pyrazon	1.6	1.8	1.2	1.0	5.6
Maximum value	4.0	4.0	4.0	4.0	16.0
Minimum value	1.0	1.0	1.0	1.0	4.0

- acute oral toxicity to rats
- acute oral toxicity to fish
- longevity
- bioaccumulation

It turned out that DDT and the chlorinated hydrocarbons have toxicity values of approximately 14.0, while organophosphorus and carbamate insecticides have values ranging from 7 to 10. Most of the herbicides have toxicity values of 7 or lower. Ethylmercury chloride, a fungicide that is no longer marketed, has a value of 13. Thus, the general indication is that all of the newly developed pesticides are much more environmentally safe than are the older chemicals.

**Additional reading**

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# Surveying Massachusetts' hazardous wastes

A recent inventory not only documented these materials by categories, but also uncovered ways of improving the management of these substances within the state

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In the field of environmental technology, the disposal of hazardous industrial waste has been a dormant issue that has recently been activated by the passage of the Resource Conservation and Recovery Act. One provision of this new law calls for each state to develop a hazardous waste management plan, the first step of which is a hazardous waste inventory. The Commonwealth of Massachusetts has made a significant head start in this direction.

Since 1970, Mass. has had a hazardous waste regulatory program; recently it completed a statewide hazardous waste inventory.

## Regulating hazardous waste

Legislation to control the handling and disposal of hazardous wastes was adopted in Massachusetts in 1970. This law established a Hazardous Waste Board, comprised of the members of the Water Resources Commission and the Commissioner of the Department of Public Safety. The Division of Water Pollution Control (DWPC) is to administer the regulations adopted by the Board.

The regulations:

- define wastes that are considered hazardous
- specify methods for the handling and disposal of such materials
- require that any firm engaged in their conveyance, handling or disposal be licensed by the DWPC.

The Mass. regulations do not contain an itemized list of specific materials by their chemical names, but rather define "hazardous wastes" as any "... waste substances which, because of their chemical, flammable, explosive, or other characteristics constitute or may reasonably be expected to constitute a danger to the public health, safety, or welfare or to the environment." Further, the regulations establish categories of hazardous materials and describe in broad terms allowable disposal methods for each category.

The categories are arranged into four classes—hydrocarbon liquids; aqueous liquids; solids and sludges; and special hazards. Typical categories include waste oils (the largest volume of hazardous materials covered by the regulations); solvents and chlorinated oils; plating and pickling waste; metal hydroxide sludges; oily solids; explosives; reactive metals; pesticides; waste cylinders of gas; and other compounds assigned a hazard rating of No. 2 or greater in the National Fire Prevention Association identification system. To date, this classification system has proven adequate in bringing those materials needing special control under the legal authority of the regulations.

The Division's licensing activities include review of applications, inspection of equipment and disposal sites, and monitoring of operating reports, which each collector or disposal facility must submit on a monthly basis. Because many disposal methods are subject to air quality standards or rules regulating the operation of sanitary landfills, coordination of activities with other state agencies is necessary. In addition, the regulations require that any disposal of wastes outside of Mass. be approved by the appropriate environmental agency of the receiving state.

Licenses, which must be renewed annually, specify which types of materials may be handled, and indicate whether licensing is for conveyance, storage, disposal, or any combination of these. Currently, about 100 firms hold hazardous waste licenses. Over half of these provide only collection of wastes, or collection and storage only, and must rely on other licensed firms for ultimate disposal. Approximately 20 of the licensed companies are located outside the state.

Two factors have limited the effectiveness of the hazardous waste program in the past. The first has been lack of sufficient manpower to ensure strict enforcement of the rules. Recent reassignment of Division personnel to hazardous wastes and the creation of two new engineering positions under a grant from EPA's Solid Waste Management Program have significantly improved this situation.

The second, more important problem, is the lack of suitable disposal options within Mass. for certain types of wastes, particularly hazardous solids and sludges that require a secure chemical landfill. Although there are several reasons for this dearth of options, the net result has been economic hardships to industry caused by long-distance transportation and the use of illegal or questionable disposal methods.

As a first step toward resolution of the problem, the DWPC in 1976 engaged GCA/Technology Division to perform a hazardous waste survey and to recommend improved methods of hazardous waste management based on the survey results.

## Reviewing state files

The primary effort in the survey was to improve the data base. To satisfy this objective the project was designed to:

- estimate the quantities of hazardous waste generated by categories and geographic distribution by using a telephone survey in conjunction with personal visits to selected industries
- identify disposal and recycling options available for improving the present manner of disposing of hazardous wastes



TABLE 1

## Hazardous waste volumes reported by licensed haulers in 1975, gal/y

Hazardous waste	Volume handled			Disposal method						
	Picked up	Delivered	Difference	Reclaimed	Burned	Landfill	Dust control	Wastewater treatment	Asphalt plants	Other
Waste oil	13 329 000	12 664 000	665 000	3 046 000	6 917 000	500 000	1 715 000	—	486 000	—
Solvents	2 602 000	1 819 000	783 000	1 544 000	223 000	34 000	—	—	—	18 000
Aqueous liquids	2 009 000	1 847 000	162 000	—	—	10 000	—	1 830 000	—	7 000
Solids and sludges	834 000	1 804 000	-970 000	—	740 000	1 009 000	—	—	—	55 000
Other	144 000	145 000	-1000	—	78 000	67 000	—	—	—	—
<b>Total</b>	<b>18 918 000</b>	<b>18 279 000</b>		<b>4 590 000</b>	<b>7 958 000</b>	<b>1 620 000</b>	<b>1 715 000</b>	<b>1 830 000</b>	<b>486 000</b>	<b>80 000</b>

• recommend disposal options on an immediate (3 months to 1 year) and long-term (1-5 y) basis.

The first step was to review the DWPC's files containing the annual permit applications and monthly reports from the waste haulers licensed and operating in Mass. The data from the permit files provide a lower limit with which to compare the results of the next phase of the project, a survey of state industries with respect to their waste quantity and disposal methods.

For each licensee, the quantities of each class of hazardous waste handled in 1975 were obtained by adding the amounts reported for each month. Table 1 summarizes these findings. A major problem encountered in reviewing the hazardous waste files in their present form is that the origin of the wastes is almost never reported and the delivery to another licensee or to a recycling/disposal facility may not be specified on each monthly report. Rather, many reports state that the wastes will be delivered to any of several alternatives that are listed on their annual permit applications. Such a system hinders the tracing of individual waste streams; nevertheless, best estimates for the disposal/recycling fates of the five classes of hazardous wastes are also displayed in Table 1.

Of the 13 329 000 gal of waste oil picked up, approximately 6 917 000 gal, or 52% are burned, either as fuel or in an incinerator. Another 1 715 000 gal or 13% are used for dust control

on roads and 486 000 gal (4%) are delivered to asphalt plants. Only 3 046 000 gal or 23% are reclaimed, while 500 000 gal or 4% are landfilled. The landfilled oils are primarily derived from spills and usually contain the absorbing media.

Solvents are reclaimed (59%), burned (9%), or landfilled (1%). Most of the 783 000 gal (30%) not accounted for is solvent sludge or distillation bottoms that are incinerated or landfilled.

Most of the aqueous chemicals picked up are treated and then discharged to sewers. A small percentage (0.5%) is reported being buried directly in a landfill. Solids and sludges are landfilled (56%), or, in the case of sludges from oil tanks or solvent reclamation, burned (41%).

Of the 1 620 000 gal of hazardous materials reported as being hauled to landfills, 503 910 gal (31%) are taken out-of-state. Forty-four percent or 713 020 gal of hazardous wastes were disposed of in Mass. landfills that today are not licensed to accept these wastes.

#### Surveying industries

To supplement the data in the DWPC files and to provide a better understanding of the flow of hazardous wastes within the state, a survey of the amount, geographic distribution, and current disposal practices was organized.

Types of industries that would be expected to generate haz-

TABLE 2

## The distribution of hazardous wastes among selected industrial categories

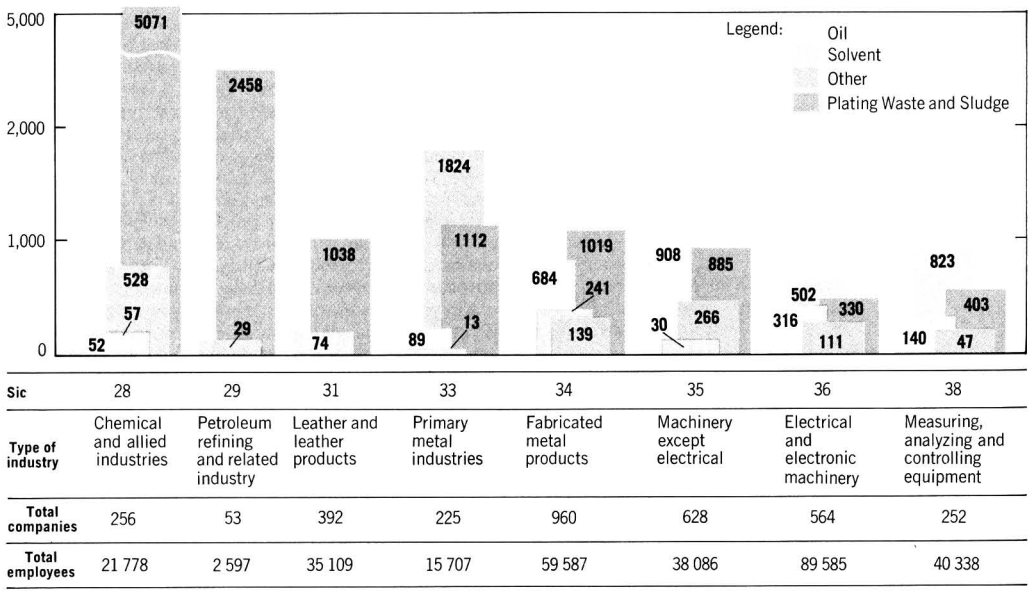
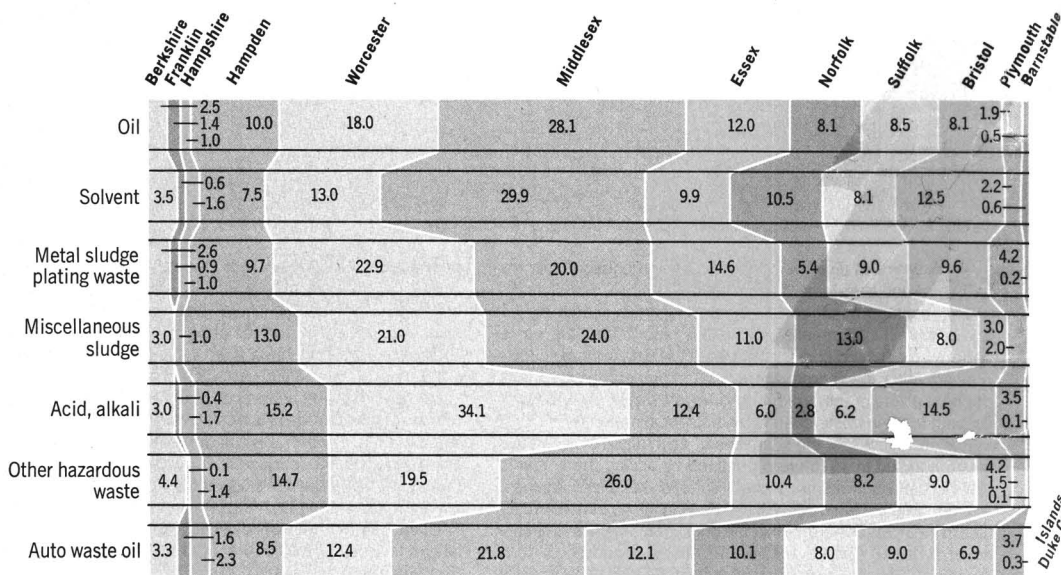


FIGURE 1

## Geographic distribution of hazardous wastes by percent



ardous wastes were identified. *The Massachusetts Industrial Directory 1974-1975*, which lists industries by Standard Industrial Classification (SIC), was used to identify the companies and number of employees within each selected SIC.

The plant manager or the environmental engineer from each facility was contacted by telephone and questioned about the types of wastes generated by his plant. Several industries (Table 2) were reluctant to release detailed information, but were willing to discuss their wastes in terms of broad classes, such as waste oils, solvents, acid, and sludges.

In all, 446 plants completed the verbal questionnaire. These account for 9.2% of the 4868 plants listed in the industrial categories selected for this survey and represent 45.4% of the employees in these industries. Ninety-one plants were either unable to estimate waste quantities or could not be contacted in follow-up calls.

Most of the information provided to the survey represents a "best guess." In many cases, exact quantities of wastes generated were unknown, but waste volumes were estimated based on factors such as number of pickups per year, size of storage tanks, and quantities of new materials used.

The data collected during the survey were extrapolated to yield statewide totals on the basis of number of employees in each industrial category. In order to represent the industries as accurately as possible, these extrapolations were performed at the 3- or 4-digit SIC level. The extrapolation procedure also assumes a linear relationship between wastes generated and number of employees. These assumptions may introduce errors and the estimates presented here are best treated as lower limits, accurate probably to within a factor of 2 or 3.

The major part of our survey dealt with hazardous waste material from manufacturing (or related) industries, but also included in the project were surveys of special classes of hazardous wastes such as automotive waste oil, fly ash from power plants, polychlorinated biphenyls (PCB's), and pesticides. These wastes were estimated from published and unpublished generation factors and discussions with key industrial and regulatory officials.

In all, 37 750 000 gal of hazardous wastes are generated each year in Mass. Of this, 18.5 million gal are waste oil, 9.2 million gal are sludges, 4.0 million gal are plating wastes and metal-containing sludges, 2.7 million gal are solvents, 2.3 million gal are acids and alkalis and 0.8 million gal are other hazardous wastes. Table 2 summarizes the distribution of hazardous waste among the various industrial sources. Waste oils from automobiles account for 83% of the state's total waste oil. Fabricated metal products and machinery are the major industrial sources, contributing 9%.

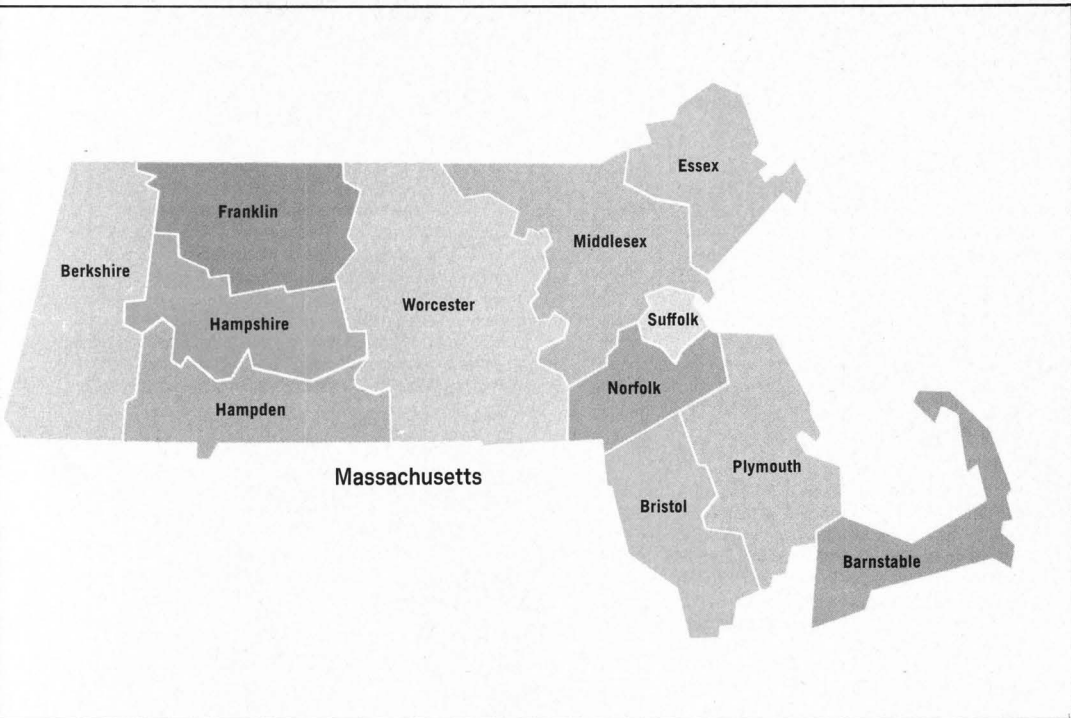
Solvents are used primarily by the electronics industry, SIC 36, and by miscellaneous industries such as jewelry and silverware manufacturers, SIC 39. Approximately 41% of the total state solvent waste is generated by these two industrial classifications.

As anticipated, metal sludges and plating wastes are generated primarily by three industries: primary metals, fabricated metal products and machinery, except electrical. The combined waste from these three classes is approximately 75% of the total metal sludge and plating waste in the Commonwealth.

Acid and alkali waste are produced almost solely from the primary metals industry, which produces approximately 80% of the state total for this type of waste. These reactive materials are used for cleaning and plating metals.

Miscellaneous sludges are mostly generated by the chemical industry. They contain numerous types of organic and inorganic components and account for 60% of the miscellaneous hazardous sludges generated in the state. Paper, printing, and textile industries generate large quantities of nonhazardous sludge.

The last major category, other hazardous waste, represents undefined wastes reported during the survey, as well as wastes that do not fit into the other five categories. Almost 60% of these wastes are generated by the chemical industry. Fabricated metals, electrical equipment, and miscellaneous manufacturing industries together generate 34% of the unclassified wastes that may include photographic chemicals, resins, inks, and polymer solutions. Most of the hazardous wastes generated by the paper and printing industries are waste inks.



In Table 3, the survey results are compared to the state permit data. The last column in the table provides the percentage of the hazardous types that the state has identified through its permit system. Note that the first three categories are readily reported—waste oils and solvents—because of their current recovery value, and aqueous liquids because of the relative ease of handling and disposal. The problems in regulating disposal of sludge and other types of waste are self-evident.

Figure 1 shows the geographic distribution of hazardous wastes generated throughout the Commonwealth on a county-wide basis. Not unexpectedly, the metropolitan areas around Boston, Worcester, Springfield, and New Bedford have the greatest quantities.

Several states have published the results of their hazardous waste surveys. Table 4 compares our survey results with those obtained in Arizona, Minnesota, Oregon, and Washington. Surprisingly close correlation is found in the ratio of industrial wastes to manufacturing employees, despite differences in the mix of industries.

#### Disposal and recycling options

The severity of the hazardous waste disposal problem is most evident with respect to sludges: There are no disposal sites within the state that are currently licensed to accept these materials. Some of these materials are being shipped to out-of-state disposal sites or waste recycling/disposal firms, but most are either being temporarily stored in company facilities or disposed of illegally. Because of the distances involved, out-of-state shipment is economically practical only for large quantities of wastes. The survey confirmed the difficulties that small waste-generating industries have in disposing of their waste sludges.

Many sludges could be landfilled within the Commonwealth if an acceptable site were available and licensed. This survey indicated that a total of approximately 13 million gal of potentially hazardous industrial waste sludges are generated per year. If these sludges (assumed to contain 10% solids) were dewatered to an 18% solids concentration (as required for disposal of

municipal treatment sludges to conventional landfills), the resulting sludge volume would be on the order of 1.0 million cubic feet (7.2 million gal). This volume of sludge would occupy only about 1 acre per year, if landfilled to a depth of 20 ft (no allowance for earth fill or cover). Small sections of existing landfills, if modified for accepting hazardous waste, would be adequate, at least over the next 1–5 years, until new facilities can be built.

With respect to solvents and waste oils, for which the preferred disposal method is reclamation or reprocessing, the capacity of Mass. firms alone is not sufficient to handle the quantities of waste materials generated within the state. For solvents, an estimated 2.8 million gal/y are generated, while in-state reclamation capacity is on the order of 1.3 million gal a year. Similarly, annual waste-oil generation is estimated at 18 million gal/y compared to an in-state reprocessing capacity of about 5 million gal annually. Despite this excess of waste oil and solvents, local reprocessors are still running considerably under capacity because of competition for waste oil and solvents from

TABLE 3  
Survey results vs. licensed hauler permit data, gal/y

Waste material	Survey results	Permit data	Percentage identified permit data
<b>Waste oil</b>	18 313 000	13 329 000	73
<b>Solvents</b>	2 784 000	2 602 000	93
<b>Aqueous liquids</b>	2 293 000 <sup>a</sup>	2 009 000	88
<b>Solids and sludges</b>	13 928 000 <sup>b</sup>	834 000	6
<b>Other</b>	756 000	144 000	19
	38 074 000	18 918 000	50

<sup>a</sup> Acids and alkalies only.

<sup>b</sup> Includes plating solutions (770 000 gal).

rerefiners in other states, as well as from other firms who burn waste oil directly as a fuel or apply it for dust control. More than 70% of the waste oil and solvents are disposed of in an acceptable manner. The current economic value of these wastes probably goes far in explaining their relatively high pickup rate.

Most of the disposal sites outside of Mass. are running well below capacity despite the strong need for adequate disposal facilities. One of the primary reasons for this is the cost of transportation. The smaller waste generators simply cannot afford to ship to some of these facilities. A potential solution for alleviating this waste disposal problem is the development of private industrial transfer stations. A transfer station is simply a centrally located area that receives, for a fee, wastes from surrounding industries. When a truckload of economic size (usually 2000–4000 gal bulk) has accumulated, wastes are removed to the out-of-state disposal firms by an independent hauler or by the disposal firms themselves. Two private transfer stations have recently begun operating in the state and the initial response is encouraging.

### Recommendations

Concerted action must be taken with respect to the management of hazardous waste disposal. In Mass. the severity of the problem is most evident with respect to hazardous sludges—there are no landfills within the state that are now licensed to accept these materials. Some of these materials are being shipped to out-of-state disposal sites, some are being temporarily stored in company facilities, but considerable amounts are being disposed of improperly and illegally.

The following recommendations, if implemented, could improve control of hazardous waste disposal in the state. The state must continue to refine its approach to hazardous waste management. The new Resource Conservation and Recovery Act of 1976 calls for the development of state-wide hazardous waste-management plans, but in many cases, the implementation of these plans will require legislative changes that can sometimes be painfully slow.

To alleviate the problem, action is required on two levels: steps that can be implemented immediately (3 months–1 y) and steps that can be implemented over a longer range (1–3 y).

Steps that can be implemented immediately include the following:

- consolidate authority for the hazardous waste program
- modify several existing landfills to accept hazardous waste
- enforce existing hazardous wastes regulations more strictly
- encourage use of transfer stations
- promote better waste-oil disposal practices
- develop public relations and educational programs.

The basic long-term recommendation is to develop a state-wide hazardous waste-management plan as required by the Resource Conservation and Recovery Act. This would address topics such as number and type of waste facilities needed, criteria for disposal site selection, schedule for developing new facilities, and manpower requirements for increased enforcement. As part of this management plan, a stricter enforcement program should be focused around a waste manifest system that requires waste generators, haulers, and disposers to file monthly reports on their hazardous waste quantities, destination, and final disposal.

### Additional reading

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TABLE 4

### Comparison of Mass. survey results with other states

State	Industrial wastes		Ratio of industrial waste to number of manufacturing employees, gal/y-person
	Industrial hazardous wastes, gal/y	No. of manufacturing employees	
Massachusetts	22 135 000	618 000	36
Arizona	12 387 000	(1460 manufacturers)	—
Minnesota	11 886 000	343 000	35
Oregon	7 717 000	197 000	39
Washington	13 390 000	252 000	53
State	Automotive waste oil		Per capita automotive waste oil, gal/y-person
	Automotive waste oil, gal/y	Population	
Massachusetts	15 435 000	5 800 000	2.7
Minnesota	6 000 000	1 914 000 <sup>a</sup>	3.1
Oregon	8 004 000	2 219 000	3.6

<sup>a</sup> 1970 population for the eight counties surveyed.

Coordinated by LRE

# The Army's drinking water surveillance program

Last year, 53 chemical and physical parameters were analyzed from 827 water sources from installations throughout the world; medically significant constituents exceeding acceptable limits are flagged and, if necessary, the water source is closed down

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In July 1970, the Public Health Service (PHS) released a report entitled "Community Water Supply Study, Analysis of Survey Findings." This report concluded that increased population and industrial development caused surface and groundwater pollution; a significant percentage of community water systems did not meet the minimum drinking water standards established by PHS in 1962, and chemical surveillance of drinking water sources was inadequate. Several years later, the "Safe Drinking Water Act," enacted by Congress in December 1974, made chemical surveillance of drinking water sources to assure compliance with standards federal law.

Until 1972, chemical surveillance of Army drinking water sources had periodically been conducted by the U.S. Geological Survey on a contractual basis for the Army Corps of Engineers. As a consequence of the PHS report, the Surgeon General of the Army charged the U.S. Army Environmental Hygiene Agency (USAEHA) in July 1972 with the mission of monitoring the quality of drinking water. Chemical analyses, number of sources to be monitored, and the establishment of an analytical quality-assurance program were efforts undertaken to upgrade surveillance.

## Surveillance program

Under the auspices of the U.S. Army Drinking Water Surveillance Program (USADWSP), water samples are collected annually from Army installations in the U.S., Puerto Rico, the Panama Canal Zone, Alaska, the Pacific area, and Asia. Both ground- and surface-water sources, treated and untreated, are sampled. For example, in calendar year 1976 a total of 827 sources were sampled (Table 1).

Surface-water sources are sampled and analyzed annually for 53 chemical constituents (minerals, nutrient, metals, pesticides and radiological analyses), and physical parameters that are grouped according to type and complexity of analysis, container, and preservation requirements. Groundwater sources are sampled and analyzed annually for all of the above constituents, excluding pesticides, which are determined on a triannual basis.

Collected samples are forwarded by mail to regional USAEHA laboratories where respective general analyses are performed. These analyses are conducted at the regional laboratory in order to minimize the time interval between collection and analyses and, hence, sample deterioration. Portions of samples are forwarded by the three regional laboratories to the main USAEHA laboratory for the more complex metals, pesticides, and radiochemicals analyses.

## Information transfer

Analytical data are collected and stored on IBM computer cards. A separate card is used for each analysis and a deck of cards corresponds to a total sample analysis. On the computer cards, each water source is identified by a six-digit installation code and by an alpha numeric code designating the respective water source as a numbered raw, treated, surface, ground or mixed source. Upon completion of the general analyses, the regional laboratory forwards the data cards to USAEHA for processing.

All samples and data cards are received, unpacked, logged, numerically labeled, and distributed by USAEHA's Analytical Reference and Quality Assurance Division to various analytical chemistry laboratories at USAEHA for specific analyses. Metal analyses are performed by the Environmental Chemistry Division (ECD), pesticide analyses by the Pest Management and Pesticide Monitoring Division (PMPMD) and radiochemical analyses by the Radiological and Biological Chemistry Division (RBCD).

Coordination of the Army's surveillance program is performed by Analytical Reference and Quality Assurance Division (ARQAD) as shown in Figure 1. Upon completion of the required analyses and confirmation of the data by ARQAD, the samples and containers are discarded. The data are collated by ARQAD into completed sample decks and forwarded to the Data Processing and Technical Information Branch (DP&TIB) for key-

punching, programming, and printout. A condensed final report for a water source is pictured in Figure 2.

To aid in interpretation of the engineering and medical aspects, the constituents are categorized as operational management, aesthetic acceptability, indicator anion, and medical acceptability. In a column adjacent to the observed analytical results, reference concentrations are printed for guidance in the interpretation of the observed results. These reference concentrations are based on the 1962 PHS standards, as revised by the U.S. EPA, with the exception of those listed for gross alpha, gross beta, and chromium; analytical procedures for these are utilized for screening purposes for radium-226, strontium-90, and chromium (VI), respectively.

The ratios of observed constituent concentrations to the reference concentrations (where applicable) are calculated and listed as percentages. All values of 100% or more initiate a "flagging action" and cause an asterisk to be placed adjacent to the constituents' names. Completed printout reports are checked by ARQAD and forwarded to the Water Quality Engineering Division (WQED) for interpretation and followup action as needed. Copies of each report are forwarded by WQED to the regional laboratories along with an interpretation of the potability or safety of the drinking water. The regional laboratories, in turn, distribute the reports to installations.

TABLE 1

### Categories of Army drinking water sources, 1976

Raw surface	49
Treated surface	75
Raw ground	432
Treated ground	237
Treated mixed	34
	<hr/>
	827

If a flagging action occurs in the category of medical acceptability for any water source, recollection is initiated and a larger sample is taken for constituent analyses. If, upon repeated analysis, the concentration of a constituent in the medical acceptability category again exceeds the reference concentration, WQED begins extensive sampling and analyses of the water source and a survey of the water system and population affected. As a result of such investigation, the water source may be declared nonpotable and the source closed or a treatment process recommended.

#### Quality-assurance program

The large amount of data generated from analyses of drinking water samples are interpreted by medical and engineering personnel with respect to health, environment, and equipment operation. Health-related aspects are considered most important. Of secondary significance are data used to assess the status of treatment and purification systems. In order to allow correct decisions to be made from the interpretation of reports, a viable analytical quality-assurance program is a major part of the surveillance program. The quality-assurance program includes:

- utilization of standard analytical procedures
- laboratory accreditation
- intra-laboratory quality control
- proficiency analytical testing
- external quality control
- anion/cation balancing of sample analytical data
- automated data transferral systems
- laboratory consultation visits and training
- calibration service

In Table 2 are listed some of the parameters measured and the detection limits established in the surveillance program. Measurement procedures are those analytical methods found in **Standard Methods for the Examination of Water and Wastewater**. For the chemical constituents in the category of medical acceptability, it is most important that the detection limits be less than the respective reference limits.

Accuracy (closeness of results to true values) and precision (reproducibility of results) guidelines have been established for those constituents found to be relatively stable in aqueous solution. These guidelines are also detailed in Table 2; accuracy is expressed as relative error and precision as relative standard deviation. These guidelines represent average laboratory performances observed over a 1-y period. ARQAD monitors adherence by the main USAEHA and three regional laboratories to these guidelines and detection limits.

Under this surveillance program, the metals and radiation laboratories participate in the accreditation program conducted by the American Industrial Hygiene Association and sponsored by the National Institute for Occupational Safety and Health (NIOSH). The accreditation provides assurance that these analytical laboratories are state-of-the-art.

#### Quality control, testing

There are many procedures that can be performed daily by a laboratory to enhance analytical performance and all can be grouped under the heading "intra-laboratory quality control." These procedures include date labeling of reagents, cleanliness of laboratories, preparation of the more unstable chemical working standards on a daily basis, proper standardization and frequent preventive maintenance of analytical equipment. The list is long and can be found in manuals published by U.S. EPA and NIOSH. Suffice to say, ARQAD promotes the use of analytical quality-control charts described in these manuals.

Duplicate results from daily repetitive analyses of a stable sample are plotted in terms of mean and range. The constituents measured for this purpose are those routinely analyzed by the various laboratories at concentrations generally encountered in the surveillance program, or concentrations equivalent to or near the health reference levels. Initial repetitive measurements are used to establish statistical control limits about the average observed concentration, and the mean range of the sets of duplicate results. The control limit values represent standard deviations about a normal distribution of results from repetitive analyses of the same sample.

Detailed contingency plans for checking instrument operation, and analytical methodology are then devised for results that fall outside of the control limits. For the pesticide laboratory, the control sample turns out to be a large volume (6 L) of aqueous solution of various pesticides (DDT, dieldrin, heptachlor epoxide and lindane) known to be stable in water for long periods. The control samples used by the other laboratories are similar in terms of volume and medium, but differ in constituents according to the analyses performed by the laboratories.

The quality-control charts are valuable in that their use allows the surveillance program laboratories to control a wide variety of systematic and random error sources in analytical systems. Daily obtaining of results within the statistical limits documents the correct operation of instruments, reagents, and techniques. Proficiency analytical-testing services are provided for the regional laboratories by ARQAD on a quarterly basis. Ampoules of concentrated controls consisting of chemical constituents categorized as general analyses are prepared, measured by ARQAD for confirmation purposes and distributed quarterly to all analysts in participating laboratories. The analysts, unaware of the true concentrations, perform quantitative analyses and report subsequent results to ARQAD. The results are statistically analyzed for accuracy and precision, and reports evaluating performances of the analysts are returned to the participating scientists.

Those constituents for which survey results indicate excessive error are identified and analytical operations for the constituents are stopped until the problems are resolved.

For pesticides and radiochemicals, proficiency testing services are provided by the U.S. EPA. Standards consisting of radioisotopes in water are distributed bimonthly by the agency's radiochemistry quality-control laboratory in Las Vegas. ARQAD then distributes them to the radiochemistry laboratory. The analytical results are forwarded to EPA for statistical treatment and comparison with numerous other laboratories; EPA then sends a report of findings to ARQAD for distribution. Pesticide standard solutions are also received occasionally from EPA as part of collaborative studies, and ARQAD coordinates the participation of the pesticide laboratory. For the Army's Environmental Hygiene Agency laboratories, ARQAD independently determines the accuracy and precision of the various analytical systems. The accuracy and precision guidelines in Table 2 are utilized by ARQAD to assess the quality of analytical data generated under the Army's surveillance program.

The samples collected by regional laboratories arrive each month at USAEHA for distribution to the pesticide, metal, and radiochemistry laboratories. The batches generally contain

50-60 samples for each laboratory. Prior to sample distribution, chemical controls are prepared and distributed to the laboratories together with the samples. After analysis by the respective laboratories, the control data are returned to ARQAD for review. If the control data are in agreement with accuracy and precision guidelines, then the corresponding sample data are sent to DP&TIB, which compiles the final report. If the control data are inaccurate or imprecise, the respective laboratories are consulted and the particular batch of samples is reanalyzed after resolution of analytical discrepancies.

#### Anion/cation balancing

Validation by ARQAD of the quality of the data received from the regional laboratories is accomplished in a different manner as geographical separation from USAEHA prevents the use of chemical controls with the incoming samples. Advantage is taken of the fact that concentrations of negatively and positively charged ionic species in water must balance to zero. All of the cations and anions normally found in relatively high concentrations in drinking water are included in the balance. This quality-assurance technique, termed "anion-cation balance", is described in **Standard Methods for the Examination of Water and Wastewater**. Limits of three standard deviations about zero are imposed on the regional laboratories. Forms for listing these standard deviations are provided to the regional laboratories, which then forwards them along with respective sample data to ARQAD.

#### Data transferral system

In any technical program involving a large amount of analytical data, an effective yet economical data transferral system is needed to minimize transcription errors. The present transferral system used in the Army's water surveillance program makes use of keypunching operations and data-acquisition systems available on some of the analytical instrumentation. Punched paper-tape data are converted by machine onto data cards, collated, and added to the pesticide, radiation, and general analyses data to complete sample decks.

A computer program has been designated to perform the anion/cation balance. Since regional laboratories have already balanced the data, failure of the data to balance under the computer program indicates keypunch errors that are subsequently corrected. The computer program also calculates total hardness values from calcium and magnesium concentrations and compares these results to the experimental values obtained by titration at the regional laboratories; specific conductance

FIGURE 1

### The water surveillance program

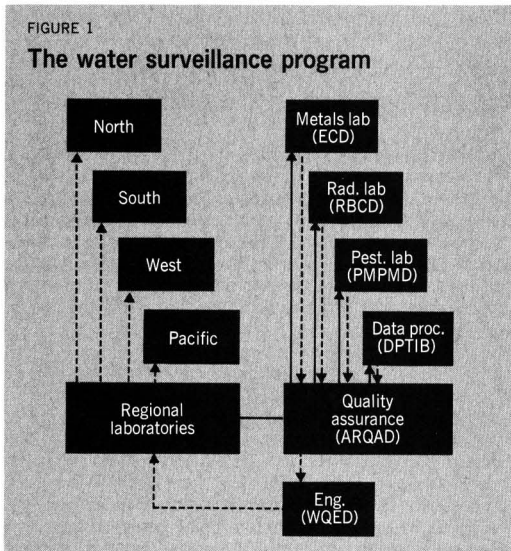


FIGURE 2

### Condensed report of a water sample

136969	ARMY INSTALLATION	SOURCE TYPE-TS	NUMBER-01	DATE COLLECTED-02 JUN 76
FLAG	CONSTITUENT	CONCENTRATION OBSERVED	REFERENCE	PERCENTAGE OBSERVED/REF
OPERATIONAL MANAGEMENT:				
	PH	(UNITS)	7.89000	
	HARDNESS, TOTAL as CaCO <sub>3</sub>	(MG/L)	75.90000	
	SPECIFIC CONDUCTANCE	(μMHOS)	257.00000	
AESTHETIC ACCEPTABILITY:				
	COPPER	(MG/L)	0.04300	1.00000 4
	IRON	(MG/L)	0.23000	0.30000 77
	MANGANESE	(MG/L)	0.02400	0.05000 48
INDICATOR ANION:				
	CHLORIDES	(MG/L)	20.20000	250.00000 8
	SULFATES	(MG/L)	32.00000	250.00000 13
MEDICAL ACCEPTABILITY:				
	ARSENIC	(MG/L)	0.01000	0.05000 20
	LEAD	(MG/L)	<0.00500	0.05000
	MERCURY	(MG/L)	<0.00020	0.00200
	NITRATES, AS NITROGEN	(MG/L)	0.25000	10.00000 2
	ENDRIN	(MG/L)	<0.00011	0.00020
	LINDANE	(MG/L)	<0.00002	0.00400
	GROSS ALPHA	(PC/L)	<0.50000	5.00000
	GROSS BETA	(PC/L)	3.50000	10.00000 35

TABLE 2

## Precision and accuracy observations

Parameter	Detection limit	Precision (Relative standard deviation, %)	Accuracy (Relative error, %)
<b>General (mg/L)</b>			
Boron	0.02	6	4
Hardness	1.0	1	4
Nitrate	0.1	4	4
Sulfate	2.0	4	9
<b>Metals (mg/L)</b>			
Calcium	1.0	3	5
Chromium	0.025	5	10
Lead	0.005	6	8
Sodium	1.0	4	3
<b>Pesticides (<math>\mu\text{g/L}</math>)</b>			
DDT	0.15	13	8
Dieldrin	0.06	10	16
Endrin	0.11	7	11
Heptachlor epoxide	0.04	10	2
<b>Radiochemical (pCi/L)</b>			
Gross alpha	0.5	23	11
Gross beta	0.7	11	3
Tritium	216.0	6	0

values are compared to total dissolved solid values; experimental total dissolved solid values are compared to dissolved solid values calculated to reflect the sum of all the constituent concentrations. Any discrepancies noted in the above data indicate keypunching errors that are corrected prior to the development of final reports.

#### Results of the surveillance program

Tabulated in Table 3 are the frequencies with which medically significant contaminants exceeded their health-reference concentration limits for total numbers of samples collected and analyzed each year. In general, it was program policy to sample the same drinking water sources each year.

The medically significant category includes radiation measurements, heavy metals, fluoride, nitrate, and pesticides. As reference limits are exceeded the problem constituents are asterisked (flagged) in final reports. These flags are the most significant results in the program as they indicate possible health problems related to drinking water sources. Most of the flags occur under the categories of radiation and heavy metal. Although a reference concentration of 3 picoCuries/liter (pCi/L) was established as the Public Health Standard for radium-226 in 1962, a reference concentration of 5 pCi/L for gross alpha radiation was used in the surveillance program. This policy was followed because of the proximity of the gross alpha detection limit to the PHS Standard.

Radiological activity, identified by flags in Table 3, appears to vary with geographic location; a majority of radiation flags tag water sources in the western part of the U.S. These radiation

flags were generated from gross alpha and beta screening determinations; no results for tritium were found to exceed the respective health-reference limit. Confirmatory analyses for radium-226 identified three groundwater sources as exceeding the health-reference limit. One source was found to contain radium-226 activities averaging 30 pCi/L; this high activity was attributed to natural activity and use of the source for human consumption was discontinued. The two other sources are currently being investigated.

Confirmatory analyses of those samples that exceeded the gross beta health limit did not identify any sources that exceed the health limit for strontium-90. This apparent discrepancy is explained by the fact that gross alpha and beta measurements are screening procedures and radiation from all alpha and beta emitters is counted. Radioactive isotopes of thorium, potassium, rubidium as well as strontium-90, radium-226 and their daughter products can contribute to gross alpha and beta activity.

The annual percentages of radiation flags to total number of sources ranged from 13–22%. This annual fluctuation for gross measurements can be attributed to variations in the number and location of water sources sampled each year, and also to the fact that so many different isotopes contribute to gross activity.

Of the metals considered to be medically significant, flags were obtained for mercury, chromium, lead, cadmium, silver, barium, and arsenic. The annual percentages of metal flags to total samples ranged from 30% in 1972 to 3% in 1976.

At the time of sample analyses the flagged results were validated by use of controls; however, upon recollection and an-

TABLE 3

## Frequency of medically significant contaminants exceeding health limits

	1972 <sup>a</sup>	1973	1974	1975	1976
Total number samples	140	762	838	746	827
Total number flags	75	230	237	169	226
Radiation (alpha and beta)	29	114	154	95	172
Metals (Hg,Cr,Pb,Cd,Ag,Ba,As)	41	74	55	41	18
Fluoride	3	22	19	21	31
Nitrate	1	2	5	6	5
Pesticides	0	0	0	0	0

<sup>a</sup> July–December



lays none of the flagged metals was found to exceed health levels and, in most cases, no metals were detected. Although the flagged data could indicate the transient existence of medically significant metals in a drinking water source, it is generally believed that the flagged results are due to contamination of samples. As these metals are sought at trace levels (0.2–50 ppb), contamination is a constant threat.

A small number of flags were obtained each year for nitrate measurements. Nitrate levels (10–15 mg/L) exceeding the health limit were confirmed for two drinking water sources. Use of these sources for human consumption has been discontinued. Recollection values for the other flags were below the health limit for nitrate, indicating either a transient existence of high nitrate levels or contamination.

Flags tagging high fluoride concentrations were found to be valid upon recollection and analysis. These results were attributed to high natural fluoride levels and the water sources are being treated with defluoridizers or personnel exposure to the source is being limited.

A small number of water sources were found to contain detectable pesticide concentrations. However, no pesticide concentrations were found to exceed the health limits.

#### Additional reading

Handbook for Analytical Quality Control in Water and Wastewater Laboratories, National Environmental Research Center, U.S. Environmental Protection Agency, Cincinnati, Ohio, June 1972.

Industrial Hygiene Service Laboratory Quality Control Manual, Technical Report No. 78, National Institute for Occupational Safety and Health, 1975.

Manual of Methods for Chemical Analysis of Water and Wastes, National Environmental Research Center, U.S. Environmental Protection Agency, Cincinnati, Ohio, EPA-625-/6-74-003, 1974.

Standard Methods for Examination of Water and Wastewater, APHA, AWWA, WPCF, Washington, D.C., 14th edition, 1976.



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**Sandra A. Costick** is a quality-assurance physical science technician with the U.S. Army Environmental Hygiene Agency. She processes the water samples, collates the analytical data, and coordinates with data processing for computer print-outs of results.

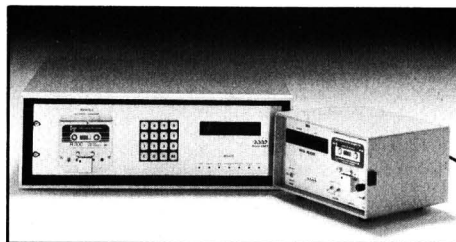
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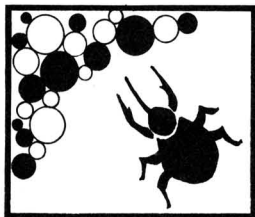


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# CURRENT RESEARCH

## Environmental Trace Metal Contamination in Kellogg, Idaho, near a Lead Smelting Complex

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■ Soil cores, grasses, and ambient air aerosols were sampled in the vicinity of a Pb smelting complex in Kellogg, Idaho. Of 34 elements analyzed by instrumental neutron activation and x-ray fluorescence, Cd, Sb, Ag, Pb, Au, Zn, Se, As, In, Ni, Cu, and Hg were the most highly enriched, ranging in surface soils up to 7900 ppm Pb, 29 000 ppm Zn, and 140 ppm Cd. For grasses, Pb ranged up to 10 000 ppm, Zn to 12 000 ppm, and Cd to 4400 ppm. Aerosol enrichments above contributions from local resuspended soils were 4100 for Cd, 180 for As, 110 for Pb, and 60 for Zn. These soil profiles, grass analyses, and aerosol enrichments indicate that other toxic elements, Cd, Se, As, Ni, and Hg, in addition to Pb, have significantly contaminated the Kellogg environment as a result of the smelting operations.

State air pollution control agencies are increasingly concerned with the environmental impact of trace metals since, in aerosols, they are an inhalation hazard to man and animals and a stress hazard to plants. Trace metals can also function as catalysts in secondary transformation of atmospheric pollutants, e.g., in converting SO<sub>2</sub> emissions into hazardous sulfates and sulfuric acid aerosols.

Trace metals are introduced to the environment from a variety of sources: industrial emissions, fuel combustion, incineration, and transportation. In this paper we report the results of a study carried out at a mining and smelting site in Kellogg, Idaho.

In 1974 it was reported (1, 2) that two Kellogg preschool children were treated for Pb poisoning and that 90% of the children subsequently tested showed abnormally high levels of Pb in their blood.

In 1976 the Shoshone Lead Health Project acknowledged that the center of abnormally high Pb concentrations in the Valley is the smelting complex. Although leaching and wind blown dusts from tailings piles still constitute an active source, the largest active source of contamination is airborne emissions from the smelting complex (3). However, the report did point out that the relative health significance of *current* emissions and *previously deposited* Pb has not yet been established (3). Furthermore, emissions, depositions, and effects of other toxic elements were not systematically studied.

We carried out multielement analyses of thirty 24-h high-volume (Hi-Vol) air particulate filters collected over a 12-month period in downtown Kellogg. To measure the soil concentrations and to evaluate the contribution of windblown soil and tailings to local aerosols, we took soil cores along with grass samples at 12 sites, and tailings and sinter samples at three sites.

Our results constitute the most comprehensive multielement aerosol, soil, and grass analysis for Kellogg, Idaho, published to date. Further analyses of soil and vegetation should provide the necessary data base for determining the levels and rates of heavy metal deposition. These data could

be used in an assessment of the resultant biological dose to man of toxic elements other than lead and, as such, are especially important because the synergistic effects of heavy metal aerosol exposure on humans in Kellogg have not yet been addressed. Preliminary results of our analyses have been presented previously (4-7).

**Area Description.** Kellogg, Idaho (Figure 1), is located in the heart of the nation's largest and richest mining district in the Coeur d'Alene River Basin in the panhandle region of northern Idaho. It has been the site of a heavy metals mining, smelting, and refining industry for the past 88 years. Lead, Zn, and Ag are the principal marketed metals, along with considerable quantities of Cd, Sb, and sulfuric acid. Located in the smelter complex in Kellogg are a concentrator, Pb smelter, electrolytic Zn plant, phosphoric acid/fertilizer plant, and sulfuric acid plant. The Pb smelter has been in operation since 1916, and the Zn plant since 1926. The operation employs about 2300 out of a population of 3900 in Kellogg.

The geomorphology of the valley is one of high, steep mountains (up to 6300 ft) enclosing a narrow ¼- to ½-mile-wide valley at an elevation of 2200 ft. The valley extends 6 miles in an east-west direction following the Coeur d'Alene River. The valley floor is filled in with river alluvium that may reach several hundred feet deep. Mine tailings and slag wastes that were discharged directly into the river before 1968 have formed a layer of silt over much of the valley floor downstream from the mining operations. These tailings have been used as land fill in various parts of the valley. The valley rocks are primarily from the Precambrian Belt, fine-grained argillites and quartzites.

The winds aloft follow a prevailing west-to-east pattern in the summer, switching over to an east-to-west pattern in the winter. A diurnal pattern for the ground-level winds is structured on top of the seasonal prevailing winds: westerly morning winds gradually becoming northerly and finally easterly in the evening. Inversion conditions occur frequently in the fall.

**Smelting Process.** The principal source of heavy metal aerosols in the ambient air is the main stack of the Pb smelter

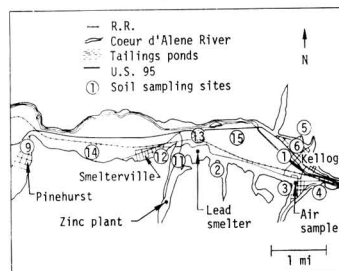


Figure 1. Map of Kellogg Valley showing sampling locations

(3). Average emissions of Pb from the main smelter stack were estimated to have been 8.3 metric tons per month from 1955 through 1964 and 11.7 metric tons per month from 1965 through 1973 (3). There are a number of steps in the smelting process that could also serve as sources of fugitive emissions. After the crude ores, principally PbS and ZnS, are crushed, screened, and blended, they are pulverized and dumped into flotation cells along with reagents. The Pb-bearing minerals are skimmed off as a froth. The other reagents are added, and Zn-bearing minerals are likewise separated.

The slurries are then dried, becoming concentrates that are mixed with crude ores and fluxes, and pelletized. These mixtures are roasted to remove S, creating sinter, which is fired along with coke in the lead smelter, forming Pb bullion and waste slag. Lead bullion carries along Cu, Au, As, Sb, and Bi. Zinc is then separated from the slag in a slag fuming furnace. Later the Cu, As, Sb, Ag, and Au are refined. The blast furnace and refinery area gases containing the metal oxides are conveyed via a flue to a baghouse where 2800 1.5 × 30 ft bags filter the dust. The collected dust is then treated to remove Cd and other metals. The Zn concentrates are refined in the electrolytic Zn plant. The SO<sub>2</sub> flue gases are captured in H<sub>2</sub>SO<sub>4</sub> units that are used in a H<sub>3</sub>PO<sub>4</sub> and (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub> fertilizer plant.

Other sources of metals related to the smelting operation include spills of concentrate from ore trains and trucks, re-suspended dust from tailings and sinter piles, and leaching of tailings piles.

#### Sampling and Analysis

**Sampling Procedures.** Air particulate samples were collected on top of the Kellogg City Hall by personnel from the

Idaho Department of Public Health at approximately 8-day intervals from January 29 to December 18, 1972. Whatman 4 filters were used with a recording flow meter and a 20 cm pump running for 24 h per sample, generally from 3:00 p.m. to 3:00 p.m. Mass loadings as determined by the Idaho Department of Public Health ranged from 60 to 251 μg/m<sup>3</sup>, as shown in Table I.

Soil cores (26 cm) were taken by driving a steel cylindrical corer, containing an interchangeable plastic liner, into the soil. Upon removal the liner was capped to protect the core.

Three core increments were analyzed: 0–2, 10–12, and 20–22 cm. The cores were air dried, and 50-g samples were ground to less than 200 mesh. Triplicate samples were analyzed; 25 mg were used for a short neutron irradiation and 200 mg were used for a long irradiation.

The grass samples were taken at the same locations as the soil cores. The grass samples were analyzed without washing to include the surface-deposited dust in the analysis. They were dried at 60 °C in a forced air oven and then ground.

**Neutron Activation Analysis.** Analyses of the trace elements of interest were performed with instrumental neutron activation analysis (INAA) and x-ray fluorescence analysis (XRFA). The INAA was performed by irradiating the samples in the 3-MW Livermore Pool-Type reactor (LPTR). Table II shows the irradiation and counting procedure that was followed.

For the 2-min irradiations, Ti flux monitors were irradiated simultaneously with the samples in pre-cleaned polyethylene vials and counted later. The flux monitors had been previously irradiated along with elemental standards for calibration. The elemental concentrations in the sample were calculated by

**Table I. Collection Data for Hi-Vol Samples Taken in Kellogg, Idaho**

Sample no.	Collection date	Total airflow, m <sup>3</sup>	Particulate wt, mg	Concn in air, μg/m <sup>3</sup>	% Day wind from west
2	01-29	1269	159.5	125.7	...
3	01-31	1390	135.1	97.2	...
4	02-07	1129	133.6	118.3	20
5	02-15	1190	114.4	96.1	20
8	03-16	1220	235.5	193.1	70
9	03-24	1423	128.5	90.3	75
10	04-03	1256	244.5	194.6	90
11	04-13	1403	218.9	156.0	80
12	04-24	1395	230.7	165.4	60
13	05-05	1330	155.2	116.7	30
14	05-11	1354	241.1	178.1	90
15	05-19	1280	198.0	154.7	30
16	05-30	1403	267.4	190.6	20
18	06-19	1618	261.7	161.7	50
20	07-06	1656	235.7	142.3	80
21	07-13	958	216.3	225.7	100
27	08-15	1585	223.8	141.2	70
28	08-21	1654	199.6	120.7	50
30	09-11	1657	198.5	119.8	60
31	09-17	1419	255.0	179.7	90
33	10-01	1283	260.3	202.9	70
34	10-05	1240	203.2	163.9	65
36	10-24	1181	300.2	254.2	30
38	11-03	1353	122.7	90.7	80
39	11-14	1160	250.6	216.1	55
40	11-24	1484	189.7	127.8	90
41	12-04	1450	86.4	59.6	0
42	12-06	1635	109.2	66.8	0
43	12-13	1192	199.8	167.6	80
44	12-18	1319	158.5	120.2	80

comparison with the elemental standard normalized by the ratio of the Ti monitor's activation.

For the 12-h irradiations elemental standards were irradiated simultaneously with the samples in rotating polyethylene containers and counted later. Triple-distilled water and speccure or reagent grade chemicals were used in the preparation of the elemental standards.

A 45-cm<sup>3</sup> Ge(Li) detector with a resolution (full width at half maximum) of 2.3 keV for the 1332-keV  $\gamma$ -ray detection was used for the  $\gamma$ -ray spectroscopy. The spectral data were accumulated in a 4096-channel pulse height analyzer, recorded on computer-compatible magnetic tape, and reduced using peak analysis computer codes (8). The accuracy and precision of the INAA system at Lawrence Livermore Laboratory (LLL) have been verified by analysis of National Bureau of Standards Reference Materials and by participation in interlaboratory comparison studies (9).

**X-ray Fluorescence Analysis.** The XRFA system consisted of an 80-mm<sup>2</sup> Si(Li) detector with a resolution of 190 eV for the 5.90-keV x-ray line from <sup>55</sup>Fe. Fluorescence spectra were obtained with a <sup>109</sup>Cd ring source as the exciter in a 180° geometry. Spectra were taken in 1000-s exposures and were stored in a 1024-channel block in a minicomputer. Calibration techniques, data reduction, and standardizations have been previously described (10). The XRFA system was used to analyze for Fe, Cu, Zn, Br, Sr, and Pb in the Hi-Vol filters and for Pb in the soils and grass samples.

The filter samples actually analyzed were 29-mm-diam discs cut out of the 8 × 10 in. high-volume filters. Homogeneous deposition on the filters was verified by repeatedly analyzing replicate discs cut from the same filter.

A series of 40 soil samples was prepared for XRFA by fusion with nine parts lithium metaborate to one part soil in a Pt-Au alloy crucible at about 900 °C. The fusion melt was cooled, weighed, reheated, and cast into 1-in.-diam preweighed Al rings, giving a glass-like disc about 1.4 mm thick. Standards for comparison were prepared by adding known weights of PbO to high-purity SiO<sub>2</sub>, preparing 9:1 fusion mixtures, and casting standard discs. A blank was prepared with SiO<sub>2</sub>.

Iron, Cu, Zn, and Br were determined in the aerosols by both INAA and XRFA and provided an internal check on our analyses. The agreement between the INAA and XRFA filter data is shown by linear correlation coefficients for Cu, Br, Fe, and Zn of 0.98, 0.96, 0.93, and 0.97, respectively.

## Results

**Soils.** Figure 1 shows the soil sampling locations in the study. Table III lists the designations and locations of the sites. Sites 4, 8, and 10 are listed as other sites because they do not fit the designations of representative valley site or background site. Site 4 (Kellogg Cemetery) is located on a hill overlooking the valley and is subject to quite different wind conditions and fallout patterns. Sites 8 and 10 are located in the town of Wallace and near the Sunshine Mine, respectively. The trace metal soil concentrations at these sites were appreciably higher than those at the background sites (#7, #9), indicating they were exposed to different sources and unsuitable in our scheme. Sites 13–15 were the existing dumping locations. Two surface samples were taken from each of these three sites; core samples were taken from sites 1–12.

Table IV shows the surface (0–2 cm) soil concentrations of the most enriched elements Cd, Sb, Ag, Pb, Au, Zn, Se, and As. The Pb data agree with the analyses in ref. 3. The surface concentrations of the tailings (and sinter) piles (sites 13–15) are included for comparison. The surface layer metal concentrations are highest at the sampling sites closest to the smelter, Nos. 11, 12, and 2.

In general, the elemental concentrations in the tailings are in the same range as those in the surface soil fraction. This

**Table II. Neutron Irradiation and Sample Counting Schedule for This Study**

Irradiation time	Neutron flux, n/cm <sup>2</sup> -s	Cooling time	Counting time	Elements detected
2 min	2 × 10 <sup>13</sup>	4 min	500 s	Al, V, Cu, Ti, Ca
		20 min	1000 s	Na, Mg, Cl, Mn, Br, I, Ba, In
12 h	4 × 10 <sup>12</sup>	20–30 h	2000 s	As, W, Ga, K, Cd
		6–10 days	100 min	Sm, Au, Hg, La, Sb
		20–30 days	8–12 h	Fe, Cr, Co, Zn, Hg, Se, Ag, Sb, Ce, Eu, Sc, Th, Ni, Ta, Hf, Ba, Rb

**Table III. Kellogg Valley Soil/Vegetation Sample Site Designations**

Distance from smelter, miles			
			Background sites
7.8 E	No. 7		Osburn
3.3 W	No. 9		Pinehurst
			Representative Valley sites
1.5 E	No. 1		Cor. Railroad and Hill Streets
0.7 E	No. 2		West Ridge Road
2.0 E	No. 3		Cor. 3rd and Gold Streets
2.0 E	No. 5		Chestnut St.
1.8 E	No. 6		Kellogg Medical Center
0.27 W	No. 11		Silver King School
0.66 W	No. 12		Smelterville Park
			Contaminated Valley sites
0.7 E	No. 2		West Ridge Road
2.0 E	No. 3		Cor. 3rd and Gold Streets
1.8 E	No. 6		Kellogg Medical Center
0.27 W	No. 11		Silver King School
			Other sites
2.3 E	No. 4		Kellogg Cemetery
11.8 E	No. 8		Wallace
5.0 E	No. 10		Big Creek
			Tailings sites
	No. 13		Sinter pile
	No. 14		Smelterville tailings pond
	No. 15		Kellogg tailings pond

agreement makes it difficult to distinguish them as separate sources. The maximum concentrations of the enriched elements do not occur at the same site: however, four valley sites, nos. 2, 3, 6, and 11, can be classified as the most contaminated. Sites 2, 3, and 11 were vacant lots; site 6 was a grassy lawn.

To compare our data to soil data at other locations and to intercompare our soil, tailings, and filter data, we have calculated enrichment factors relative to average crustal abundances.

The enrichment factor ( $EF_i$ ) for a given element of a single site ( $i$ ) is expressed as follows:

$$EF_i = R_i (\text{Site})/R (\text{Earth's crust}) \quad (1)$$

**Table IV. Kellogg Valley Trace Element Concentrations in Surface Soils (0–2 cm) (ppm)<sup>a</sup>**

Site <sup>a</sup>	Distance from smelter, miles	Cd	Sb	Ag	Pb	Au	Zn	Se	As
1	1.5	...	32	6.0	1700	0.07	970	...	69
2	0.7	140	150	25	7600	0.37	4 300	6.7	93
3	2.0	32	260	31	6700	0.22	1 400	5.1	94
4	2.3	...	28	2.7	2000	...	200	...	24
5	2.0	65	72	14	170	0.47	2 600	3.4	44
6	1.8	82	104	24	5300	0.25	5 700	1.6	110
7	7.8	...	20	3.7	890	...	804	...	24
8	11.8	...	40	10	2200	...	3 000	...	37
9	3.3	18	18	2.8	1000	0.06	940	...	36
10	5.0	...	20	3.6	300	...	320	...	53
11	0.27	83	155	30	7900	0.23	13 000	4.6	100
12	0.66	25	5	9.3	3200	0.12	870	0.76	49
13	...	...	52	3.2	290	...	29 000	5.5	18
14	...	26	70	13	3700	0.12	3 200	...	210
15	...	37	79	24	7900	0.24	7 500	0.75	260

<sup>a</sup> See Figure 1 and Table III for sampling locations.

**Table V. Mean Surface Soil Concentrations at Seven Kellogg Valley Sites: Enriched Elements**

Element	Concn, <sup>a</sup> ppm	Crustal (Wedepohl), ppm	EF <sub>w</sub>	Contam/bkgd <sup>b</sup>
Cd	70.9 ± 41.0	0.1	1540	5.6
Sb	111 ± 86	0.2	1150	13.0
Ag	20.0 ± 10.2	0.06	680	11.0
Pb	4640 ± 3030	15	560	9.4
Au	0.25 ± 0.14	0.004	160	5.2
Zn	4160 ± 440	60	130	8.5
Se	3.69 ± 2.23	0.09	100	8.5
As	80.3 ± 26.3	1.7	86	4.1
W	90.0 ± 44.8	1.3	86	2.6
In	2.05 ± 1.33	0.07	70	12.0
Ni	1200 ± 670	44	39	...
Cu	278 ± 108	30	24	>1.5
I	4.9 ± 0.3	0.5	16	>0.68
Br	16.6 ± 9.3	2.9	13	>0.74
Hg	0.112 ± 0.093	0.03	9.3	13.0

<sup>a</sup> Mean values of concentrations at sites 1–3, 5, 6, 11, and 12. <sup>b</sup> Ratio of average surface concentrations at contaminated sites 2, 3, 6, and 11 to average background sites 7 and 9.

where  $R$  is the ratio of the concentration of a given element to that of Sc. If one calls  $R_i$  the elemental ratio, then the average element ratio  $R$  over all valley sites is:

$$R = \frac{1}{n} \sum_i R_i \quad (2)$$

when  $n$  is the number of sites. We redefine the average valley soil enrichment factor ( $EF_w$ ) as:

$$EF_w = \frac{R}{R_w} \quad (3)$$

where  $R_w$  is the ratio of the element to Sc for crustal rock using the values of Wedepohl (11).

Elemental enrichment factors are used for analysis because absolute concentrations are affected by winds, precipitation, inversions, etc. Ratioing absolute elemental concentrations to another single element removes variations caused by particulate loading changes. A second normalization to soil

abundances allows the determination of the relative amounts of soil particulate and nonsoil particulate loadings on the air filters.

We selected Sc as the normalizer element because it is detected with high accuracy and precision and because the only reasonable source of Sc was the soil. Other studies have normalized to Al (12). Since Al might possibly be emitted from the smelter operations, however, we chose Sc as a better soil indicator element.

Table V contains the mean surface-soil concentrations of those elements having  $EF_w$  values greater than 10. The elemental data from sites 1–3, 5, 6, 11, and 12 were averaged to represent valley soil. The variations represent one standard deviation from the mean values. Elements with  $EF > 10$  were arbitrarily considered enriched relative to crustal abundances; those with  $EF < 10$  as nonenriched elements. Table VI shows similar data for nonenriched elements. The scandium  $EF_w$  is by definition, unity. The cutoff between enriched and nonenriched elements is arbitrary; however, elements with  $EF < 10$  appear nonenriched on the aerosols, as discussed below.

An additional indicator of contamination is the surface-soil concentrations at the valley sites compared to those at the background sites. The ratio contam/bkgd in Tables V and VI are ratios of the averages of the elemental surface-soil concentrations at the most contaminated valley sites 2, 3, 6, and 11 to the average of the nonvalley background sites 7 and 9. All of the calculated ratios are greater than four for the enriched metals with the exception of W (2.6), whereas all the nonenriched elements have ratios less than four. The rare earths have  $EF_w$  values and contam/bkgd values near one, as expected.

Since a high enrichment or a high contam/bkgd factor does not necessarily prove an unnatural source of an element, it is worthwhile to examine the soil profiles of the elements. Figure 2 shows some typical profiles of selected elements taken at sites 2, 3, 9, and 12. Sites 2 and 3, vacant lots, are contaminated valley sites. Site 12, a valley site, is a grassy lawn area and appears to have been disturbed in some fashion. Site 9 is a background site.

At sites 2, 3, and 9 the enriched elements Pb, As, Ag, Sb, Br, Hg, Cd, In, Se, Ni, and Au show a sharp decrease with depth. The only enriched metal element that shows a zero slope is W. The high  $EF_w$  indicates a concentration higher than Wedepohl's, but the zero slope and the low contam/bkgd ratio (2.6)

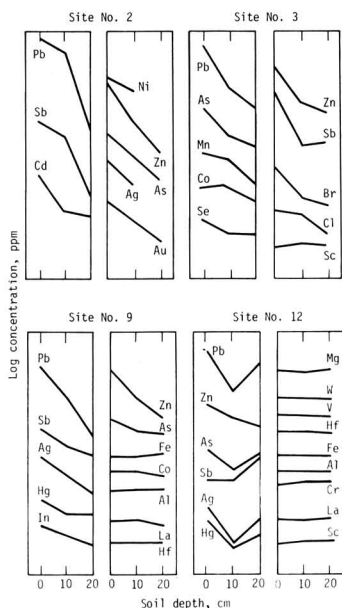
**Table VI. Mean Surface Soil Concentrations at Seven Kellogg Valley Sites: Nonenriched Elements**

Element	Concn, ppm	Crustal (Wedepohl), ppm	$EF_w$	Contam/bkgd <sup>a</sup>
Mg	5.37 ± 2.82%	1.39%	6.6	1.5
Hf	10.1 ± 3.7	3.0	5.8	0.93
Mn	2090 ± 2881	690.0	4.9	2.9
Co	20.7 ± 21.4	12.0	3.0	3.0
Ga	21.7 ± 8.5	17.0	2.8	1.4
Fe	4.57 ± 3.17%	3.54%	2.1	2.1
Sm	5.93 ± 2.35	6.6	1.6	0.89
Ce	62.8 ± 23.9	75.0	1.4	0.90
Cl	213 ± 133	320.0	1.4	>2.0
Ba	504 ± 204	590.0	1.4	0.91
Eu	1.16 ± 0.47	1.4	1.4	1.1
Th	8.57 ± 3.58	11.0	1.4	0.86
La	31.9 ± 4.5	44.0	1.2	0.94
Cr	44.6 ± 22.0	70.0	1.1	1.3
Sc	8.14 ± 2.81	14.0	1.0	0.92
K	1.52 ± 0.41%	2.82%	0.93	0.92
Ti	2.49 ± 0.96	4700.0	0.93	0.97
Ca	1.34 ± 1.56%	2.87%	0.79	3.8
V	43.8 ± 7.5	95.0	0.79	1.3
Al	3.27 ± 1.23%	7.8%	0.71	0.79
Na	0.544 ± 0.249%	2.45%	0.38	0.75

<sup>a</sup> Ratio of average surface concentrations at contaminated sites 2, 3, 6, and 11 to average background sites 7 and 9.

**Table VII. Surface Soil, Tailing, and Sinter Enrichments ( $EF_w$ )**

Element	Soils	Tailings	Sinter
Cd	1540	1210	<23
Sb	1150	1360	585
Ag	680	1250	120
Pb	560	1430	45
Au	160	190	...
Zn	130	370	1100
Se	100	32	145
As	86	530	24
W	86	41	1320
In	70	67	44
Ni	39	...	...
Cu	24	410	70
I	16	<240	<225
Br	13	<130	...
Hg	9.3	4.6	0.70
Mg	6.6	2.5	13
Hf	5.8	12	4.4
Mn	4.9	33	50
Co	3.0	4.2	22
Ga	2.8	1.9	6.5
Fe	2.1	10	18
Sm	1.6	2.7	2.3
Ce	1.4	2.3	1.6
Cl	1.4	<7.3	<7.5
Ba	1.4	<4.3	4.7
Eu	1.4	4.6	3.8
Th	1.4	1.7	1.4
La	1.2	1.4	1.4
Cr	1.1	0.87	4.6
Sc	1.0	1.0	1.0
K	0.93	1.6	0.55
Ti	0.93	0.87	<0.65
Ca	0.79	0.40	8.0
V	0.79	0.37	1.2
Al	0.71	0.67	0.50
Na	0.38	0.01	0.23



**Figure 2.** Concentration profiles of various elements in Kellogg Valley soil

Curves plotted to various logarithmic scales and cannot be compared directly except by slope. Change in Pb at site nos. 2 and 3, for example, is 100-fold

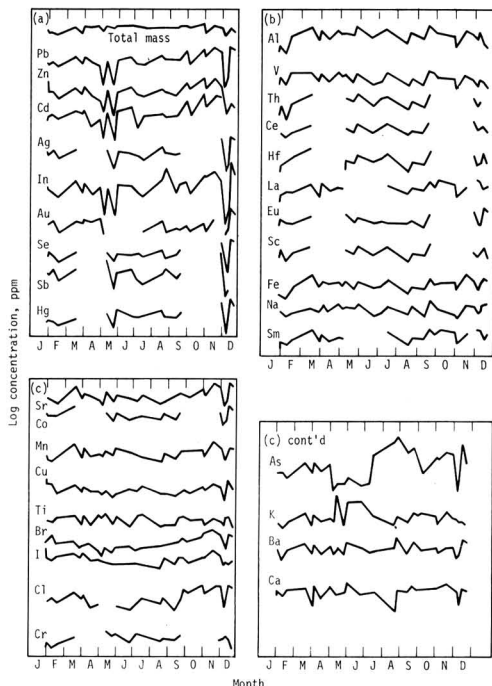
demonstrate that W is probably not deposited in the soil by the same mechanism as the metals listed above.

The background site 9, Pinehurst, shows a similar decrease with depth of the enriched element soil concentrations as do the valley sites 2, 3, and 12. This may indicate that the heavy metal aerosol fallout is not limited to the Kellogg Valley but extends to Pinehurst, although the absolute values of con-

tamination at the Pinehurst background site are far smaller. Nonenriched elements La, Sc, Hf, Cr, Al, Fe, Mg, and V show zero slopes. Even though Mn ( $EF_w = 4.9$ ) and Cl ( $EF_w = 1.4$ ) are not enriched, they do show a definite decrease with depth and therefore may result from atmospheric deposition.

Surface samples from two different tailings piles and one sinter pile were also analyzed for trace metal concentrations. Table VII contains the average enrichment factors relative to Sc for the tailings and the sinter. The soil factors are also listed in Table VII for comparison. Since the concentrations in the two tailings pile samples were similar, they were averaged. The  $EF_w$  values for the soil, tailings, and sinter are generally similar, with some notable exceptions. The tailings are very much more concentrated in As and Cu than the soils and sinter. The sinter is more concentrated in Zn and W than the soils and tailings. Both the tailings and sinter have significantly higher concentrations of Mn and Fe than the soil. The sinter is depleted in Pb, Cd, Sb, Ag, Hg, and As.

**Hi-Vol Air Filters.** The relative concentrations of 33 of the 36 elements measured in the Kellogg ambient air are plotted in Figure 3. Three elements Mg, Ga, and W were not plotted because they were detected in too few samples to establish a distribution. Total mass is also shown in Figure 3 for comparison. The complete listing of all of the filter elemental analyses is contained in ref. 6.



**Figure 3.** Trace element concentrations in air at Kellogg, Idaho, of samples collected throughout the year

Curves plotted to various logarithmic scales and cannot be compared directly except by time of fluctuation. Overall variations in most elements were between 10- and 100-fold

From these data we have calculated average concentrations for the 36 elements in Table VIII. The average concentration  $\langle C \rangle$  for a given element was calculated as follows:

$$\langle C \rangle = \frac{1}{n} \sum_i C_i \quad (4)$$

where  $n$  = number of samples in which the particular element was detected, and  $C_i$  = concentration of the element in sample  $i$ . For the elements Fe, Br, Cu, and Zn the INAA and XRFA results were averaged. The Pb concentration ( $10.8 \mu\text{g}/\text{m}^3$ ) agrees with the  $8.6 \mu\text{m}^3$  reported in ref. 3 for the same time period. Since Whatman 4 filter paper is less efficient for submicron particles than glass filters (13), comparisons of these data with other Hi-Vol results using glass filters and flow rates of 40–55 cfm are not appropriate. This difference is mitigated by the fact that Whatman 4 filters become rapidly loaded and thus develop higher efficiencies for small particles with increasing sampling time.

We believe the smelting operation to be the origin of all those elements that vary with Pb. Scandium displays a concentration pattern completely unlike that of Pb; therefore, it must have a separate source unrelated to the smelter operation. Previous studies (12) have shown that the only other significant source of atmospheric Sc is resuspended soil dust. Since our results are in agreement with that hypothesis, we consider Sc and those elements that vary with Sc to be soil derived.

Using the average concentrations, we have calculated air  $EF_w$  values based on Sc shown in Table IX. The air  $EF_w$  values are divided into high and low  $EF_w$  groups as was done for the soil  $EF_w$  values in Tables V and VI.

**Table VIII.** Mean Concentrations of Trace Elements on Hi-Vol Filters Collected at City Hall, Kellogg, Idaho ( $\text{ng}/\text{m}^3$ )

Trace element	$\langle C \rangle$	$C_{\text{min}}$	$C_{\text{max}}$
Ti	95.7	<40	170
Mg	718	264	1 270
Cu	186	51.7	513
V	2.01	0.716	3.98
Al	1 050	203	2 500
Ca	583	80.6	1 310
Ba	39.0	<10	106
I	1.94	0.770	6.05
Br	99	23.1	323
In	5.79	0.0635	43.3
Na	207	84.8	412
Cl	498	106	1 300
Mn	71.3	26	214
As	329	8.28	2 510
K	1 110	277	6 210
Cd	748	<30	2 890
Ga	2.36	0.867	4.42
W	4.44	1.97	9.43
Sm	0.184	0.0491	0.337
Au	9.76	2.97043.1	
La	1.09	0.279	2.07
Eu	0.0663	0.0293	0.173
Se	5.23	0.644	17.6
Ce	2.07	0.961	3.96
Hg	113	10.8	504
Th	0.243	0.0438	0.465
Cr	6.82	2.61	14.9
HF	0.140	0.0457	0.354
Sb	146	5.21	1 210
Ag	10.5	0.936	36.5
Sc	0.322	0.134	0.518
Fe	1 835	650	4 880
Zn	4 620	270	15 700
Co	3.21	1.16	7.49
Sr	22.5	6.62	74.9
Pb	10 800	501	30 200
Mass	148	60	254

The meteorological data available during the sampling periods (Table I) show only the basic wind direction as easterly and westerly. This is partially justified by the fact that, in the sampling situation, the surface winds are channeled by the narrow valley. Examination of the wind patterns during the particular day when the lowest measured concentration of each element was obtained shows that those elements with  $EF_w > 10$  were sampled on days when the wind was (on an average) blowing from the sampler toward the smelter 85% of the sampling day. The minimum values for nonenriched elements ( $EF_w < 10$ ) occur on days that have the same wind direction (i.e., E to W) 44% of the average sampling day. From this we conclude that the minimum concentrations of enriched elements were obtained when the direct contribution from the smelter was also minimum. Concentrations of the nonenriched elements seem to be relatively independent of wind direction.

An inspection of the  $EF_w$  values shows that the elements are generally ranked in the same order for air and soil, although the absolute values are very different for the enriched elements. For the nonenriched elements the  $EF_w$  values are



**Table IX. Elemental Enrichments for Hi-Vol Air Filters ( $EF_w$ )**

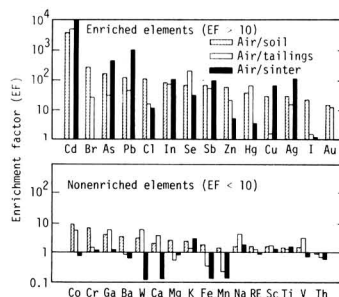
Enriched group		Nonenriched group	
Element	$EF_w$	Element	$EF_w$
Cd	3 650 000	Ga	6.2
Sb	46 000	Mn	4.6
Pb	36 000	Sr	3.9
Ag	11 000	Cr	3.9
As	8 700	Ba	2.9
Zn	4 600	Eu	2.5
Se	3 700	Fe	2.1
In	3 300	Hf	2.0
Br	2 000	K	1.3
Au	1 400	Ce	1.2
Cu	370	Sm	1.1
I	210	Sc	1.0
Hg	204	La	0.97
W	140	Mg	0.95
Cl	70	Ca	0.90
Co	14	Th	0.72
		Ti	0.71
		V	0.58
		Al	0.40
		Na	0.34

quite similar; only Co and Cl appear enriched on the air filters and nonenriched in the soils. All elements that appear enriched in the soils also are enriched on the air filters, except Ni, which was not detected on the air filters.

To compare directly the air filters and soils, we have calculated enrichment factors of the air filters relative to the surface-soil, tailings, and sinter concentrations, again normalized to Sc (Figure 4). A large  $EF$  (soil, tailings, or sinter) value indicates a significant enrichment of that element from some source other than windblown soil, tailings, or sinter. On the other hand, a low  $EF$  value for an element relative to either soil, tailings, or sinter would indicate that either soil, tailings, or sinter is a possible source of that element. The  $EF$  values less than unity for the nonenriched elements mean that the material has a higher relative concentration of that element than the aerosols and could be a source. This plot (Figure 4) shows that aerosols contain higher concentrations of Cd, As, Pb, In, Br, Cl, I, Se, Sb, Zn, Hg, Cu, Ag, and Au that could be injected into valley air by erosion of soil or by resuspension of tailings and sinter. These enrichments are caused by other sources, presumably by active emissions from the smelter complex.

Cascade impactor measurements taken near the main smelter complex have shown that discharged metals predominate on small (<3  $\mu\text{m}$ ) particles (14). Therefore, resuspended soil particles (that tend to be small) might have higher amounts of effluent metals than would a bulk soil analysis. This effect would decrease the aerosol  $EF_{\text{soil}}$  values. This decrease would imply a greater contribution of resuspended soil to the Kellogg atmosphere and a lesser contribution of active smelter emissions. However, of course, the total contribution of smelter operations to the Kellogg environment would remain unchanged.

**Grasses.** We see analogous enrichments of the metals in the grass samples collected at each site that a soil core was taken. Table X shows the concentrations for Cd, Sb, Ag, Pb, Zn, and As in the surface grass. Unlike the soils, sites 1, 4, 6, and 11 tend to have the highest concentrations of the enriched elements. Table XI contains the concentration ranges of the enriched trace elements in grasses in the Valley and in the



**Figure 4.** Enrichment factors for various elements, comparing air/soil, air/tailings, and air/sinter. RE = rare earth elements

background sites. For comparison we list the average concentrations of trace elements in forage crops compiled from the literature (15, 16).

The elemental enrichments in the grasses are large; Cd ranges up to 9840 times more concentrated than the forage number, Sb is 1110 times, Ag is 180 times, and Pb is 4000 times. Note that the concentration of K, which is listed for comparison, is similar to the forage number.

Other attempts to compare washed and unwashed grasses showed that the variance among individual samples was much greater than the difference between washed and unwashed samples (3).

**Sources of Trace Metals.** In Kellogg Valley the sources of atmospheric and terrestrial contaminants can be summarized as follows: point sources: smelter blast furnace and main stack, fugitive emissions, and milling operations; area sources: automobiles, resuspended soils and dust, resuspended dust from tailings and sinter piles, ores and concentrate spills from trains and trucks, and stack effluents from private and commercial fossil fuel combustion.

The fossil fuel use in the town of Kellogg has been apportioned (17): coal, 64%; natural gas, 27%; and fuel oil, 9%. To evaluate the contribution of coal fly ash from chimneys near the Hi-Vol sampler, we calculated  $EF_w$  values of fly ash using the trace element concentrations in the National Bureau of Standards Standard Reference Material fly ash #1633 (9). Local Kellogg fly ash values were not available. A comparison with other published fly ash analyses indicated that the NBS #1633 fly ash was an acceptable representation of trace element abundances. Only for As, Se, and Sb were the  $EF_w$  values significantly greater than unity. In other words, the trace element concentrations in coal fly ash are very similar to those in soil. The slight enrichment in As, Se, and Sb is not enough to account for the observed aerosol enrichments.

Table XII summarizes our conclusions on the sources of the trace elements that were observed on the air filters and in the soils and grasses. The smelter operation has been the major source of atmospheric Cd, As, Pb, In, Sc, Sb, Zn, Ag, Au, Ni, and possibly Cu. These elements have high aerosol enrichments, their soil concentrations decrease with depth, and they are present in high concentrations in the grasses. Natural soils are the major source of Fe, Mg, Hf, Th, Al, Sm, W, V, La, Ti, Ce, Sc, Na, Ca, K, and possibly Mn and Co. These elements have low aerosol enrichments, show no decrease in soil concentrations with depth, and have normal concentrations in grass. Resuspension of tailings dust might be a significant source of As. The As aerosol concentration does not seem to vary with those of Sc (soil) or Pb (smelter), but is enriched on the air filters. Since As is present in relatively high concentrations in the tailings ( $EF_w = 530$ ), we believe that the resuspension of tailings might be another source of As. The concentration of halogens decreased with soil depth. The

**Table X. Kellogg Valley Trace Element Concentrations in Grass<sup>a</sup> (ppm)**

Location	Distance from smelter, miles	Cd	Sb	Ag	Pb	Zn	As
1	1.5	4300	110	18	10 000	...	48
2	0.7	2000	6.2	0.9	540	600	4.9
3	2.0	2000	6.9	1.1	670	560	4.8
4	2.3	3100	50	7.0	2 800	990	41
5	2.0	...	...	...	...	...	...
6	1.8	4400	39	6.4	2 800	1 400	30
7	7.8	830	3.5	0.8	320	800	2.7
8	11.8	...	...	...	...	...	...
9	3.3	17	4.5	1.0	480	420	3
10	5.0	...	...	...	...	...	...
11	0.27	9500	91	17	5 000	12 000	59
12	0.66	160	26	5.5	2 300	1 900	19

<sup>a</sup> See Figure 1 for locations of sampling sites.

**Table XI. Ranges of Enriched Trace Element Concentrations in Grass**

Element	Valley concn, <sup>a</sup> ppm	Background concn, <sup>b</sup> ppm	Forage crops, <sup>c</sup> ppm
Cd	200-9480	57-82	1
Sb	6.2-111	3.5-4.5	0.1
Ag	0.92-18	0.800-1.02	0.1
Pb	540-9990	320-480	2.5
Au	0.31-11.5	1.7-480	0.001
Zn	560-11 900	420-810	25.0
Se	0.130-3.20	0.062-0.078	0.05
As	4.9-59	2.7-3.2	1.0
W	ND	ND	0.1
In	0.078-2.1	0.075-0.092	0.1
Ni	ND	ND	1.5
Cu	38-110	21-26	7.5
I	<1	<1	0.1
Br	24-212	22-88	10.0
Hg	(6.0-77) × 10 <sup>-3</sup>	(6.5-6.6) × 10 <sup>-3</sup>	0.1
K	0.46-2.71%	0.90-1.10%	2.0%

<sup>a</sup> Concentrations at sites 1-3, 5, 6, 11, and 12. <sup>b</sup> Concentrations at sites 7 and 9. <sup>c</sup> Refs. 14 and 15.

**Table XII. Sources of Trace Elements in Kellogg Valley Aerosols**

Source	Elements
Smelter complex	Cd, As, Pb, In, Se, Sb, Zn, Hg, Ag, Au, Ni, (Cu)
Natural soils	Mg, Hf, Th, Al, Sm, V, La, Ti, Ce, Sc, Na, Fe, Ca, K, (Mn), (Co)
Other	Br, Cl, I

aerosol concentration of Br and Cl varied with that of Pb. The bulk of the halogens apparently did not originate from the soils and at least originated in part from the smelter operations.

### Conclusions

We have demonstrated that the smelting industry in Kellogg, Idaho, has made a measurable impact on the valley environment. The elements Cd, Sb, Pb, Ag, Cu, As, Zn, Se, In,

Au, Ni, and Hg are enriched in the soils and grasses and have been deposited by fallout. The variations in aerosol concentrations of these metals were similar, and the absolute concentrations of these metals were high. These results also demonstrate that Pb was not the only metal of concern. We found high average ambient air concentrations of 11 µg Pb/m<sup>3</sup>, 800 ng Cd/m<sup>3</sup>, 300 ng As/m<sup>3</sup>, and 5 µg Zn/m<sup>3</sup>, among others. The synergistic effects of these high air concentrations of metals on humans in Kellogg should be addressed, and the body burden of these metals should be investigated.

### Acknowledgments

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## Fractionator for Size Classification of Aerosolized Solid Particulate Matter

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■ A system is developed for collecting kilogram quantities of size-fractionated particulate matter which can be subsequently used for biologic testing purposes. The apparatus consists of a series of two cyclones and a centripeter and yields four size fractions. When used over a 12-day period to classify fly ash from stack gas passed through the electrostatic precipitator of a coal-fired power plant, the collected fractions have volume median diameters of 20, 6.3, 3.2, and 2.2  $\mu\text{m}$  with geometric standard deviations of approximately 1.8. A total of 8.08 kg of fly ash is collected.

The increasing national demand for electrical power generation requires further assessment of present pollution abatement technologies and the potential health hazards associated with energy technologies. Particulate matter from coal combustion has received special emphasis in recent years. To evaluate the health hazards of coal combustion and to develop new and improved pollution abatement technologies, relatively large quantities of size-classified particulates are required. Although cascade impactors are routinely used for aerodynamic size classification in emission testing, these instruments are designed to classify milligram quantities of particulates. To achieve our goals for biologic testing, we have developed a stack-sampling system capable of classifying kilogram quantities of aerodynamically size-fractionated fly ash.

The particle fractionator is designed to provide fly ash in volume-size classes for biological testing, namely, with median sizes of diameters: 2, 3, 6, and 20  $\mu\text{m}$ . The 2- $\mu\text{m}$  fraction represents the size region suggested of most interest for pulmonary deposition after inhalation in humans (1, 2). The 3- and 6- $\mu\text{m}$  size classes will predominately be deposited in the nasopharyngeal region, i.e., the upper regions of the respiratory tract where most particles will be removed by ciliary action, swallowed, and ingested. Although the largest size class (20  $\mu\text{m}$ ) is probably not of concern in inhalation exposure due to the short atmospheric residence time, these particles may ultimately be ingested after foliar deposition on food crops.

### System Description

The apparatus which was developed to fractionate and collect fly ash is shown schematically in Figure 1. Basically it consists of a set of two cyclones in series followed by a centripeter—an arrangement which permits separation of the particulate matter into four size fractions. With reference to Figure 1, stack gas is drawn through the inlet probe into the heated enclosure which contains the fractionation devices. Heating to about 100 °C is necessary to prevent condensation of moisture due to the high dew point associated with power plant stack gases. The first cyclone through which the gas flows was designed from use of the data and model of Ancel (3) to have a cut size of 10  $\mu\text{m}$  for unit density particles. Cut size is defined as the diameter of a spherical particle for which the probability of collection is 50%. After passing through the first cyclone, the gas flows through the second cyclone which has a design cut point of 7  $\mu\text{m}$  and thence into the centripeter.

The centripeter principle, developed almost simultaneously by Hounam and Sherwood (4) and Conner (5), is illustrated in Figure 2. Aerosol is drawn through an acceleration nozzle wherein it achieves a velocity on the order of 10–100 m/s. A

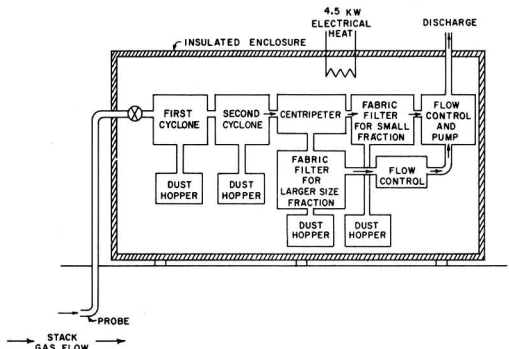


Figure 1. Schematic diagram of fractionation system

collection nozzle is placed at a distance of approximately one diameter of the acceleration nozzle downstream from the exit plane of the acceleration nozzle. Typically the entrance size of the collection nozzle is 1.4 times as large as the acceleration nozzle diameter. Only a small portion (2–10%) of the flow which effluxes from the acceleration nozzle is drawn into the collection nozzle with the remainder being diverted around it. Large particles, due to the high inertia associated with the acceleration jet exit-plane velocity, are driven into the collection nozzle and carried away from the classification zone by the small flow of transport gas. Small particles contained within the 2–10% transport air are also drawn along with the large particles. The majority of the total gas flow and the small particles are diverted around the collection nozzle and passed out of the collection system. Particle cut size for the centripeter was calculated from the expression (6):

$$\text{Stk} = \text{Stokes' Number} = \frac{C_{\rho p} D_p^2 V_j}{9 \mu d_j} = 0.32 \quad (1)$$

where  $C$  = Cunningham's correction =  $1 + 2.46 \lambda/D_p$ ;  $\lambda$  = gas mean free path length, m;  $D_p$  = particle diameter, m;  $\mu$  = gas viscosity, kg/m-s;  $d_j$  = acceleration jet diameter, m;  $\rho_p$  = particle density, kg/m<sup>3</sup>; and  $V_j$  = particle velocity at acceleration jet exit plane, m/s.

Since a total air flow rate of approximately 0.85 m<sup>3</sup>/min and particle cut size of from 3 to 5  $\mu\text{m}$  were desired, it was necessary to design the prototype system with multiple jets operating in parallel. Two versions have been employed, the first with 25 jets each 0.5 cm diameter and the second which also has 25 jets with each having a size of 0.65 cm. Results presented herein are those obtained with the latter design. The critical design parameters which were used in the centripeter system are given in Table I.

Gas containing the larger particles (Figure 1) is processed through a fiberglass fabric filter and then drawn through a flow meter and control valve. Similarly, the small particle stream is drawn into a fiberglass fabric filter, through a control valve, and then is joined with the gas from the large particle fabric filter. The combined stream goes through a blower and thence is discharged to the atmosphere.

Filtered, high-pressure building supply air (100 psig) is pulsed at approximately 2-min intervals for cleaning of the fabric filters. The particles which are removed in the cleaning cycle are collected in dust hoppers.

With respect to the ability of the fabric filters to collect the fly ash particles, Billings and Wilder (7) reported that for six applications of reverse-jet fabric filters on fly ash, the minimum efficiency noted was over 99.9%. Peterson and Whitby (8) reported that the fractional efficiency of a fabric filter media loaded with NBS fly ash was greater than 99% over the size range of 0.06–1.0  $\mu\text{m}$ .

In application, the fly ash fractionator system was mounted on the breeching after the electrostatic precipitator of a 750-MW coal-fired electric power plant and operated for a period of 12 days at a flow rate of 0.85 m<sup>3</sup>/min. Fuel combusted contained approximately 0.3% sulfur, 22% ash, and 10% moisture. The probe was located along the vertical centerline of the 10-m-high rectangular shaped breeching at a position 2.5 m below the top of the ducting. Operating temperature was maintained at 92–102 °C which precluded condensation of the 73 °C dew point stack gas.

#### Methods

The analysis of system performance consisted of determining for each size fraction the total mass collected over the operating period, the size distributions of representative fly ash samples, and the basic average particle densities.

Size distribution data were obtained by first ultrasonically dispersing a 0.3-g fly ash sample in a methanol–electrolyte

solution for a 2-min period. An aliquot of the dispersion was then analyzed with a Coulter Counter Model T system. Each size distribution determination represents the composite of duplicate dispersions and analyses. As a backup a Particle Data Inc., Celloscope was employed to analyze the finest size fraction. With a saline solution used as the electrolyte, the apparatus yielded data identical to that of the Coulter approach.

The basic particle density in the four sized fractions was determined in triplicate utilizing a gravimetric, liquid displacement technique. After dispersing the fly ash in 1-propanol and degassing in vacuo, the suspension and tared container were weighed completely immersed in 1-propanol. The displaced liquid volume was calculated from this gravimetric determination.

#### Results

The quantities of material collected during the 12-day period in each fraction are given in Table II and show that the total accumulation of post-precipitator fly ash was 680 g/day with 9.9% in the smallest size fraction. Size distribution of the material drawn through the probe into the system is shown in Figure 3. The volume median diameter is 13  $\mu\text{m}$  with 90% of the distribution associated with particles of size less than 37  $\mu\text{m}$  and 10% with sizes less than 2.5  $\mu\text{m}$ .

The resulting volume size distributions of the four fly ash fractions are shown in Figure 4. Assuming that the distributions are approximately logarithmic normal, the statistical

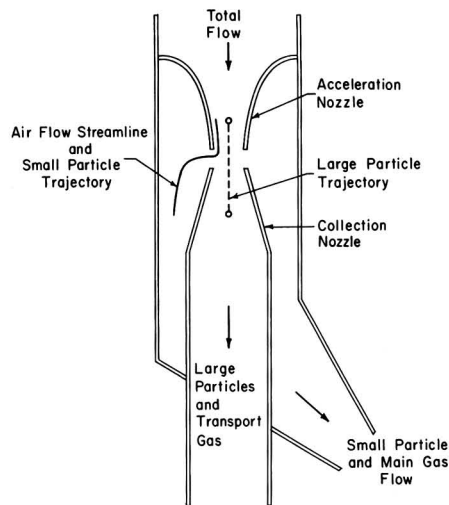


Figure 2. Centripeter concept—single jet

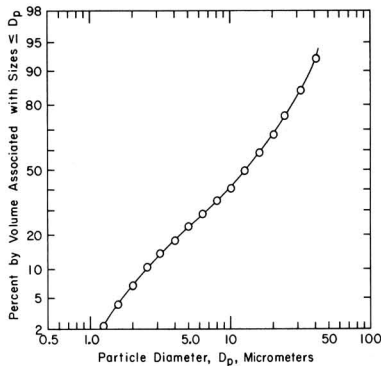
Table I. Centripeter Design Parameters

Number of jets	25
Acceleration nozzle diameter	0.65 cm
Collection nozzle diameter	0.91 cm
Gap between acceleration and collection nozzles	0.65 cm
Acceleration nozzle Reynolds number	3900
Collection nozzle Reynolds number	280
Total flow rate through system	850 L/min
Large particle transport flow rate	85 L/min
Particle cut size (aerodynamic diam)	5.2 $\mu\text{m}$

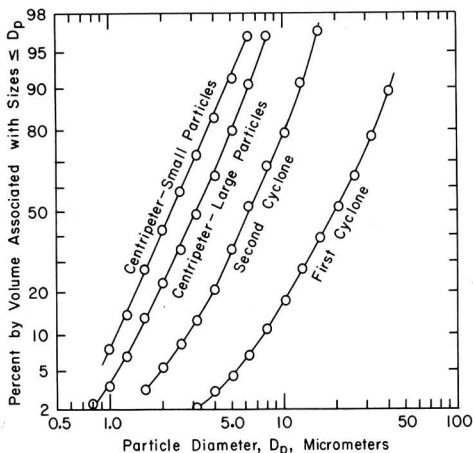
**Table II. Material Collected by System**

Fraction	Mass collected, kg <sup>a</sup>	%
First cyclone	5.38	66.6
Second cyclone	1.31	16.2
Centripeter—large particles	0.59	7.3
Centripeter—small particles	0.80	9.9

<sup>a</sup> Twelve-day collection period.



**Figure 3.** Size distribution of fly ash drawn into system



**Figure 4.** Size distribution of fly ash fractions

**Table III. Characteristics of Fly Ash Fractions**

Fraction	Mean particle density, g/cm <sup>3</sup>	SD	Vol median diam, μm <sup>a</sup>	Geometric SD
First cyclone	1.852 <sup>b</sup>	0.019	20.0	1.8
Second cyclone	2.186 <sup>b</sup>	0.023	6.3	1.8
Centripeter—large particles	2.358 <sup>c</sup>	0.015	3.2	1.8
Centripeter—small particles	2.445 <sup>b</sup>	0.014	2.2	1.9

<sup>a</sup> Mean of two determinations. <sup>b</sup> Mean of three determinations. <sup>c</sup> Mean of four determinations.

description of each fraction may be represented as shown in Table III. Volume median sizes of the fractions range from 20 μm for the first cyclone to 2.2 μm for the small particles from the centripeter. Photomicrographs of the collected fly ash fractions (Figure 5) show the quality of size separation which is achieved by the system.

The basic performance of a particle fractionation stage can be represented by its fractional efficiency, that is, the efficiency as a function of particle diameter. For the three fractionation stages employed in the system, these relationships were determined through knowledge of the total mass of each fraction and the corresponding Coulter Counter mass frequency size data. The computational scheme for efficiency was to compare the fraction of mass in each size interval which was removed by the collection stage with that which entered the stage.

To convert the Coulter Counter particle size to a more general size parameter, the aerodynamic equivalent size, the following expression was employed:

$$D_a^2 = \rho_p D_p^2 \quad (2)$$

where subscript *a* refers to the aerodynamic size parameter. The values of particle density appropriate to each of the size fractions were determined by a liquid displacement technique and are shown in Table III. Note that the density of the fly ash varied from 1.85 to 2.45 g/cm<sup>3</sup> depending upon the size fraction. This is consistent with the results of Fisher et al. (9), who reported on the presence of plerospheres (hollow spheres packed with smaller spheres) and cenospheres in hopper fly ash. Based upon microscopic analysis of the four fly ash fractions, we have quantitated the relative abundance of morphologic particle types (10). From this analysis it appears that vesicular particles are predominantly associated with the coarser fractions and solid spheres predominate in the finer fractions. It therefore appears that the variation in particle density may be explained primarily on the basis of the relative abundance of vesicular particles and solid spheres within the fly ash fractions.

Note that the apparent reduction in slope of the centripeter fractional efficiency (Figure 6) for the smallest particles reflects the presence of the small particles which are carried with the transport air in the fractionation zone. This causes introduction of up to 10% fine particles in the coarse fraction.

### Summary

Through the use of a specially developed particle fractionation system, it has been possible to collect kilogram quantities of size-fractionated particulate matter from an air pollution emission source. These quantities are compatible with the needs of biologic testing programs. Also, since the material is fractionated directly from the stack gas rather than from reaerosolized samples of bulk powders (e.g., laboratory classification of electrostatic precipitator hopper fly ash), it should provide a more representative biological challenge in health-hazard evaluation studies.

Aerodynamic cut sizes of the fractionation stages for the system which was developed were 10, 6.6, and 5.2 μm; however, other values for the cut sizes can easily be obtained through a combination of operating conditions and design parameters.

When employed in the collection of fly ash from a power plant, the system provided kilogram quantities of material with volume median sizes of 20, 6.3, 3.2, and 2.2 μm. Geometric standard deviations of the fractions were approximately 1.8.

Aside from the obvious requirement for biological testing of large quantities of aerodynamically sized particulates, the fractionator has utility in laboratory development and evaluation of pollution abatement instrumentation. Another

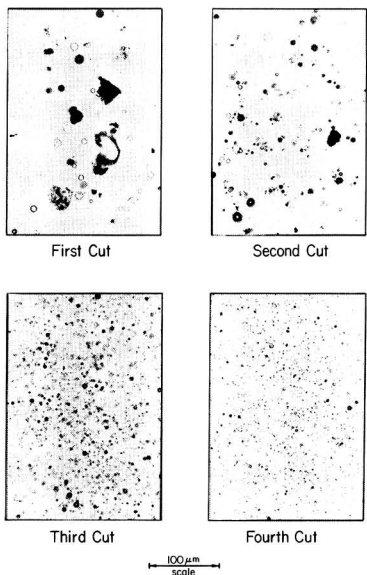


Figure 5. Photomicrographs of collected samples

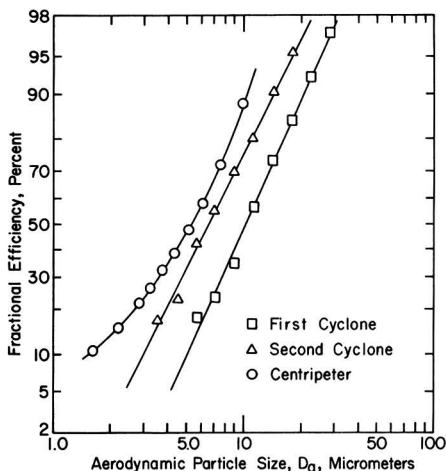


Figure 6. Fractional efficiencies of system stages

important application of this system involves the collection of sufficient quantities of materials for particulate standards to be used in the development and testing of analytical techniques. In this regard, a hopper fly ash standard certified for concentrations of 12 trace elements is available from the National Bureau of Standards (NBS-SRM 1633). This ma-

terial is a blend of fly ashes collected by electrostatic precipitators and mechanical collectors at five electric power plants. Since this standard is a blend of ashes which were collected by the particle emission abatement technologies at the various plants, the particle size is relatively large ( $11 \mu\text{m}$ —mass median Stoke's diameter) (11), and the collected material is not characteristic of that which escapes the control systems.

By use of the system described here, fly ash was collected and fractionated in situ after the ESP. This material is representative of fly ash that is released from the stack of the power plant, and the fractionation provides sufficient quantities of fly ash size fractions of environmental and biomedical importance for analytical technique development and testing. Furthermore, with additional fractionation of the size-classified material, such as by employing a spiral-duct aerosol centrifuge (12), essentially aerodynamically monodisperse particles may be obtained. The availability of monodisperse particles derived from actual air pollutants will provide the opportunity to evaluate important particle properties such as aerodynamic shape factors, morphologic heterogeneity (10), and chemical composition (10) within well-defined size classes. Such studies are ultimately required to provide specifications for the design of control technologies for specific components of particulates within size classes.

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# Reduction of Aqueous Free Chlorine with Granular Activated Carbon—pH and Temperature Effects

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■ A mathematical model, developed previously by the authors, is used to analyze the effect of pH and temperature on the reaction between free chlorine and activated carbon in batch and packed bed reactors. The  $\text{OCl}^-$  species reacts more slowly than  $\text{HOCl}$ , but apart from the effect of pH on the distribution of free chlorine between  $\text{HOCl}$  and  $\text{OCl}^-$ , no effect of pH is noted. An apparent activation energy of 10.5 kcal is found for the rate constant for dissociation of free chlorine on the carbon surface. The kinetic constants determined in this study permit the prediction of column breakthrough curves for various design and operation conditions.

Free chlorine ( $\text{HOCl} + \text{OCl}^-$  at pH values of importance in water purification) has been used in water treatment for many years for disinfection, ammonia removal, and taste and odor control. Free chlorine residual is sometimes in excess of desired levels; thus, it has to be removed or reduced in concentration. This may be the case, for example, after breakpoint chlorination, especially of wastewater. A number of industries also require chlorine-free water because of the interference of chlorine with some industrial processes. Dechlorination is also of interest since minimizing the time of chlorine contact with certain waters should reduce the extent of formation of chlorinated organics. These reasons illustrate the importance of having a well-understood process for the removal of chlorine from water.

A number of processes have been developed for eliminating or reducing free chlorine residuals from water as reviewed by Snoeyink and Suidan (1), and those which involve the use of sulfur compounds or activated carbon appear to be the most common. Because activated carbon can also be used for adsorption of organics and catalysis of the breakpoint reaction, its dechlorination properties were more closely examined in this study.

A mathematical model for the reaction between aqueous  $\text{HOCl}$  and activated carbon was developed previously (2). It was based upon both surface reaction and pore diffusion as rate limiting steps and accounted for the reduction in reaction rate owing to the buildup of reaction products on the carbon surface. Constants for the model were determined by analysis of data obtained from a small scale batch reactor, and the model was then used to predict chlorine concentration vs. time for various carbon particle sizes, chlorine doses, and carbon doses in batch reactors as well as chlorine effluent concentration vs. time for packed bed reactors as a function of detention time, particle size, and chlorine concentration. The applicability of the model to both types of reactors was then verified by laboratory experimentation. A brief outline of the model is presented here to aid in interpretation of the data.

The objective of the research reported herein was to determine the effects of pH and temperature on the reactions of  $\text{HOCl}$  and  $\text{OCl}^-$  with activated carbon with the aid of the model of Suidan et al. (2) and to predict the behavior of packed beds of carbon for various pH and temperature values.

## Mathematical Model

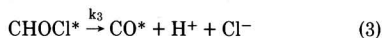
The reaction between  $\text{HOCl}$  and activated carbon can be represented by (3):



where  $\text{C}^*$  represents a reactive site on the carbon surface and  $\text{CO}^*$  represents a surface oxide. If  $\text{OCl}^-$  is the free chlorine species, no  $\text{H}^+$  is expected as an end product, except in the event the oxide is acidic and gives off a proton. To develop the reaction rate expression, the assumption was made that it proceeds by a reversible adsorption step:



followed by irreversible dissociation:



where  $\text{CHOCI}^*$  represents an adsorbed  $\text{HOCl}$  molecule and  $k_1$ ,  $k_2$ , and  $k_3$  are rate constants. Reaction rate decreases as oxides build up on the carbon surface, but not all oxides remain on the surface. The fraction of active sites occupied by the oxides,  $f_o$ , can be given by

$$f_o = \frac{Q}{k_5 + Q} \quad (4)$$

where  $Q$  represents the amount of chlorine reacted per unit surface area of the carbon. Assuming the reaction in Equation 3 to be rate limiting and the reaction in Equation 2 to be at equilibrium, the following surface reaction rate expression was developed:

$$R_c(C, f_o) = \frac{k_3 SC}{k_4 + C} (1 - f_o) \quad (5)$$

where  $k_4$  is  $k_2/k_1$ ,  $S$  refers to the total number of reactive sites, and  $C$  represents the concentration of  $\text{HOCl}$ . The model for reaction within the carbon pores was based on the assumption that a carbon particle can be represented by a flat slab with sealed ends having straight cylindrical pores of diameter  $d_p$  and length  $2L_p$ . The two ends of each pore are exposed to the concentration of the free chlorine species at the external surface of the carbon particle. Such a model is roughly equivalent to a spherical particle of diameter  $6L_p$  (4). Surface film diffusion resistance was shown to be negligible compared to pore diffusion under the conditions employed (2). Incorporating the surface rate expression, Equation 5, into a mass balance in the pore, the following was obtained:

$$\frac{\partial C}{\partial t} = \left[ \frac{D_c}{L_p^2} \right] \frac{\partial^2 C}{\partial \eta^2} - \left[ \frac{4k_3 S}{d_p} \right] \frac{C}{C + k_4} (1 - f_o) \\ \frac{\partial f_o}{\partial t} = \left[ \frac{k_3 S}{k_5} \right] \frac{C}{C + k_4} (1 - f_o)^3 \quad (6)$$

where  $\eta$  is a reduced position variable measured from the mouth of the pore,  $D_c$  is the diffusivity of the chlorine species, and

$$\eta = 0 : C = C_B \\ \eta = 1 : \frac{\partial C}{\partial \eta} = 0 \quad (7)$$

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are the boundary conditions. The initial conditions were taken to be the state of fresh carbon with  $f_o = 0$ .

The bulk fluid expression for  $C_B$  depends on the type of reactor employed. In the case of the semibatch reactor in which the bulk concentration is maintained constant,  $C_B = C_0$  in Equation 7. For a perfectly mixed closed batch reactor, a material balance on free chlorine yields

$$\frac{\partial C_B}{\partial t} = V_p \left( \frac{m}{\epsilon} \right) \left( \frac{D_c}{L_p^2} \right) \left( \frac{\partial C}{\partial \eta} \right)_{\eta=0} - R_d \quad (8)$$

where  $V_p$  represents the pore volume per unit weight of carbon,  $m$  represents the concentration of carbon in the reactor,  $\epsilon$  is the porosity of the reactor, and  $R_d$  is the rate of decrease of the chlorine concentration in a comparable blank reactor.

The model for the packed bed reactor was based on the experimental observation that the rate of reaction at a given time was not dependent on the previous concentration history of the reactor, but only on the amount of chlorine which had reacted per unit weight of carbon. An algebraic expression,  $R(\bar{Q}, C_B)$ , was then developed to represent the rate of chlorine mass removed per unit weight of carbon. The packed bed problem was thus reduced by one dimension, and the cost of numerically solving the problem was significantly reduced. Incorporation of  $R(\bar{Q}, C_B)$  into a mass balance on a packed bed with axial dispersion yielded

$$\frac{\partial C_B}{\partial t} = -\frac{m}{\epsilon} R(\bar{Q}, C_B) + D_A \frac{\partial^2 C_B}{\partial z^2} - v \frac{\partial C_B}{\partial z} \quad (9)$$

$$\frac{\partial \bar{Q}}{\partial t} = R(\bar{Q}, C_B)$$

where  $C_B$  is the concentration of free chlorine,  $v$  is the interstitial liquid velocity in the bed,  $m$  is the mass of carbon per unit bed volume,  $\epsilon$  is the porosity of the packed bed,  $z$  is the distance dimension as measured from the entrance end of the bed, and  $D_A$  is the axial dispersion coefficient. The boundary conditions are:

$$z = 0 : vC_o = vC_B - D_A \frac{\partial C_B}{\partial z}$$

and

$$z = L_b : \frac{\partial C_B}{\partial z} = 0 \quad (10)$$

where  $L_b$  is the bed length. The initial state of  $C_B$  was the steady-state solution obtained from Equation 9 with  $\bar{Q}$  set to zero. The models were solved numerically using an implicit finite difference scheme (5).

#### Experimental Materials and Methods

The activated carbon, Filtrasorb 400 (Calgon Corp., Pittsburgh, Pa.), was prepared by mechanical grinding followed by sieving into a number of particle size ranges. It was then thoroughly washed with deionized water and dried at 105–110 °C. The DPD ferrous titrimetric procedure (6) was used to

determine the concentration of aqueous chlorine. For experiments run at pH 10, samples were acidified prior to free chlorine measurements. Free chlorine solutions were prepared by adding measured volumes of the stock free chlorine solution to deionized water containing  $7 \times 10^{-3}$  M phosphate buffer. Carbonate salts ( $2 \times 10^{-4}$  M at pH 7.6 and  $5.5 \times 10^{-2}$  at pH 10) were added to minimize pH variation owing to  $\text{CO}_2$  absorption. HCl and NaOH were used to adjust pH. For closed batch experiments carried out at pH 4.0, a Fisher Titrimeter (Fisher Scientific Co., Pittsburgh, Pa.) was used to maintain constant pH. At pH 7.6 and 10, the buffer capacity was sufficiently strong to permit manual pH control.

Four-liter systems were used for the closed batch tests. A blank reactor containing all reagents except activated carbon was run to determine the rate of disappearance of free chlorine owing to factors other than reaction with activated carbon. Stirrers with Teflon stirring rods were used, and the stirring speed was maintained at 764–917 rpm. The experiments were run at room temperature, 22.5–23.5 °C with 23 °C as a mean, 35 °C (temperature bath), and 2 °C (constant temperature cold room). After the solutions were mixed for about 3 h, activated carbon was added to the reactors; the initial concentration of chlorine was measured just prior to carbon addition.

A 1.5-cm i.d. column was used for the packed bed experiment. The carbon, 2.35 g of 60 × 80 U.S. standard mesh, bed length,  $L_b = 2.6$  cm, column diameter/particle diameter = 74, was sandwiched between inert Ottawa sand of the same particle size. Approximately 15 cm of sand were used above and below the carbon to control the flow regime through the carbon. A flow rate of 32.78 mL/min (4.26 gpm/ft<sup>2</sup>) was used. A positive displacement pump (Fluid Metering Inc., Oyster Bay, N.Y.) was used to provide a constant flow rate. The influent solution was prepared in 60-L batches and was stabilized 3 h prior to applying it to the carbon.

#### Results and Discussion

**Determination of Constants.** The rate of disappearance of free chlorine from the blank reactors was observed to follow first order kinetics rather closely. Thus, the term  $R_d$ , the decay rate term in Equation 8, was replaced by

$$R_d = k_d C_B \quad (11)$$

where  $k_d$  is a first order rate constant. Values of  $k_d$  for all experiments are given in Table I. The diffusivity coefficient,  $D_c$ , was assigned the value  $10^{-5}$  cm<sup>2</sup>/s at 23 °C. This value is an order-of-magnitude estimate for similar molecules in liquids and was used for both HOCl and OCl<sup>-</sup>. (Approximation of  $D_c$  by the Wilke-Chang model (7) gave a value of  $1.5 \times 10^{-5}$  cm<sup>2</sup>/s for HOCl). The value used for  $V_p$  was 0.94 cc/g (8).  $L_p$  was always taken as one-sixth of the arithmetic mean diameter of the particle size range. The remaining constants [ $4k_3S/d_p$ ], [ $k_3S/k_5$ ], and  $k_4$  were evaluated for each set of conditions by a trial and error fit of closed batch reactor experimental data.

**Table I. Values of Constants in Mathematical Model**

Constant	pH 4		pH 7.6, $T = 23$ °C	pH 10		
	$T = 23$ °C	$T = 35$ °C		$T = 2$ °C	$T = 23$ °C	$T = 35$ °C
$4 k_3 S/d_p$ , g/cm <sup>3</sup> -s	$6.08 \times 10^{-3}$	$1.22 \times 10^{-2}$	$3.82 \times 10^{-3}$	$4.06 \times 10^{-4}$	$1.56 \times 10^{-3}$	$3.13 \times 10^{-3}$
$k_3 S/k_5$	2.17	4.34	1.36	0.145	0.557	1.12
$k_4$ , g/cm <sup>3</sup>	$1.81 \times 10^{-5}$	$1.81 \times 10^{-5}$	$1.81 \times 10^{-5}$	$1.81 \times 10^{-5}$	$1.81 \times 10^{-5}$	$1.81 \times 10^{-5}$
$k_d$ , s <sup>-1</sup>	$2.23 \times 10^{-7}$	$5 \times 10^{-7}$	$2.23 \times 10^{-7}$	$2.23 \times 10^{-7}$	$2.23 \times 10^{-7}$	$2.23 \times 10^{-7}$
$D_c$ , cm <sup>2</sup> /s	$1 \times 10^{-5}$	$1.34 \times 10^{-5}$	$1 \times 10^{-5}$	$0.52 \times 10^{-5}$	$1 \times 10^{-5}$	$1.34 \times 10^{-5}$
$L_p$ (60 × 80), cm	0.0035					
$V_p$ , cm <sup>3</sup> /g	0.94					



**Effect of pH.** Data showing the effect of pH on the reaction of  $60 \times 80$  mesh carbon with chlorine in closed batch reactors are given in Figure 1. Two experiments using the same conditions were conducted at pH 4, and excellent reproducibility was obtained. The remaining constants in the model were determined by a trial-and-error fit of the data; the constants are given in Table I, and the solid lines in Figure 1 were calculated using these constants. Additional experiments using different initial concentrations and carbon dosages were fit equally well using these constants.

HOCl is a weak acid with a  $pK_a$  of 7.6 at  $23^\circ\text{C}$  (9). Thus, at pH 4, HOCl predominates; at pH 10,  $\text{OCl}^-$  predominates; and at pH 7.6, the concentrations of each are equal. When determining the constants at pH 10 and 7.6, the assumption was made that  $k_4$  was the same for  $\text{OCl}^-$  as for HOCl. This assumption yields an overall surface reaction rate expression for a combination of the two species similar to that obtained for the single species. The dissociation rate constant,  $k_3$ , in this case is a function of the relative concentrations of HOCl and  $\text{OCl}^-$ . The overall surface reaction rate expression becomes

$$R_c(C, f_o) = \frac{SC(1 - f_o)}{k_4 + C} (k_{3\text{HOCl}}f_{\text{HOCl}} + k_{3\text{OCl}^-}f_{\text{OCl}^-}) \quad (12)$$

where  $C$  represents the total free chlorine concentration,  $k_{3\text{HOCl}}$  and  $k_{3\text{OCl}^-}$  represent the surface dissociation rate constants of HOCl and  $\text{OCl}^-$ , respectively, and  $f_{\text{HOCl}}$  and  $f_{\text{OCl}^-}$  represent the fractions of the total free chlorine residual in the form of HOCl and  $\text{OCl}^-$ , respectively. At pH 7.6, a rather good fit of the data was obtained for values of  $[4k_3/d_p]$  and  $[k_3S/k_5]$  which are the average of the values of the two constants at pH 4 and 10, consistent with the assumption that the pH effect is dependent only on the relative distribution of HOCl and  $\text{OCl}^-$ , and indicating that Equation 12 is valid. Magee (3) presented values of a first order rate constant vs. pH which are consistent with this conclusion.

The data shown in Figure 2 represent a breakthrough curve for a packed bed experiment with an influent pH of 10. The effluent pH remained at 10 with no noticeable variation during the run. The experiment was stopped after 250 h prior to the appearance of any brown color material. Using the values for the constants obtained from the batch data at pH 10, an algebraic expression for  $R(\bar{Q}, C_B)$  was obtained using the procedure of Suidan et al. (2). The packed bed model was solved using an axial dispersion coefficient of  $0.0167 \text{ cm}^2/\text{s}$ , and the predicted curve is shown in Figure 2. In this case, the prediction is not quite as good as was observed at pH 4 by Suidan et al. (2), but it is considered satisfactory for most purposes.

**Effect of Temperature.** Temperature is expected to affect both the diffusivity and the reaction rate constants. The diffusivity at 2 and  $35^\circ\text{C}$  was calculated, based on the assumption that the effect of temperature in the carbon pore was similar to that in free solution, using the equation,

$$D_c(\bar{T}_2) = D_c(\bar{T}_1) \frac{\mu_1 \bar{T}_2}{\mu_2 \bar{T}_1} \quad (13)$$

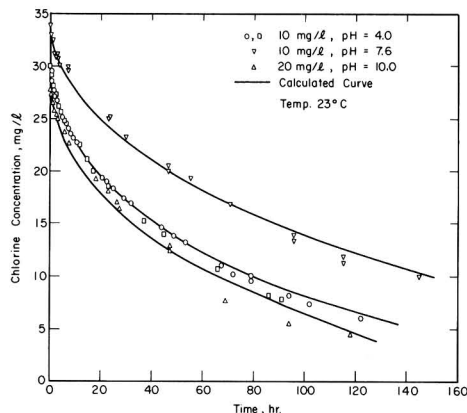
where  $\mu$  is the viscosity and  $\bar{T}$  is the absolute temperature (10). These diffusivities are given in Table I.

Closed batch reactor data are shown in Figure 3 for pH 10, at 2 and  $35^\circ\text{C}$ , and pH 4 at  $35^\circ\text{C}$ . Trial-and-error fit of the data yielded the constants  $k_4$ ,  $[4k_3S/d_p]$ , and  $[k_3S/k_5]$  as given in Table I, and the solid lines in Figure 3 are the model predictions using these constants. Additional runs using other values of  $C_o$  and carbon dose showed equally good correspondence between data and predicted curves. The value of  $k_4$ , the equilibrium constant, in all cases was the same as it was at  $23^\circ\text{C}$ , thus indicating that the major effect of temperature was to change the value of  $k_3$ .

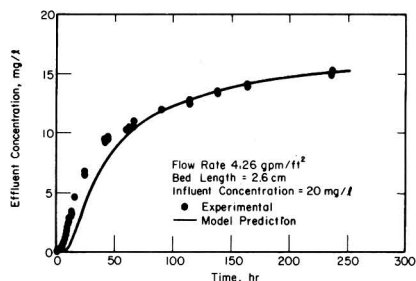
Figure 4 shows an Arrhenius plot of the temperature effect data. The three values of  $[4k_3S/d_p]$  available at pH 10 fall on

a straight line, and the two values at pH 4 form a line parallel to it. Based on these limited data, the apparent activation energy for  $k_3$ , the only rate constant which is part of  $[4k_3S/d_p]$ , is  $10.5 \text{ kcal/mol}$ . The constant  $k_4$  represents the adsorption-desorption equilibrium constant, and it likely varies with temperature. In this study, however, it was assumed that  $k_4$  did not vary with temperature in fitting the data; thus, the variation observed in  $k_3$  includes the effect of temperature on  $k_4$ , if any.

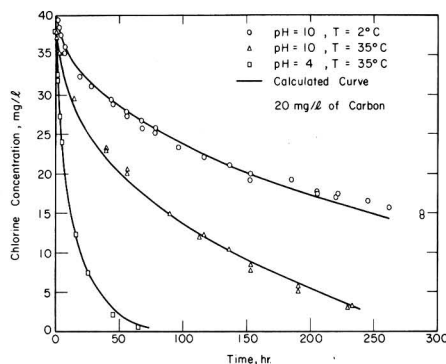
**Predicted Breakthrough Curves for Packed Bed Reactors.** The constants determined by analyzing the closed



**Figure 1.** Effect of pH on carbon-chlorine reaction in closed batch reactor



**Figure 2.** Chlorine breakthrough curve at pH 10,  $23^\circ\text{C}$



**Figure 3.** Effect of pH and temperature on carbon-chlorine reaction in closed batch reactor

batch reactor data can now be used to calculate breakthrough curves for packed bed reactors at various pH, temperature, influent concentration, particle size, and flow rate. The curves shown in Figure 5 were calculated assuming a column bed depth of 10 cm, an application rate of 4 gpm/ft<sup>2</sup>, and 18 × 20 mesh carbon size, a bed porosity of 0.43, and a C<sub>0</sub> of 5 mg/L. (See ref. 11 for complete families of curves for a variety of conditions.) These curves are specific for the carbon used in this study, but the magnitude of the pH and temperature effects is expected to be similar for other commercially available carbons.

### Conclusions

This study shows the magnitude of the effects of pH and temperature on the reaction between HOCl and OCl<sup>-</sup> and activated carbon and also that constants can be obtained from small scale batch reactor data which enable the prediction of packed bed reactor performance. The mathematical model satisfactorily describes the effects, but it should be noted that this does not necessarily confirm the assumed mechanism. The constants determined in this study are specific for the carbon used; the magnitude of the pH and temperature effects is expected to be similar for other commercially available carbons, though, and the procedure for studying the other carbons would be similar to that outlined here.

The pH was observed to influence the reaction rate only in

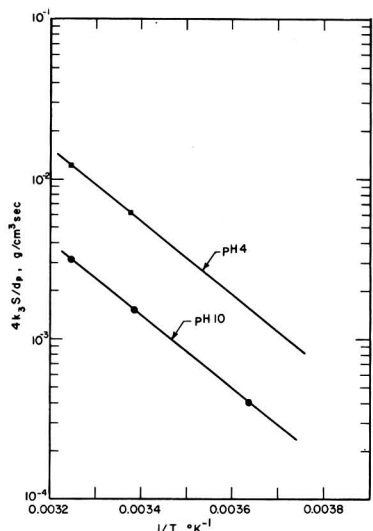


Figure 4. Effect of temperature on parameter  $4 k_3 S/d_p$

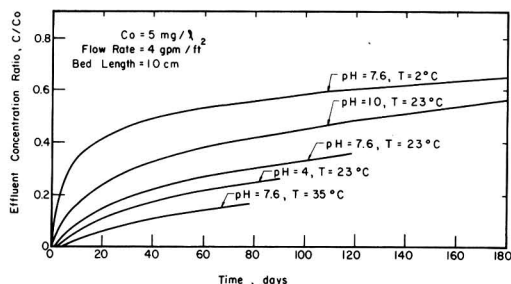


Figure 5. Effect of pH and temperature on chlorine removal in packed beds of 18 × 20 mesh carbon

that it affects the distribution of free chlorine between HOCl and OCl<sup>-</sup>.

Having established the pH and temperature effects, general expressions were developed for  $[4 k_3 S/d_p]$  and  $[k_3 S/k_5]$  as functions of temperature and pH

$$\left[ \frac{4 k_3 S}{d_p} \right]_{pH, \bar{T}} = \frac{5.325 \times 10^4 [6.08 + 1.57 \times 10^{(pH - pK\bar{T})}]}{1 + 10^{(pH - pK\bar{T})}} \exp\left(\frac{-5266}{\bar{T}}\right)$$

$$\left[ \frac{k_3 S}{k_5} \right]_{pH, \bar{T}} = \left[ \frac{4 k_3 S}{d_p} \right]_{pH, \bar{T}} \times 357.2 \quad (14)$$

White (12) gave values of the pK<sub>a</sub> at six different temperatures which could be used to compute an enthalpy for the HOCl dissociation reaction, ΔH°, of 4.0 kcal. With this value, the pK<sub>a</sub> at temperature  $\bar{T}$  can be computed using the following expression:

$$pK\bar{T} = 7.6 + 874.27 \frac{(296 - \bar{T})}{296 \times \bar{T}} \quad (15)$$

Since  $k_4$  is constant for all cases, Equations 14 and 15 can be used to calculate the parameters needed to compute breakthrough curves for pH and temperature values other than those studied here.

The effect of the presence of organic compounds on the rate of uptake of free chlorine by activated carbon has not yet been investigated. This is a very important parameter which is difficult to evaluate because of the wide variability of the type of organic compounds present in water and wastewater and because of the possibility that free chlorine may react with some of the adsorbed and nonadsorbed organic compounds. The effects presented in this paper are for pure solutions and should thus be used as "baseline" values in any design calculations. A factor of safety should be used to protect against short filter runs owing to the presence of organic matter.

### Nomenclature

- C = free chlorine concentration, M/L<sup>3</sup>
- C<sub>B</sub> = bulk free chlorine concentration, M/L<sup>3</sup>
- C<sub>0</sub> = initial or influent bulk chlorine concentration, M/L<sup>3</sup>
- CHOC1\* = free chlorine molecule adsorbed on carbon surface, SITE/L<sup>2</sup>
- C\* = reactive surface sites on carbon surface, SITE/L<sup>2</sup>
- CO\* = oxidized surface sites on carbon surface, SITE/L<sup>2</sup>
- D<sub>A</sub> = packed bed axial dispersion coefficient, L<sup>2</sup>/T
- D<sub>c</sub> = free chlorine pore diffusion coefficient, L<sup>2</sup>/T
- d<sub>p</sub> = diameter of straight cylindrical pore, L
- f<sub>o</sub> = fraction of active sites occupied by surface oxides
- f<sub>HOCl</sub> = fraction of free chlorine present in HOCl form
- f<sub>OCl<sup>-</sup></sub> = fraction of free chlorine present in OCl<sup>-</sup> form
- k<sub>1</sub> = adsorption rate constant for free chlorine on carbon surface, L<sup>3</sup>/T·M
- k<sub>2</sub> = desorption rate constant for free chlorine from carbon surface, T<sup>-1</sup>
- k<sub>3</sub> = surface reaction rate constant, M/T·SITE
- k<sub>3HOCl</sub> = k<sub>3</sub> for HOCl
- k<sub>3OCl<sup>-</sup></sub> = k<sub>3</sub> for OCl<sup>-</sup>
- k<sub>4</sub> = equilibrium constant for adsorption-desorption step = k<sub>2</sub>/k<sub>1</sub>, M/L<sup>3</sup>
- k<sub>5</sub> = denominator constant in f<sub>o</sub> expression, M/L<sup>2</sup>
- k<sub>d</sub> = first order rate of decay constant, T<sup>-1</sup>
- L<sub>b</sub> = length of packed bed, L
- L<sub>p</sub> = pore half length, L
- m = mass of carbon per unit reactor volume, M/L<sup>3</sup>
- Q = mass of free chlorine reacted per unit surface area of carbon, M/L<sup>2</sup>
- $\bar{Q}$  = average mass of chlorine reacted per unit weight of carbon

$R_c(C, f_o)$  = rate of surface reaction of free chlorine, M/L<sup>2</sup>.  
 $T$   
 $R_d$  = rate of decay of free chlorine in blank reactor, M/L<sup>3</sup>.  
 $T$   
 $R(\bar{Q}, C_B)$  = rate of chlorine mass removed per unit weight of carbon, T<sup>-1</sup>  
 $S$  = total surface sites on carbon surface, SITE/L<sup>2</sup>  
 $\bar{T}$  = absolute temperature, K  
 $t$  = cumulative time for a batch or column run, T  
 $V_p$  = pore volume per unit mass of carbon, L<sup>3</sup>/M  
 $v$  = interstitial liquid velocity through packed bed, L/T  
 $z$  = distance coordinate as measured from entrance end of packed bed reactor, L  
 $\epsilon$  = packed bed porosity  
 $\eta$  = nondimensionalized distance coordinate as measured from pore mouth  
 $\mu$  = absolute viscosity of solution, M/L·T

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## Evaluation of Particulate Trace Species in Southwest Desert Atmosphere

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■ A sampling program using high-volume filter samples for studying the concentration and composition of particulate matter in the arid southwest (in and near Tucson, Ariz.) was established in January 1974. Through the use of statistical techniques and examination of enrichment factors, it is possible to make a number of suggestions regarding the sources for and the cycle of various species in the, desert rural and urban atmosphere. Large particle airborne soil or crustal materials dominate the aerosol population found in both the urban and rural atmosphere with over a dozen of the measured species directly attributable to this source. Nonsoil species, in general, appear to be fairly well mixed and probably result primarily from nonurban anthropogenic and natural sources. The acid-base nature of airborne gases and particles would appear to control the gas and particle distribution of ammonia and to largely define the particulate sulfate speciation [primarily (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>]. Large seasonal fluctuations, consistent with the climatology and meteorology for the area under investigation, are seen in the concentration and composition of particulate matter in the desert atmosphere.

In recent years particulate trace species in the atmosphere have received an increasing amount of attention. Studies by a number of investigators around the country and world have produced a large amount of information concerning the particulate concentration and distribution of trace elements in polluted (1-6) and clean airsheds (7, 8). To date, such studies have been largely confined to major urban centers on the east and west coasts of the United States and to the very remote areas of the world. Currently, there is little information available regarding the concentration and behavior of particulate trace species in the rural and smaller urban areas of inland United States localities. The arid western and southwestern region of this country is an area where information

of this type is especially needed. The arid West is receiving increasing attention and activity with regard to energy production (coal fired) and nonferrous metallurgical processing. An understanding of the composition and distribution of the aerosol population is required if the cause and effect relationships in atmospheric quality are to be defined and predicted.

The present particulate sampling program in and near Tucson was established to characterize the chemical composition of atmospheric particulate constituents in the metropolitan population of approximately 300 000. The city, at an elevation of 800 m, is essentially surrounded by mountains ranging in altitude from 3000 m (to the north) to about 1500 m (to the west). Tucson is perhaps a typical western community with relatively low density population occupying the 80 square miles encompassing the city. The sprawling nature of the city is responsible for a large automobile dependent commuting population. Tucson is predominantly a service community with essentially no heavy industry. Economically, the city is dependent upon tourism, agriculture, government services (Davis Monthan Air Force Base, University of Arizona), and the mining industry. Approximately half of the copper produced in the United States is mined and refined within about a 120-mile radius of Tucson, although the actual sites are removed from the immediate area. Electric power for the city is supplied locally by both gas- and oil-fired generators. A substantial portion of the city's power needs is supplied by remote coal-fired units. Currently, the home and city heating needs are dependent upon natural gas.

It is the purpose of this report to define the composition of particulate species in an urban and rural portion of the southern Arizona atmosphere. A survey study of the particulate species distribution and behavior in this region of the country is described. The term "background" as used here and in the companion paper (9) refer to areas removed from urban and local anthropogenic activities and is not meant to imply

a true desert background in which man's influence on the atmosphere is absent or necessarily minimized. Urban centers, metal processing, power generation, and other industrial activities in the southwest portion of the United States are expected to significantly influence the airborne particulate composition of both rural and urban atmospheres. This paper and the companion paper are aimed at defining ambient particle composition and evaluation techniques which can be used to suggest improved sampling (source and ambient) and analysis procedures to obtain a more complete picture of sources, sinks, and chemistry of various atmospheric species in this section of the country. The information available from the ambient composition data coupled with these improved and more detailed future studies should provide for an efficient means of evaluating the impact current anthropogenic activities and those to be developed do, or may, have on the air quality (e.g., visibility, species burden, etc.) of the arid southwestern atmosphere.

### Experimental

**Sampling Program.** In December of 1973 a sampling program was established at 11 locations in and around Tucson. These stations included eight urban locations, two near urban locations (20 miles south and southeast of Tucson), and a "background" station (the Research Ranch) approximately 60 miles southeast of the city. The Research Ranch was established to preserve a sizable area of generally high desert grassland. Established primarily to support biological research, conservation and education, this facility is ideally suited for various aspects of atmospheric chemistry research through the absence of local anthropogenic activities and the native desert conditions maintained on the land. It is a protected land-laboratory which includes 3 215 acres of private, 2 350 acres of state, and 2 275 acres of U.S. Forest Service land. The ranch is situated in the transition zone between the Sonora Plains and the Huachuca Mountains in southeastern Arizona, and the nearest small town, Elgin (population ~50), is 4.8 miles to the north.

The sampling stations for this work consisted of two high-volume samplers (Bendix Model 500, Bendix Corp., Baltimore, Md.) equipped with flow meters. Glass fiber filters (Gelman Type A) were used as the collection media on one of the samplers. The other sampler was used with polystyrene filters (Microsorban Type 99197, Delbag Luftfilter GMBH, Berlin, Germany). The sampling program was carried out through 1974 sampling for 24 h at each location every sixth day. Sampling rates were approximately 85 m<sup>3</sup>/h for each sampler. The hi-vol flow rates were calibrated and adjusted monthly with a manometer and set of meter calibration orifices.

**Analytical Techniques. Trace Metal Analysis by Atomic Absorption.** One half of the polystyrene filter was used for the analysis of 23 elements by atomic absorption spectrometry. The filters were ashed in a muffle furnace at 400 °C, and the residue was digested in Parr acid digestion bombs (Parr Instrument, Co., Moline, Ill.) with HF, HCl, and HNO<sub>3</sub>. After suitable dilutions and matrix additions, the samples were analyzed by conventional atomic absorption for Si, Al, Ca, Fe, K, Na, Mg, Pb, Ti, Zn, Cu, Cd, Mn, Sr, Rb, Ni, Li, Cr, Co, and Cs. Complete details of the analytical procedure are given by Ranweiler and Moyers (10).

**Sulfate-Nitrate-Ammonium Analysis.** For the analysis of sulfate, nitrate, and ammonium ions, 8 in.<sup>2</sup> (1/8) of the glass fiber filter were used. The fraction of the filter being used for analysis was cut into small pieces with stainless steel scissors and added to the Teflon beaker of a Parr acid digestion bomb. Ten milliliters of distilled deionized water was added, and the beaker sealed in the stainless steel jacket and heated to 100 °C for 1 h to remove the water soluble NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>.

After cooling, the solution was diluted to 20 mL and separated from the filter material by filtration. With approximately 5% (1 mL) of this solution, NH<sub>4</sub><sup>+</sup> was measured with the Indophenol method (11). Approximately 10% (2 mL) of the above solution was used for the NO<sub>3</sub><sup>-</sup> determination by modification of the Greise-Saltzman reaction (12). Approximately 40% of the solution from the sample digestion was used for the determination of SO<sub>4</sub><sup>2-</sup>, by use of the standard Barium turbidity method (13).

Standard Reference Materials (NBS Fly Ash and Orchard Leaves) were analyzed routinely with the atmospheric samples. Results from the analysis of these materials have shown the analytical techniques to provide the degree of accuracy and precision required for these studies (RSD of 10% or less) (14).

### Results

Table I presents the average and standard deviations for the 1974 samples at the rural and urban locations. In the design of the sampling network the Research Ranch was specifically chosen to provide a rural site not influenced by local activities. The urban location for which the data are presented here was selected by statistically determining which urban location closely approximated the urban average for all orthogonal species measured. The urban locations show increased concentrations relative to the rural location for every species measured in this program. The near urban locations showed trace species concentrations in every case intermediate to that found at the urban and rural locations. The data in Table I show that the increased burden of trace species in the urban air relative to rural air varies from species to species. These data do, however, suggest apparent urban sources (although relatively small in some cases) for every species measured in this program.

In addition to examining averages, ranges, composition, and frequency distributions for each species, the interspecies

**Table I. Concentration of Species in Southern Arizona Rural and Urban Atmosphere**

	Urban, µg/m <sup>3</sup>		Rural, µg/m <sup>3</sup>	
	$\bar{x}$	$\sigma$	$\bar{x}$	$\sigma$
Mass	111	72.9	29.1	13.0
Si	18.4	13.4	3.9	2.5
Al	5.7	4.4	1.2	0.68
Ca	5.3	3.4	0.79	0.47
SO <sub>4</sub> <sup>2-</sup>	4.8	4.8	3.7	2.6
Fe	2.9	2.1	0.66	0.58
K	2.6	2.1	0.53	0.34
NO <sub>3</sub> <sup>-</sup>	1.9	0.8	0.83	0.41
Na	1.3	0.89	0.28	0.21
Mg	1.1	1.0	0.18	0.13
NH <sub>4</sub> <sup>+</sup>	1.1	1.2	0.77	0.78
Pb	0.69	0.45	0.067	0.056
Ti	0.39	0.30	0.10	0.08
Zn	0.17	0.11	0.11	0.07
Cu	0.19	0.07	0.11	0.09
Mn	0.055	0.044	0.012	0.008
Sr	0.020	0.014	0.0031	0.0027
Rb	0.011	0.008	0.0024	0.0015
Ni	0.0060	0.0036	0.0032	0.0030
Li	0.0044	0.0036	0.0089	0.0006
Cr	0.0040	0.0034	0.0031	0.00022
Cd	0.0024	0.0039	0.0020	0.00021
Co	0.0019	0.0019	0.0007	0.0005
Cs	0.0015	0.0029	0.0006	0.0011

relations which exist in this geographic area have also been examined. These relationships have been evaluated to date primarily by linear least-squares regression analysis. These statistical evaluations have been applied to all data collected in this study. In general, least-squares regression analysis showed that a number of interspecies relationships do exist. Furthermore, there appear to be significant differences in these relationships at the "background location" (Research Ranch) and the Tucson locations. In Tables II and III those data are presented for which samples were collected simultaneously at the urban and rural sampling sites.

Table II presents the linear correlation coefficients for the data collected at the representative urban location for all possible elemental pairs. With the number of data used in this study, correlation coefficients of about 0.3 and greater would indicate a statistically significant ( $p = 0.05$ ) relationship (15). The degree of correlation is, of course, improved (i.e., scatter reduced) as the absolute value of the coefficient increases. Certainly, caution must be used in interpreting the significance of correlation coefficients obtained from data of this type. Statistical data evaluation of the type used in this work is parametric and may suffer when applied to non-Gaussian parameter distributions.

From Table II, one should note the following features: The elements Al, Fe, Si, Ti, Li, Rb, K, Na, Ca, Mg, Mn, Sr, and Cr all are correlated with each other (Co, Cs, and Ni show reduced correlations with these same elements and with each other); the total mass of suspended particulates shows the most significant relationship with these same elements; the elemental pair  $\text{SO}_4^{2-}$ - $\text{NH}_4^+$  is very highly correlated with each other in the Tucson atmosphere; Pb and Cu appear to have some correlation with  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  as does Pb with  $\text{NO}_3^-$ ; and the elements Cd and Zn show no apparent relationship to any other chemical component measured in this investigation.

Table III presents the linear correlation coefficient matrix for the Research Ranch data collected in 1974. The following facts are suggested in this information: The elements Al, Fe, Si, Ti, Li, Rb, Mg, Na, Ca, Mn, and Sr would appear to be correlated to each other (Cr is apparently not in this group as it was at the Tucson locations); mass is also related to the above species; again,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  are apparently strongly correlated; however, at this location, the elements Pb, Cu, Cd, and Zn also show a significant correlation with the  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  and with each other; and the species Cr, Ni, Co, Cs, and  $\text{NO}_3^-$  show only weak or no correlation to the other chemical parameters examined in this work.

One of the most interesting and significant results evident from Table II is the high sulfate-ammonium correlations. Linear least-squares correlation coefficients greater than 0.8 were obtained for  $\text{SO}_4^{2-}/\text{NH}_4^+$  at all sampling locations. This high correlation may be expected from the acid-base nature of atmospheric sulfur dioxide and ammonia, and such relationships have been demonstrated in humid climates (16). For arid climates, however, this apparent association of  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  has not been previously studied. Figure 1 presents a scatter diagram for the urban ammonium and sulfate concentrations measured in this program. Figure 2 is a similar diagram for the rural samples. The sulfate-to-ammonium ion relationship was remarkably consistent at all sampling locations (i.e., essentially identical correlations, slopes, and intercepts). For both the urban and rural location, the least-squares line intercepts the sulfate axis at a value of about  $1 \mu\text{g}/\text{m}^3$ . This may suggest that before apparent buffering by ammonia occurs, sulfuric acid generated or condensed at the particulate surface is initially neutralized by basic materials in the particles. Alternatively, this intercept may indicate that portion of the sulfate which does not have a sulfuric acid (or  $\text{SO}_2$ ) origin (i.e., primary sulfate aerosols vs. secondary aerosols).

Table II. Linear Correlation Coefficients for Urban Samples (Location 2)

	$\text{NH}_4^+$	$\text{SO}_4^{2-}$	Cu	Cd	Pb	$\text{NO}_3^-$	Zn	Ni	Ca	K	Fe	Mg	Na	Cr	Rb	Ti	Mass	Al	Si	Sr	Li	Mn	Co	Cs	
$\text{NH}_4^+$	1.00																								
$\text{SO}_4^{2-}$	0.87	1.00																							
Cu	0.54	0.64	1.00																						
Cd	0.22	0.20	0.22	1.00																					
Pb	0.49	0.49	0.36	0.24	1.00																				
$\text{NO}_3^-$	0.35	0.27	0.16	0.34	0.54	1.00																			
Zn	0.36	0.32	0.25	0.38	0.31	0.17	1.00																		
Ni	0.14	0.20	0.30	0.30	0.21	0.38	0.26	1.00																	
Ca	0.13	0.09	-0.05	0.07	0.11	0.23	0.31	0.45	1.00																
K	0.06	0.04	-0.04	0.07	0.21	0.22	0.36	0.51	0.92	1.00															
Fe	0.03	0.01	-0.09	0.04	0.13	0.20	0.31	0.49	0.93	0.98	1.00														
Mg	0.01	0.01	-0.00	0.05	0.04	0.17	0.25	0.56	0.92	0.90	0.92	1.00													
Na	0.02	0.01	0.00	0.12	0.31	0.31	0.34	0.54	0.88	0.92	0.89	0.86	1.00												
Cr	-0.03	-0.04	0.13	0.12	0.03	0.18	0.23	0.65	0.71	0.75	0.76	0.80	0.71	1.00											
Rb	0.01	0.02	0.04	0.14	0.16	0.26	0.02	0.49	0.65	0.71	0.73	0.73	0.68	0.76	1.00										
Ti	-0.05	-0.10	-0.14	0.01	-0.04	0.11	-0.02	0.40	0.78	0.78	0.82	0.83	0.68	0.77	0.85	1.00									
Mass	0.10	0.10	-0.06	-0.02	0.11	0.18	0.11	0.41	0.76	0.78	0.78	0.75	0.64	0.80	0.77	0.84	1.00								
Al	-0.05	-0.07	-0.06	0.04	0.05	0.20	0.01	0.49	0.83	0.83	0.87	0.91	0.77	0.80	0.85	0.94	0.79	1.00							
Si	-0.03	-0.06	-0.06	0.03	0.02	0.18	0.05	0.50	0.82	0.84	0.87	0.88	0.76	0.84	0.90	0.96	0.85	0.96	1.00						
Sr	-0.04	-0.07	-0.04	0.07	0.10	0.26	0.08	0.49	0.81	0.79	0.82	0.90	0.79	0.81	0.86	0.89	0.73	0.95	0.92	1.00					
Li	-0.06	-0.07	0.04	0.11	0.06	0.19	0.05	0.55	0.75	0.80	0.80	0.86	0.78	0.86	0.85	0.89	0.70	0.91	0.91	0.92	1.00				
Mn	-0.09	-0.11	0.03	0.11	0.03	0.19	0.00	0.56	0.76	0.79	0.80	0.86	0.77	0.87	0.83	0.88	0.71	0.83	0.92	0.89	0.96	1.00			
Co	-0.02	0.00	0.16	0.11	0.04	0.18	0.09	0.51	0.47	0.57	0.56	0.62	0.51	0.65	0.56	0.60	0.57	0.68	0.64	0.58	0.64	0.73	1.00		
Cs	-0.10	-0.08	0.09	0.04	0.03	0.03	-0.04	0.48	0.51	0.62	0.61	0.68	0.52	0.71	0.65	0.72	0.66	0.76	0.75	0.65	0.72	0.82	0.88	1.00	

Table III. Linear Correlation Coefficients for Rural Samples (Location 11)

	NH <sub>4</sub> <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	Cu	Cd	Pb	NO <sub>3</sub> <sup>-</sup>	Zn	Ni	Ca	K	Fe	Mg	Na	Cr	Rb	Ti	Mass	Al	Si	Sr	Li	Mn	Co	Cs
NH <sub>4</sub> <sup>+</sup>	1.00																							
SO <sub>4</sub> <sup>2-</sup>	0.93	1.00																						
Cu	0.44	0.64	1.00																					
Cd	0.45	0.60	0.84	1.00																				
Pb	0.72	0.78	0.73	0.78	1.00																			
NO <sub>3</sub> <sup>-</sup>	0.27	0.28	-0.05	-0.07	0.15	1.00																		
Zn	0.49	0.59	0.75	0.68	0.59	-0.03	1.00																	
Ni	-0.04	0.10	0.43	0.37	-0.03	-0.03	0.55	1.00																
Ca	0.26	0.23	0.08	0.10	0.30	0.38	0.31	-0.05	1.00															
K	0.40	0.38	0.12	0.13	0.17	0.19	0.18	0.07	0.47	1.00														
Fe	0.04	0.10	0.15	0.16	0.17	0.31	0.30	0.21	0.87	0.36	1.00													
Mg	0.03	0.06	0.02	0.06	-0.03	0.19	0.19	0.35	0.61	0.47	0.74	1.00												
Na	-0.16	-0.07	0.10	0.08	-0.01	0.19	-0.15	0.10	0.29	0.15	0.49	0.57	1.00											
Cr	0.15	0.17	0.09	0.03	-0.02	0.18	0.43	0.52	0.31	0.20	0.39	0.34	-0.10	1.00										
Rb	0.03	0.09	0.07	0.08	0.17	0.39	0.23	0.14	0.82	0.28	0.92	0.64	0.33	0.37	1.00									
Ti	-0.23	-0.17	-0.12	-0.09	-0.16	0.28	0.03	0.11	0.65	0.28	0.79	0.56	0.37	0.32	0.69	1.00								
Mass	0.38	0.36	0.17	0.17	0.31	0.38	0.38	-0.02	0.80	0.54	0.71	0.61	0.28	0.30	0.62	0.53	1.00							
Al	0.10	0.12	0.01	0.02	0.14	0.41	0.23	0.04	0.93	0.46	0.90	0.68	0.31	0.40	0.87	0.77	0.76	1.00						
Si	0.06	0.09	0.07	0.08	0.09	0.30	0.19	0.16	0.78	0.34	0.88	0.72	0.49	0.41	0.79	0.77	0.66	0.82	1.00					
Sr	-0.09	-0.11	-0.07	-0.03	-0.11	0.19	0.06	0.23	0.65	0.39	0.80	0.81	0.62	0.16	0.69	0.61	0.54	0.65	0.73	1.00				
Li	-0.07	-0.05	-0.01	0.03	-0.03	0.28	0.09	0.23	0.71	0.42	0.86	0.86	0.65	0.29	0.74	0.69	0.64	0.76	0.83	0.92	1.00			
Mn	-0.04	-0.01	0.06	0.08	0.03	0.27	0.14	0.24	0.75	0.41	0.91	0.83	0.64	0.29	0.80	0.70	0.66	0.79	0.84	0.92	0.98	1.00		
Co	-0.28	-0.13	0.07	0.07	-0.12	0.01	-0.11	0.21	-0.03	0.13	0.04	0.19	0.17	-0.01	0.01	0.14	-0.10	0.08	0.05	0.03	0.15	0.11	1.00	
Cs	0.25	0.30	0.11	0.03	0.18	0.38	0.27	-0.08	0.48	0.22	0.34	0.17	-0.04	0.52	0.30	0.42	0.50	0.47	0.41	-0.06	0.20	0.17	-0.07	1.00

The calculated slopes of the linear regression lines of NH<sub>4</sub><sup>+</sup> to SO<sub>4</sub><sup>2-</sup> are 0.29 and 0.28 for the urban and rural locations, respectively. Figures 1 and 2 show the expected regression lines for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>SO<sub>4</sub> and a sulfate excess of 1 μg/m<sup>3</sup>. Inspection of the ammonium-to-sulfate molar ratios for (NH<sub>4</sub>)HSO<sub>4</sub> (0.19) and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (0.38) would suggest the existence of sulfate to a large extent in the form of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The remaining sulfate may exist in a combination of chemical forms: (NH<sub>4</sub>)HSO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, and the metal salts of sulfate and bisulfate. These results are in good agreement with the data presented by Junge for more humid atmospheres (17).

Attempts were also made to determine how nitrate concentrations might affect the acid-base character of particulate matter. Nitrate is apparently not strongly correlated to the sulfate and ammonium concentrations (although a statistically significant relationship is suggested). The average equivalent concentration of sulfate is approximately 2.5 and 5 times that of nitrate at the urban and rural locations, respectively. Addition of the nitrate concentration to that of sulfate and examination of the relationship with ammonium concentration showed essentially the same results as the regression of NH<sub>4</sub><sup>+</sup> on SO<sub>4</sub><sup>2-</sup>. Multiple regression analysis indicated that the effect of NO<sub>3</sub><sup>-</sup> on NH<sub>4</sub><sup>+</sup> was insignificant compared with the effect of SO<sub>4</sub><sup>2-</sup>. Thus, for the data and conditions included in this work, nitrate would appear to play only a minor role (compared to SO<sub>4</sub><sup>2-</sup>) in accounting for particulate ammonium ion concentrations. Halide concentrations were not regularly monitored in this work. However, analysis of selected (and specially collected) samples for bromine and chlorine showed the contribution of these species to also be small in comparison to the sulfate concentration (18). The samples which were analyzed for halogens showed average concentrations of approximately 0.1 and 0.2 μg/m<sup>3</sup> for Br<sup>-</sup> and Cl<sup>-</sup>, respectively.

Table II also suggests that some type of relationship exists between SO<sub>4</sub><sup>2-</sup> and several metals. For the urban location, a relationship between SO<sub>4</sub><sup>2-</sup> concentration and the concentrations of Pb and Cu (at a 1% significance level) is indicated. At the rural location, these same elements as well as Cd and Zn show apparent significant correlations with SO<sub>4</sub><sup>2-</sup>. Whether these relationships are a reflection of: similarities in the par-

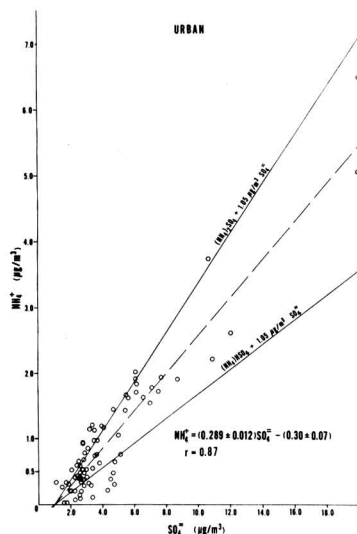


Figure 1. Ammonium-sulfate relationship observed in urban atmosphere. (—) regression line

ticle size distribution (i.e., transport and residence time phenomena); identical sources; or an actual chemical association of the  $\text{SO}_4^{2-}$  with these metals is yet to be determined.

The interspecies correlations suggest a number of possibilities concerning the distribution, concentration, and composition of particulate species present in the local atmosphere. The correlation which is observed between the elements Al, Fe, Si, Ti, Li, Rb, Mg, Na, Ca, K, Mn, and Sr at all locations examined in this investigation would suggest a common source (or type of source) for these species. Certainly, an obvious source for many of these elements would be the airborne crustal or soil material which is generated by an erosion process.

An increasingly popular method of examining the relative importance of selected sources on the measured atmospheric burden of trace species is to compare the relative abundance of species in source material to that found in the atmosphere (8). In the case of a soil source, this comparison is made by examining the enrichment of elements in the air over what is found in crustal or soil material. This enrichment is calculated by obtaining the ratio of the air concentration of an element

normalized to a reference element to the crustal concentration normalized to the same reference element. For this work, Al has been chosen as the reference element since soil is almost certainly the source for Al. One might note that perhaps Si should be chosen for the reference element since Si is the most abundant element in the soil and crust. Al (the second most abundant crustal element) was chosen, however, since the analytical precision and accuracy were somewhat better than that for Si (i.e., analytical uncertainty of approximately 3% for Al and 8% for Si). The enrichment figures are calculated according to:

$$E = \frac{\frac{\text{Air concentration of indicated element}}{\text{Air concentration of Al}}}{\frac{\text{Crustal concentration of indicated element}}{\text{Crustal concentration of Al}}}$$

An enrichment factor of 1 would indicate that the relative concentration of a given element is identical to that which is present in soil. An enrichment factor greater than 1 indicates the element is more abundant in the air relative to that found in soil. Crustal ratios were taken from Taylor (19). Values less than 1 for  $E$  would suggest a depletion of the element in air over that found in soil.

Figure 3 presents a comparison of the average enrichment factors for urban and "background" particulates. The elements attributed to the airborne soil material at both locations (Mn, Sr, Fe, Na, Si, Mn, Ti, Rb, Ca, K, and Li) show essentially identical enrichment factors with  $E$ 's very close to unity ( $E = 1$ , for Al by definition). The species Zn, Cu, Cd, Pb, In, Tl, Bi,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$  are enriched in the atmosphere relative to soil by factors ranging from 50 to 2000, and nonsoil sources for these species in both urban and background particulate matter are suggested. The elements Cr, Co, Ni, and Cs show enrichment factors relatively close to one. However, since these elements do not show a strong correlation with the other soil elements, it is suggested that either the local crustal composition of these elements is highly variable or that a mechanism other than soil erosion is responsible for introducing a significant fraction of these species into the atmosphere. The contribution of soil material to the total atmospheric burden of particulate matter (assuming an Al concentration of 8.2% in soil) is estimated to be 50% at the rural sampling site and from 60 to 80% at urban locations monitored in this investigation. If we consider that the obvious nonsoil elements (with the exception of Pb) show higher enrichment values at the "background" location relative to the urban locations and that the elements Cr, Co, Cs, and Ni also show higher enrichment at the background location, a combination of soil and nonsoil sources for these latter four elements may be hypothesized.

The higher enrichment factors for the nonsoil species at the "background" location may suggest that nonurban sources (i.e., smelters, power plants, and natural sources) contribute in a large part to the total atmospheric burden measured at the urban locations. The correlation which exists between the  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , Pb, Cu, and Cd at the background location (as discussed previously) may reflect the similarity in particle size and thus the long-range transport and diffusion similarities, and does not necessarily indicate a common source for these species.

In addition to evaluating the chemical data, attempts have been made to make evaluations of the effect of meteorological parameters upon the chemical concentrations, composition, and interspecies relationships. To make these evaluations, the local climatological information which is collected and compiled at Tucson International Airport by the National Oceanic and Atmospheric Administration has been used. Information on temperature, relative humidity, dew point, precipitation,

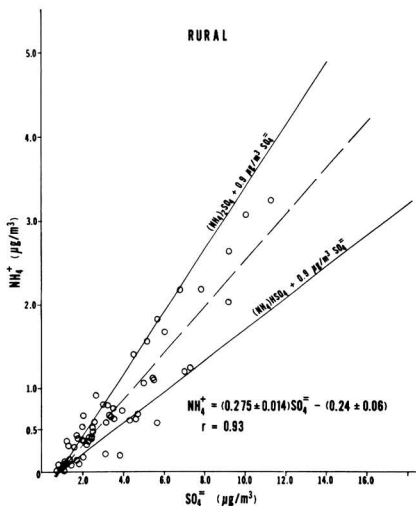


Figure 2. Ammonium-sulfate relationship observed in rural atmosphere. (— regression line)

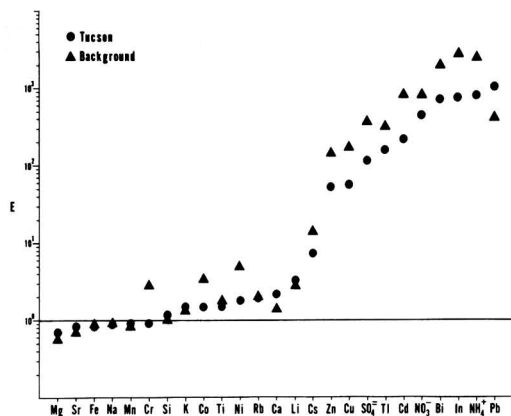


Figure 3. Crustal enrichment factors for particulate species in desert rural and urban atmosphere

wind speed, direction, and visibility was compiled and included in the data evaluation procedures. Statistical analyses of the weather parameters (for collection day, day before, and two days before) and the chemical information were carried out using the same techniques as for examining interspecies relationships. Table IV presents correlation coefficients for selected chemical and meteorological parameters. While it was possible to observe some effect of various weather parameters upon the composition and concentration of species present in the atmosphere, these relationships have proved to be weaker and more complex than is the case for the chemical-chemical relationships. The effect of wind direction is not observable on species concentration and not included in Table IV. In the Tucson area, winds prevail southeasterly and westerly. These winds are generally diurnal with southeasterly winds in the morning and westerly winds in the afternoon and evening. Since the sampling period is 24 h, these wind effects tend to average out over the course of the day. The weak relationships undoubtedly result from a combination of averaging effects throughout the sampling period and the effect of other parameters upon the measured chemical species. These data suggest the need for more sophisticated evaluation procedures if the meteorological effects are to be more completely defined.

While the meteorological effects upon composition and concentration of atmospheric trace species are not straightforward, it is possible to qualitatively observe the influence of the local meteorology and climatology. Figure 4 shows the bimonthly variations observed for mass, soil,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , Pb, Cu, Zn, and Cd. Soil is a calculated value from the measured Al concentrations and is representative of the variation seen with all the previously defined soil elements. Additionally, the  $\text{NH}_4^+$  concentrations show the same patterns as are seen in the case of  $\text{SO}_4^{2-}$ . The nonsoil species show a general tendency toward winter maximums and summer minimums. The soil (and mass) tends to show a maximum in the spring-summer and minimum in the summer-fall, with winter values being intermediate. Certainly, the local climatology is largely responsible for the apparent patterns shown in Figure 4. The climatology of Tucson, located on the edge of the Sonoran Desert, is typical of the desert environment with mild winters, hot summers, and low annual amounts of precipitation. In the summer the daytime heating produces intense vertical and horizontal mixing of the air mass. This instability results in increasing the injection and residence time in the atmosphere of the large soil-like particles. At the same time, those species whose introduction into the atmosphere is independent of the atmospheric turbulence (the nonsoil species) are most rapidly mixed and diluted in the air mass and hence would be expected to show minimum concentrations under such conditions. The desert winters are characterized by intense night

time radiational cooling, resulting in the development of very shallow and stable inversions. Under such conditions large particles (such as soil) are rapidly removed by sedimentation and thus show lower atmospheric concentrations than occur with more turbulent conditions. The small particles, however, have relatively small settling velocities, and removal by sedimentation is less significant.

Thus, as a result of containment in a smaller dilution volume, species associated with small particles are expected to show an increased winter time concentration relative to dry summer time conditions. The data presented in Figure 4 tend to support the suggestion of the soil particles being primarily large particles and nonsoil species being distributed on smaller particles. These particle size suggestions have been supported by recent high-volume impactor studies using the techniques and locations discussed here. These studies have shown the apparent soil species to be concentrated on particles larger than  $2 \mu\text{m AD}$  and the nonsoil species contained predominantly in the less than  $2\text{-}\mu\text{m AD}$  particle size range (14). The summer-fall minimum generally seen for all species may be explained by the increased precipitation during these months.

### Conclusions

These findings, which should apply to other arid (and in some cases nonarid) airsheds, include:

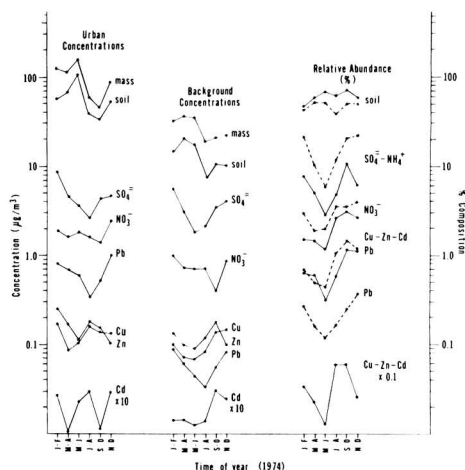


Figure 4. Absolute and relative concentration of several species in desert atmosphere (— relative urban abundance) (--- relative rural abundance)

Table IV. Dependence of Chemical Composition on Meteorological Parameters (Urban Location)

	Mass	Al	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	Pb	Zn	Cu	Cd
WS <sup>a</sup>	0.28 (0.02) <sup>b</sup>	0.18 (0.14)	-0.11 (0.40)	-0.12 (0.34)	-0.27 (0.02)	-0.15 (0.24)	-0.15 (0.22)	-0.15 (0.24)
RH	0.48 (0.00)	-0.55 (0.00)	0.03 (0.84)	0.01 (0.94)	0.07 (0.58)	0.07 (0.58)	0.10 (0.42)	-0.03 (0.82)
DP	-0.46 (0.00)	-0.39 (0.00)	-0.17 (0.17)	-0.13 (0.30)	-0.31 (0.00)	-0.05 (0.72)	0.08 (0.52)	-0.02 (0.88)
T	0.00 (0.99)	0.18 (0.14)	-0.29 (0.02)	-0.12 (0.34)	-0.42 (0.00)	-0.20 (0.12)	-0.06 (0.66)	0.07 (0.60)
P	-0.41 (0.00)	-0.54 (0.00)	0.31 (0.01)	0.12 (0.34)	0.39 (0.00)	0.30 (0.015)	0.26 (0.05)	0.13 (0.29)
VIS	-0.34 (0.01)	-0.26 (0.03)	-0.21 (0.09)	-0.28 (0.02)	-0.01 (0.94)	-0.10 (0.45)	-0.01 (0.94)	0.00 (0.99)
WS (DB)	0.42 (0.00)	0.36 (0.01)	-0.14 (0.255)	0.02 (0.87)	-0.21 (0.10)	-0.21 (0.09)	-0.21 (0.10)	-0.16 (0.20)
RH (DB)	-0.48 (0.00)	-0.57 (0.00)	0.17 (0.18)	0.06 (0.66)	0.15 (0.23)	0.06 (0.66)	0.13 (0.29)	-0.04 (0.73)
DP (DB)	-0.52 (0.00)	-0.39 (0.001)	-0.10 (0.42)	-0.05 (0.69)	-0.25 (0.04)	-0.03 (0.80)	0.09 (0.50)	0.01 (0.91)

<sup>a</sup> WS, wind speed; RH, relative humidity; DP, dew point; T, temperature; P, barometric pressure; VIS, visibility; WS (DB), wind speed (day before sampling); RH (DB), relative humidity (day before sampling); DP (DB), dew point (day before sampling). <sup>b</sup> Values in parentheses indicate the probability of true correlation coefficient being zero (i.e., no correlation exists).



Airborne soil material accounts for the majority of the mass of suspended atmospheric particulate matter in both urban (80%) and rural (50%) locations in southern Arizona. Over a dozen of the 28 chemical species monitored in this program can be attributed either entirely or to a large extent (a majority) to the airborne crustal material.

The urban activities are apparently a source for every chemical species measured in this program. For several nonsoil species, however, the urban source is small relative to non-urban sources.

The acid-base nature of the atmospheric gases and aerosols is apparently largely responsible for defining sulfate speciation and the gas-particle distribution of volatile acid-base species.

Meteorological parameters are probably most important in defining the concentration and fluctuation of various species suspended in the desert atmosphere. These meteorological effects are, however, quite complicated, and improved sampling and evaluation methodologies for quantitatively evaluating these relationships are required.

#### Acknowledgment

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## Application of Pattern Recognition and Factor Analysis for Characterization of Atmospheric Particulate Composition in Southwest Desert Atmosphere

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■ Measurements made of the composition of atmospheric particulate matter collected in the greater Tucson, Ariz., area are examined by use of pattern recognition and factor analysis. Cluster analysis shows Si, Ti, Cs, Li, Rb, Al, K, Fe, Ca, Mg, Na, Mn, Sr, Co, and Cr to be primarily of soil origin. Factor analysis is used to separate the variance of the data base into a small number of factors. Examination of these factors suggests that it is possible to interpret their chemical and physical significance in terms of sources, source strength, and gas-to-particle conversion processes. The results suggest that  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  distributions can be explained by a diffuse area-wide gas-to-particle conversion process which produces these species in a chemically combined state. The species  $\text{NO}_3^-$ , Zn, Cu, Ni, and Cd would appear to result from multiple processes (sources). Relative to a remote desert location, all elements measured in this study show an enrichment in urban particulates, with Pb being the most enriched (1300%) and  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , Zn, Cu, and Cd among the least enriched (150%). These data evaluation techniques show great potential for helping to reduce the dimensionality and explaining the complicated problems associated with atmospheric chemistry and air quality investigations.

A previous paper (1) has described the atmospheric sampling and analysis program of the University Analytical Center at the University of Arizona. To gain a maximum of information from the data, a number of multivariate statistical methods, which have been found useful with increasing frequency in numerous widely divergent areas, were utilized. Multivariate techniques provide insight into the interrelationships among the chemical species.

A primary objective of this sampling, analysis, and evaluation program is to identify processes which influence the concentration and distribution of atmospheric particulate species. These processes can include sources for various species and chemical and physical changes responsible for species generation or removal.

The sampling program was conducted from December 1973 through December 1974. Twenty-four-hour, high-vol samples were collected at 11 locations in and around the Tucson area during that period. Twenty-four species were monitored: total particulate mass,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , Si, Ti, Cs, Li, Rb, Al, Zn, K, Fe, Ca, Mg, Na, Pb, Cu, Mn, Sr, Ni, Co, Cr, and Cd. Most of the locations are within the city of Tucson, but several stations are located outside the city in an effort to provide background information (i.e., nonurban) about the southwest desert aerosol population. Figure 1 locates the sampling sta-

tions in relation to Tucson. Station 11, which is 50 miles from the city, shows the smallest influence from the urban plume and localized activities (1). There are 40–65 samples taken at each location for which all of the measurements were available. (For a more detailed description of the sampling and analysis program, see ref. 1.)

### Results and Discussion

Table I contains the means and relative standard deviations of the species sampled at two different locations. Location 2 is an urban location at which the most samples were collected. Location 11 is an outlying desert (background) location as

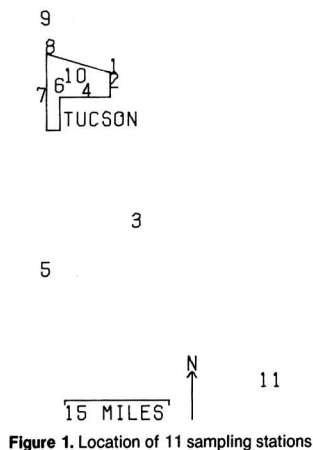


Figure 1. Location of 11 sampling stations

Table I. Mean Concentrations, Relative Standard Deviations ( $s/\bar{X}$ ), and Ratios of Means for Location 2 (Urban) and Location 11 (Outlying)

Feature	Location 2		Location 11		Ratio
	Mean, $\mu\text{g}/\text{m}^3$	$s/\bar{X}$	Mean, $\mu\text{g}/\text{m}^3$	$s/\bar{X}$	
Pb	0.72	0.68	0.055	0.96	13.1
Ca	4.9	0.59	0.79	0.60	6.2
K	2.5	0.64	0.42	0.66	5.8
Sr	0.019	0.54	0.0035	0.85	5.4
Mg	0.93	0.69	0.18	0.78	5.3
Li	0.0046	0.91	0.0009	0.77	5.2
Rb	0.011	0.68	0.0025	0.66	4.4
Si	18.0	0.62	4.1	0.67	4.4
Al	5.4	0.53	1.3	0.60	4.3
Mn	0.054	0.65	0.013	0.72	4.3
Na	1.2	0.64	0.29	0.76	4.3
Fe	2.8	0.69	0.68	0.59	4.1
Mass	101.0	0.56	28.0	0.49	3.6
Ti	0.37	0.65	0.12	0.80	3.1
Cs	0.0013	0.68	0.0004	1.00	3.0
Co	0.0018	0.86	0.0006	0.77	2.9
NO <sub>3</sub> <sup>-</sup>	1.8	0.44	0.74	0.53	2.5
Ni	0.0058	0.54	0.0030	0.83	1.9
NH <sub>4</sub> <sup>+</sup>	1.2	1.21	0.70	1.06	1.6
Zn	0.16	0.72	0.099	0.50	1.6
SO <sub>4</sub> <sup>2-</sup>	5.0	1.03	3.4	0.73	1.5
Cd	0.0022	1.51	0.0015	1.15	1.5
Cr	0.0038	0.70	0.0028	0.63	1.4
Cu	0.13	0.60	0.093	0.67	1.4

identified in Figure 1. Also listed is the urban/background ratio of the means of each measurement, using only those days for which sampling was done at both locations. This ratio provides information on which species are the most enriched in the city relative to the desert background.

Not surprisingly, lead is the most enriched element in the city. It is to be noted that all of the enrichment ratios exceed 1.0, which suggests the city as a source for all of the monitored species. However, some species are only slightly enriched within the city, relative to the background. For these species (NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Zn, Cd, Cr, Cu), the apparent Tucson source may be minor (approximately half) compared to a nonurban source.

Reference 1 contains the correlation matrices of the monitored species for locations 2 and 11. Examination of each correlation matrix suggests the existence of groups of species with mutually high correlations. Very likely, each species in any one of these groups arises from similar sources or from similar chemical and physical transformation processes in the atmosphere. Pattern recognition methods were used to locate these clusters of species, as described below.

**Pattern Recognition.** Pattern recognition has been applied to a variety of chemical problems. It has been used to identify the presence or absence of functional groups from mass spectra (2), from nuclear magnetic resonance data (3), and from infrared spectra (4); to identify structure/activity relationships (5); and for other problems (6). Pattern recognition was used in a pollution study of lake sediments (7). The method of pattern recognition employed in this study is known as cluster analysis (also called unsupervised learning). Two complementary cluster analysis techniques were used, nonlinear mapping and hierarchical clustering. Nonlinear mapping is a display technique which allows human recognition of clusters but may suffer from mapping errors. Mapping errors do not occur in the hierarchical clustering technique, but the algorithms employed have difficulty separating odd-shaped clusters.

**Nonlinear Mapping (8, 9).** This mapping technique plots  $n$ -dimensional points in 2-dimensions and attempts to preserve structure by minimizing the differences between the  $n$ -space and the corresponding 2-space interpoint distances. The scheme is iterative and is halted when the mapping error,  $E$ , of the  $N$  points appears to converge.

$$E = \left( \sum_{i < j}^N d_{ij} \right)^{-1} \sum_{i < j}^N (d_{ij} - d_{ij}^*)^2 / d_{ij} \quad (1)$$

The  $d_{ij}$  symbol designates the distance between points  $i$  and  $j$  in  $n$ -space, and  $d_{ij}^*$  is the corresponding distance in 2-space.

Since chemical species are to be clustered based on their correlation coefficients, the distance between two species was defined as  $d_{ij} = 1 - r_{ij}$ , where  $r_{ij}$  is the correlation coefficient between species  $i$  and  $j$ . The measure behaves as a distance in that, for two perfectly correlated species, the measure equals zero. In this study negative correlations are infrequent and of small magnitude. All the information contained in a nonlinear mapping is found in the interpoint distances. The two coordinate axes have no physical significance.

Nonlinear mappings of the species from the urban and outlying locations, 2 and 11, respectively, are shown in Figures 2A and 2B. At the urban location there is clustering of the species Co, Cs, Rb, Li, Mn, Ti, Si, Al, Sr, Cr, Mg, Fe, K, Na, and Ca. These elements are probably of a crustal origin. Note that the total mass is also in this cluster which is not surprising since the species having the greatest concentrations—Si, Al, and Ca—are in this cluster. From Table I, the soil elements are the most enriched species in the city except for Pb. Because of the enriched quantities, the soil particulates can be considered to result primarily from various urban activities.

Except for  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$ , the remaining species (Ni,  $\text{NO}_3^-$ , Cd, Cu,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , Pb, and Zn) are well separated from the soil cluster and from each other. Separation suggests different sources and/or different chemical and physical cycles in the atmosphere. The high degree of correlation between  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  is probably explained by the chemical combination of these species in the atmosphere (10). This combination results from acid-base processes after  $\text{SO}_2$  is oxidized to  $\text{H}_2\text{SO}_4$  (11).

In contrast to the urban location, the soil cluster is more dispersed at the outlying location. The reduced concentrations of these elements may be allowing the effects of minor sources (such as a marine source) to be visible. Six nonsoil species (Cu, Cd, Pb, Zn,  $\text{NH}_4^+$ , and  $\text{SO}_4^{2-}$ ) show greater correlation at the outlying location, perhaps reflecting similar particle size and transport behavior. For the four metals a common source might also contribute in part to the observed correlation.

**Hierarchical Clustering** (12, 13). Hierarchical clustering initially considers each entity as a separate cluster. Then the clusters are joined one at a time according to an agglomerative algorithm, until all the entities are joined into a single cluster. The results of a hierarchical clustering are displayed in a *dendrogram*—a diagram of the clusters existing at each level of clustering.

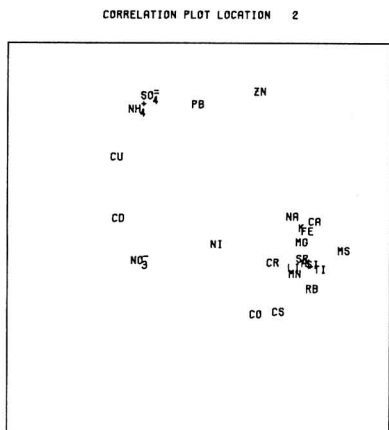


Figure 2A. Nonlinear map of features at location 2

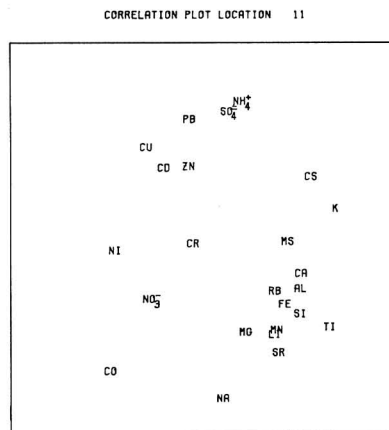


Figure 2B. Nonlinear map of features at location 11

Figures 3A and 3B are dendrograms resulting from the hierarchical clustering of the species at locations 2 and 11, respectively. The same distance measure was used in this clustering as in the nonlinear mappings. The soil species are very evident by their tight clustering. Ni exhibits a behavior intermediate between soil and nonsoil, indicating that a portion of the Ni concentration may have a soil origin.

A matrix of correlations among the locations provides information about both the locations and the species that is used to construct the matrix. Table II contains correlation matrices among locations using  $\text{NH}_4^+$  and Al features.  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  show the same behavior in that all interlocation correlations are very high. This behavior is expected and consistent with the suggested chemical oxidation and acid-base processes responsible for generating particulate  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  on an area-wide basis. Al is typical of all the soil elements. Correlations among the urban locations are seen, but the outlying location is obviously different.  $\text{NO}_3^-$ , Ni, Zn, Cd, Cu, and Pb have lower interlocation correlations, probably because they are influenced by localized urban sources (e.g., for Pb, traffic patterns may account for these lower correlations).

**Factor Analysis.** The pattern recognition techniques condense the information present in the correlation matrices and present it graphically. This form allows general trends to be viewed more efficiently. However, nothing is learned from use of these techniques which would not have been observed in a careful study of the matrices which noted sets of species with mutually high correlations and similar behavior. It would be very desirable to have a model which explains the behavior of each chemical species in terms of the physical and chemical influences on that species in the atmosphere. Determining the number of major influences and identifying them will require a more sophisticated analysis and are the objectives of the remainder of this paper.

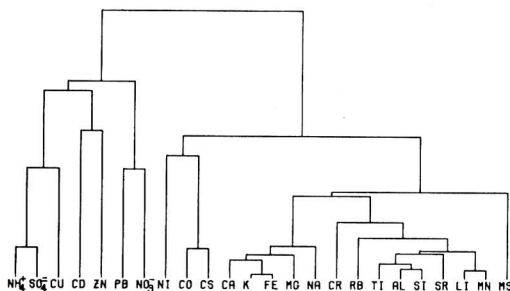


Figure 3A. Dendrogram showing clustering of features at location 2

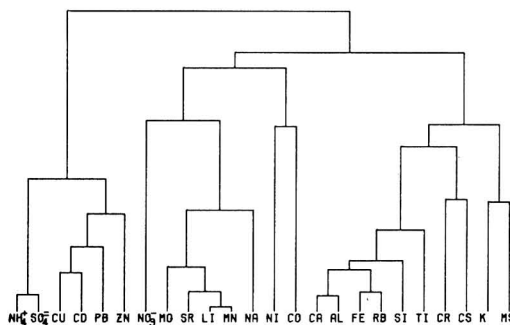


Figure 3B. Dendrogram showing clustering of features at location 11

There are several reasons why factor analysis may be useful in testing the atmospheric particulate data. Since it is not possible to change experimentally the values of the variables, the researcher must rely on natural variations and use a statistical method to deduce the interrelationships among the variables. This is a common problem in the natural and social sciences and has led to many multivariate analysis methods. Factor analysis has particularly found use in the psychological and political sciences. The common reference works are written by researchers in those fields (14, 15). Several applications of factor analysis to pollution problems have been published (7, 16). These works have used factor analysis to identify or confirm the presence of pollution sources. Related eigenvector analysis techniques have been used in a study of meteorological effects on air pollution (17, 18). The introduction of particulates into the atmosphere from a number of different point and area sources fits the factor analysis model of a variable being a weighted sum of factor values.

It is not the purpose of this paper to describe computationally how to perform a factor analysis. Programs are available as part of statistical packages at computing centers. Alternatively, it may be more convenient to write the necessary programs for use on a laboratory computer as was done with this work. A description of the factor analysis model, some implicit assumptions, and limitations of the technique will be offered here.

In the factor analysis model each variable ( $z_j$ ) is expressed as a linear combination of  $m$  factors ( $F_i$ 's) common to all variables and a unique factor ( $U_j$ ). The factors are hypothetical variables chosen so that the correlations among the observed variables can be reproduced as well as possible by only a few factors.

$$z_j = a_{j1}F_1 + a_{j2}F_2 + \dots + a_{jm}F_m + d_jU_j \quad (2)$$

The coefficients in the above equation are called *loadings*. We use an orthogonal factor analysis model which means that the factors are orthogonal to one another and the loadings are also

correlation coefficients between the observed variable and the factor. By noting which species have high loadings on a particular factor, it may be possible to assign a physical interpretation to that factor. The factor analysis computes the values of the loadings starting with the correlation matrix of the observed species. The values of the factors themselves for each sampling day were not computed.

Several assumptions are implicit in the use of factor analysis for the atmospheric particulate study. All the major influences on particulate composition should be reflected in the correlation matrix. It is further assumed that the major influences are different enough in their effects on the correlation matrix to produce factors which represent only one influence, not combinations of several influences. One limitation of factor analysis lies in the interpretation of factors. Interpretations are based on the magnitudes of the loadings but also rely on previous knowledge and common sense. Of the factors resolved in this study, some were expected, some were unanticipated but interpretable, and others represent unknown influences.

*Rotation.* The factors were rotated using the orthogonal varimax rotation (14). The purpose of rotation is to point a factor at a cluster of variables so the factor may be easier to interpret. The algorithm will tend to cause loadings to be either high or low with few medium loadings.

The loadings of the rotated six-factor solutions of locations 2 and 11 are found in Table III. Co and Cs were omitted from the analysis because there was too much uncertainty in these measurements. The Co values were near the detection limit, and there were contamination problems with Cs measurements.

A measure of adequacy of a factor analysis solution is whether the factors can reproduce the observed correlation matrix. For the six-factor solution of location 2, the average difference between an observed correlation and a reproduced correlation is 0.01, and the maximum difference is 0.06. Five to eight factors are needed to adequately reproduce the correlation matrices of each location.

The "Fraction of Total Variance" row of Table III shows that most of the variance of the standardized variables is contained in just a few dimensions. The six-factor solution contains 84% of the total variance. By examining the loadings of the corresponding factors and recalling that a loading is a correlation coefficient between a variable and a factor, it is possible to interpret the factors. Most of the factors can be interpreted as resulting from physical and chemical sources of particulates.

The first factor of location 2 has high loadings from Na, K, Fe, Ca, Mg, Rb, Sr, Al, total mass, Ti, Si, Li, Mn, and Cr. The variance that is common to these species is due to their source, the soil. In the factor analysis of any of the locations, this apparent soil factor always appears first with high loadings for these same elements. Ni shows variable loadings on this factor at the different locations. The variability of Ni loading on this factor is consistent with the previous suggestion that atmospheric Ni concentrations result from both a soil and nonsoil source. At several locations Zn also shows some loading on the soil factor. The loadings of Cr, Na, and K are reduced at location 11. The reduced quantities of particulates from the soil source have allowed variance from more minor sources to be visible.

Factor 2 of location 2 has high loadings from  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , and Cu. Pb, Zn, and possibly a few other species have some variance in this direction. The factor analyses of other locations always have high  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  loadings on the second factor. Locations which are outlying or at the edge of the city, such as 1, 3, 5, 9, and 11, have 5-7 high loadings on this factor from among the features  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ , Pb, Cu, Zn,  $\text{NO}_3^-$ , Cd, and Ni. The urban locations 6, 7, and 10 have high loadings from

**Table II. Interlocation Correlations of  $\text{NH}_4^+$  and Al**

	1	2	3	4	5	6	7	8	9	10	11
$\text{NH}_4^+$											
1	1.00										
2	0.93	1.00									
3	0.91	0.93	1.00								
4	0.94	0.96	0.96	1.00							
5	0.86	0.88	0.93	0.90	1.00						
6	0.86	0.91	0.88	0.71	0.86	1.00					
7	0.93	0.94	0.93	0.95	0.92	0.63	1.00				
8	0.93	0.96	0.92	0.94	0.88	0.76	0.94	1.00			
9	0.93	0.90	0.91	0.88	0.94	0.61	0.90	0.90	1.00		
10	0.92	0.94	0.92	0.97	0.89	0.96	0.87	0.95	0.77	1.00	
11	0.81	0.76	0.86	0.85	0.75	0.73	0.82	0.83	0.71	0.76	1.00
Al											
1	1.00										
2	0.90	1.00									
3	0.49	0.56	1.00								
4	0.69	0.78	0.64	1.00							
5	0.74	0.80	0.68	0.76	1.00						
6	0.88	0.78	0.42	0.68	0.75	1.00					
7	0.80	0.71	0.41	0.45	0.60	0.87	1.00				
8	0.65	0.67	0.73	0.76	0.76	0.70	0.51	1.00			
9	0.46	0.51	0.53	0.65	0.63	0.47	0.27	0.78	1.00		
10	0.94	0.92	0.52	0.71	0.81	0.92	0.75	0.61	0.42	1.00	
11	0.54	0.48	0.20	0.31	0.38	0.28	0.31	0.21	0.17	0.40	1.00

only  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$ . Since the interlocation correlations suggest that  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  are produced on a diffuse area-wide basis, it is inferred that factor 2 corresponds to a background well-mixed aerosol from nonlocal sources. This explains why outlying locations have more species loaded on this factor, since local sources at these locations are absent or of minor importance.

The third factor of location 2 has a high loading from Zn and medium loadings from K, Ca, Na, Fe, and Mg. A factor like this is present at nearly every location although it is not necessarily the third factor. At several locations the loadings from all six species are nearly the same. There may be a source which introduces quantities of these six elements into the atmosphere. It is curious, however, that in the chemical analysis procedure, when a sample is divided into aliquots for analysis, one of the aliquots is diluted and analyzed for just these six species (1). This could explain why Na, Ca, K, Fe, and Mg are more tightly clustered than the other soil elements in the nonlinear map and the dendrogram. Zn does not cluster with these species because its origin is from other sources, but the factor analysis can separate the common variation of the elements in this aliquot. This factor is not visible in location 11 because there are other nonsoil sources. Identification of the aliquot dilution factor illustrates the power of the factor analysis technique. It is doubtful that examination of pairwise relationships would have separated this small common variance from the much larger physical source variance. A multivariate approach is called for in these situations.

Cd is the major contributor to factor 4 of location 2. Species having intermediate loadings are Ni,  $\text{NO}_3^-$ , and Zn. At outlying locations Cd is loaded only on the distant source factor (factor 2). At all urban locations Cd has a high loading on a factor with other high or intermediate loadings from the set of  $\text{NO}_3^-$ , Ni, Zn, Cu, and Pb. This may suggest that this factor is due to a high-temperature or combustion process since these elements

have been identified as being enriched in power plant fly ash (19, 20). This factor is not visible at the outlying location.

Factor 5 of location 2 is loaded from Pb and  $\text{NO}_3^-$ . This is unique for the particular location considered since these species are usually found on separate factors with no other high loadings, or on the distant source factor if the location is outlying. A Pb-loaded factor would reflect the automotive source, while a  $\text{NO}_3^-$ -loaded factor would reflect a source which is unique for  $\text{NO}_3^-$ , possibly an area source in which locally produced  $\text{NO}_x$  is converted to particulate  $\text{NO}_3^-$  in the atmosphere. The reason for the apparent convergence of these two factors at location 2 is unknown. At location 11,  $\text{NO}_3^-$  is found alone on factor 6, and Pb is among the species loaded on factor 2. These loadings happen to be negative, but this has no physical significance. The factor could be redefined with an opposite sign, and in fact at some other locations these factors do have positive loadings.

Factor 6 at location 2 has no high loadings but contains intermediate loadings from Cr, Ni, and Cu. These three elements appear together loaded on factors at other locations as well, and may be from some common but unknown source. Factor 3 of location 11 has loadings from Ni and Cr also. Quite possibly, this factor reflects mining activity in the area.

Na is the only species with a high loading on factor 4 of location 11. Only location 5 has a similar factor. This may be variation from the marine source which is not visible at urban locations due to the higher Na concentration.

A few factors appear at locations other than locations 2 and 11. A factor with loadings from Li, Mn, Cr, and Cu is present at eight locations (sometimes one of these elements is missing). Five locations have a factor whose only high loading is Rb.

Table IV lists the observed significant factors for all of the locations and the proposed sources of variation. These may correspond to physical sources, chemical processes, contamination, or measurement variance.

Table III. Factor Analysis Loadings—Rotated Six-Factor Solutions

	Location 2						Commun- ality	Location 11						Commun- ality
	1	2	3	4	5	6		1	2	3	4	5	6	
Zn	0.05	0.25	0.73	0.33	-0.03	0.03	0.71	0.20	0.73	-0.46	0.25	0.16	0.14	0.90
Pb	0.02	0.38	0.12	0.05	-0.75	0.05	0.73	0.12	0.90	0.22	0.06	0.15	-0.17	0.92
Cu	-0.04	0.67	-0.00	0.16	-0.06	0.39	0.64	0.01	0.91	-0.20	-0.10	-0.02	0.07	0.88
Cd	0.02	0.13	0.15	0.61	-0.20	0.04	0.46	0.04	0.90	-0.12	-0.12	-0.00	0.11	0.85
$\text{NH}_4^+$	-0.02	0.86	0.14	0.09	-0.22	-0.15	0.84	-0.05	0.59	0.04	0.16	0.66	-0.35	0.93
$\text{SO}_4^{2-}$	-0.03	0.92	0.11	0.03	-0.18	-0.02	0.90	-0.02	0.73	-0.05	0.08	0.51	-0.38	0.95
$\text{NO}_3^-$	0.17	0.17	0.02	0.30	-0.62	0.00	0.53	0.32	0.03	0.03	-0.07	0.11	-0.68	0.58
Ni	0.51	0.17	0.13	0.34	-0.16	0.39	0.60	0.01	0.21	-0.88	-0.17	-0.06	0.12	0.87
Cr	0.84	0.01	0.11	0.21	0.06	0.32	0.87	0.35	0.02	-0.65	0.26	0.13	-0.18	0.66
Li	0.94	-0.04	-0.04	0.10	-0.05	0.20	0.94	0.82	-0.06	-0.15	-0.48	0.16	0.00	0.96
Mn	0.94	-0.07	-0.06	0.10	-0.03	0.22	0.95	0.86	0.02	-0.12	-0.45	0.13	-0.00	0.97
Sr	0.94	-0.06	-0.01	0.07	-0.13	0.05	0.91	0.76	-0.11	-0.09	-0.51	0.18	0.12	0.89
Al	0.97	-0.05	-0.03	0.00	-0.07	-0.00	0.96	0.95	0.05	-0.02	0.06	0.14	-0.17	0.95
Si	0.99	-0.03	-0.02	0.05	-0.01	-0.05	0.98	0.87	0.06	-0.13	-0.19	0.07	-0.12	0.83
Rb	0.88	0.03	-0.16	0.18	-0.15	-0.02	0.86	0.90	0.11	-0.08	-0.05	-0.05	0.21	0.87
Ti	0.96	-0.05	-0.08	0.03	0.05	-0.16	0.96	0.81	-0.18	-0.11	-0.06	-0.11	-0.05	0.72
Mass	0.84	0.12	0.05	-0.05	-0.04	-0.25	0.79	0.73	0.22	0.03	-0.00	0.41	-0.13	0.77
Na	0.79	-0.07	0.41	-0.06	-0.34	0.17	0.94	0.39	0.03	0.06	-0.76	-0.05	-0.07	0.75
Mg	0.92	0.01	0.29	-0.03	-0.00	0.11	0.94	0.69	-0.03	-0.28	-0.43	0.32	0.05	0.85
Fe	0.89	-0.04	0.40	-0.08	-0.11	-0.04	0.97	0.95	0.16	-0.12	-0.17	0.01	-0.08	0.98
Ca	0.85	0.05	0.42	-0.07	-0.09	-0.09	0.92	0.91	0.16	0.10	0.07	0.23	-0.13	0.94
K	0.86	-0.01	0.45	-0.08	-0.18	0.02	0.97	0.37	0.10	-0.04	-0.08	0.62	-0.02	0.54
Fraction of total variance														
	0.53	0.11	0.07	0.04	0.06	0.03	0.84	0.38	0.19	0.08	0.08	0.07	0.04	0.84

**Table IV. Element Loadings on Individual Factors and Possible Explanations for Factor Significance**

	1	2	3	4	5	6	7	8	9	10
Elements, major loading	Mass, Al, Ti, Si, Sr, Rb, Li, Mn, Ca, K, Fe, Mg, Na, Cr	NH <sub>4</sub> <sup>+</sup> , SO <sub>4</sub> <sup>2-</sup> , Cu	Zn	Pb	NO <sub>3</sub> <sup>-</sup>	Cd				Na
(Minor loading)	(Ni, Zn)	(Ni, Cd, Zn, Pb, NO <sub>3</sub> <sup>-</sup> )	(Mg, Na, Fe, Ca, K)			(Zn, Ni, Cu, Pb, NO <sub>3</sub> <sup>-</sup> )	(Li, Mn, Cr, Cu)	(Ni, Cr, Cu)	(Rb)	
Physical or chemical significance	Soil Large particle	Distant and/or diffuse source Small particles Gas-particle conversion	Common aliquot dilution variance	Auto-motive	Gas-particle conversion	Unknown (may have combustion and/or transport significance)	Urban only may suggest signature of one or more urban sources	Mining activity	Un-known	Back-ground only Marine source?

### Conclusions

The multivariate approach to data analysis appears to be particularly useful for studies of atmospheric aerosols. Many observations reported here could not have been made without the aid of these powerful methods. For example, the solid element cluster, ammonium and sulfate correlation, partial soil character of Ni, and the diversity of Pb, Zn, Cu, Cd, and NO<sub>3</sub><sup>-</sup> behavior were observations that were made by simple pairwise comparison of variables (correlation coefficients). These observations were also evident from the factor analysis. However, the factor analysis went even further in resolving a number of hypothetical variables which contained portions of the variance that is common to at least several of the species. Interpretation of these factors by the researcher is then the most critical part. These factors may correspond to known physical sources, chemical processes in the atmosphere, common attributes of the chemical analysis procedure, or some unknown cause. From these studies it is suggested that improved sampling and analysis strategies can be designed to study specific processes (chemical and physical) responsible for defining the distribution and behavior of trace species in the atmosphere. The application of these (and similar) evaluation techniques may provide an important new dimension in our ability to understand and quantitatively define the effects various sources and processes may have on the composition and distribution of species in the atmosphere. Work is currently under way to improve both the data base and the techniques for studying such data.

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# Modeling Study of Seasonal Effect on Air Pollution at 60°N Latitude

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■ A computer modeling study of the effect of temperature and solar altitude variation on the chemical processes which take place in a general photochemical air pollution system at 60°N latitude was performed. Eleven photochemical and 100 dark reactions of 11 initial reactants were considered. The results indicated that temperature changes corresponding to seasonal variations have little effect on the overall chemistry, but changes in solar intensity and wavelength distribution estimated to correspond to seasonal variations have a marked effect on the chemical evolution of the system. One of the key factors governing overall rates was the concentration of the peroxy radicals HO<sub>2</sub> and RO<sub>2</sub>. The temporal behaviors of the major pollutants were calculated, and their role is discussed.

Modeling by computer integration of sets of first order differential equations, representing the independent behavior of the individual chemical species, has become a major tool in the elucidation of chemical changes in photochemical air pollution systems and the complex interrelationship of the numerous kinetic factors influencing them (1-4).

In extending computer modeling studies to the environmental conditions of northern Alberta and the Northwest Territories, it is necessary to take into account the differences in geographical situation and climatic conditions. Owing to the northerly location, approximately 60°N latitude, great seasonal variations in both solar altitude and temperature are experienced. Such factors have not been considered in previous modeling studies. Moreover, it has recently been shown that lowering the temperature and the intensity of solar radiation does not completely suppress photochemically induced air pollution (5). This study was therefore initiated to determine how these factors influence the ongoing chemistry of an air pollution mixture.

After completion of this work, a publication by Nieboer et al. appeared (6) in which the potential for photochemical smog formation was investigated as a function of latitude. The effect of solar altitude and temperature on the chemistry of an air pollution mixture was not studied, but the ozone and PAN dosage was calculated as a function of integrated UV light intensity. In their calculations, the authors took into account the diurnal variation of light intensity as a function of latitude, while in the present work, for reasons which will be given shortly, a constant average light intensity as a function of season was assumed.

Since the subject of this work is the study of chemical changes occurring in a polluting system under the above conditions, it was decided to carry out the study within the framework of the extended model developed by Demerjian et al. (2). In these calculations it is assumed that there is no atmospheric dilution of products and reactants, and solar radiation and temperature are kept constant for one particular calculation.

Obviously, such assumptions greatly oversimplify the actual case. In particular, the effects of the diurnal variation in temperature and solar altitude are neglected. These effects can readily be incorporated into the existing model, but would not allow unambiguous rationalization of the effects of temperature and a particular solar altitude as such on the chemical evolution of the system. Although our conclusions could

be experimentally verified with smog chamber studies, these do not seem to have been performed.

The seasonal variation of the solar wavelength-intensity distribution at 60°N latitude has not been studied. We therefore estimated photochemical rate constants following the often applied method developed by Leighton (7). A recently published, much more elaborate calculation of light fluxes available for photochemical reactions in the lower boundary layer of the atmosphere (8) results in values less than 10% different from those calculated by Leighton's method.

As far as nonphotochemical reactions are concerned, we used the rate constants recommended by Hampson and Garvin (15) wherever possible, or more recently published data. However, the model of Demerjian et al. encompasses many reactions which in theory appear to be important but have not been studied in detail. In view of the reasonable success of this model in explaining the data of several independently performed smog chamber studies, we decided to use the best estimates for the rate constants in these cases, as discussed by Demerjian et al. We used established procedures (9) to evaluate those Arrhenius parameters which have not been reported.

## Photochemical Reactions

The photochemical reactions considered in this study are shown in Table I, together with their estimated specific absorption rates. The latter values were determined following the method developed by Leighton from the relation

$$k_a = \sum_{\lambda} 2.303 \alpha_{\lambda} \phi_{\lambda} J_{\lambda} \quad (I)$$

where  $\alpha_{\lambda}$  is the absorption coefficient of the reactant at wavelength  $\lambda$ ,  $\phi_{\lambda}$  is the quantum yield at wavelength  $\lambda$ , and  $J_{\lambda}$  is the actinic irradiance over a wavelength interval  $\lambda$  and  $\lambda + \Delta\lambda$ , given by:

$$J_{\lambda} = I_{o\lambda} T_{a\lambda} [T_{s\lambda} + g i (1 - T_{s\lambda}) \cos z] (1 + a) \quad (II)$$

where  $I_{o\lambda}$  is the solar intensity outside the atmosphere at  $\lambda$ ;  $T_{a\lambda}$  is the transmissivity of the atmosphere, mainly due to ozone absorption;  $T_{s\lambda}$  is the transmissivity of the atmosphere due to scattering and diffusion;  $g$  and  $i$  are fractional constants, usually taken as 0.5 and 2, respectively;  $z$  is the solar zenith angle; and  $a$  is the albedo factor.

In determining the seasonal variation of the actinic irradiance,  $I_{o\lambda}$  and  $T_{s\lambda}$  were taken from ref. 7;  $a = 0.5$  during winter conditions to take into account reflectance from snow and is set equal to zero for all other conditions. The albedo factor is in fact wavelength dependent and has a value of less than 0.1 over the important wavelength region 3000-4000 Å for most natural surfaces (10). The average value  $a = 0.5$  for snow-covered areas suggested by Leighton (7) might be low, although  $a = 0.4$  has been recently quoted for old, dirty snow (11). The values for  $z$  and the equivalent ozone layer thickness of the atmosphere which determines  $T_{a\lambda}$  are shown in Table II and represent average values for the season indicated. In the cases of HNO<sub>2</sub>, HNO<sub>3</sub>, and O<sub>3</sub>, more recent values of  $\alpha_{\lambda}$  and  $\phi_{\lambda}$  were used in the calculations of  $k_a$  than had been available to previous investigators. One referee has indicated to us that the data of Johnston and Graham (17) for  $\alpha_{\lambda}$  (HNO<sub>2</sub>) are actually too low by a factor of three. This correction would make the absorption coefficient closer in mag-

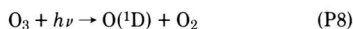
**Table I. Specific Absorption Rates<sup>a</sup>**

	Winter	Spring	Summer	Autumn	Ref <sup>b</sup>
P1. NO <sub>2</sub> + hν → NO + O	0.098	0.33	0.48	0.33	2
P2. HNO <sub>2</sub> + hν → OH + NO	0.0057	0.019	0.028	0.020	17
P3. HNO <sub>3</sub> + hν → OH + NO <sub>2</sub>	2 × 10 <sup>-7</sup>	9 × 10 <sup>-6</sup>	3 × 10 <sup>-5</sup>	1 × 10 <sup>-5</sup>	17
P4. H <sub>2</sub> CO + hν → H <sub>2</sub> + CO	7.7 × 10 <sup>-4</sup>	3 × 10 <sup>-3</sup>	4.9 × 10 <sup>-3</sup>	3.1 × 10 <sup>-3</sup>	18
P5. → H + HCO	2 × 10 <sup>-4</sup>	9.4 × 10 <sup>-4</sup>	1.7 × 10 <sup>-3</sup>	1.0 × 10 <sup>-3</sup>	18
P6. CH <sub>3</sub> CHO + hν → CH <sub>4</sub> + CO	2 × 10 <sup>-6</sup>	1.2 × 10 <sup>-5</sup>	2.4 × 10 <sup>-5</sup>	1.3 × 10 <sup>-5</sup>	19
P7. → CH <sub>3</sub> + HCO	3.4 × 10 <sup>-5</sup>	2.4 × 10 <sup>-4</sup>	4.8 × 10 <sup>-4</sup>	2.7 × 10 <sup>-4</sup>	19
P8. O <sub>3</sub> + hν → O( <sup>1</sup> D) + O <sub>2</sub>	1.1 × 10 <sup>-6</sup>	1.1 × 10 <sup>-4</sup>	6.3 × 10 <sup>-4</sup>	2 × 10 <sup>-4</sup>	12-14
P9. → O( <sup>3</sup> P) + O <sub>2</sub>	2.6 × 10 <sup>-3</sup>	7.3 × 10 <sup>-3</sup>	1 × 10 <sup>-2</sup>	7.7 × 10 <sup>-3</sup>	12-14
P10. CH <sub>3</sub> ONO + hν → CH <sub>3</sub> O + NO	1.8 × 10 <sup>-2</sup>	6.2 × 10 <sup>-2</sup>	9.2 × 10 <sup>-2</sup>	6.3 × 10 <sup>-2</sup>	19
P11. H <sub>2</sub> O <sub>2</sub> + hν → 2OH	2.1 × 10 <sup>-4</sup>	8.4 × 10 <sup>-4</sup>	1.4 × 10 <sup>-3</sup>	8.8 × 10 <sup>-4</sup>	2

<sup>a</sup> In min<sup>-1</sup>. <sup>b</sup> References used in determining absorption and quantum yield data.

nitude to that estimated by Cox (39) and also to the data used by Demerjian et al. (2) who equated the values of α<sub>λ</sub> (HNO<sub>2</sub>) with α<sub>λ</sub> (CH<sub>3</sub>ONO). Although such changes will have some effect on the numerical results of our calculations, no major changes in the relative findings and conclusions should be expected.

Recent work (12-14) has shown that the quantum yield of O(<sup>1</sup>D) formation from the photolysis of O<sub>3</sub> declines much more rapidly with increasing wavelength than previously assumed (2); thus, much less O(<sup>1</sup>D) formation is to be expected in the lower atmosphere. In the calculations it is assumed that over the wavelength range 3050-3150 Å, φ[O(<sup>1</sup>D))] = 0.25 and φ[O(<sup>3</sup>P))] = 0.75 and that at higher wavelengths only O(<sup>3</sup>P) atoms are formed. Even under these assumptions the calculated rate of formation of O(<sup>1</sup>D) atoms, especially under winter conditions, might be overestimated since a combination of the long effective path length of solar radiation through the atmosphere (z = 80°) and the lower temperature, where φ[O(<sup>1</sup>D))] will be smaller (16), might completely suppress the formation of O(<sup>1</sup>D). Our estimated values compare very well with those of Nieboer et al. (6), with the exception of the reaction



We believe this discrepancy is due to the fact that Nieboer et al. used older data for calculating the quantum efficiency as a function of excitation wavelength.

### Nonphotochemical Reactions

One hundred nonphotochemical reactions were considered in the calculations. These reactions together with their rate constants are listed in Table III. Comments as to the choice of rate parameters for some of the reactions are given in the Appendix. Reactions 12, 14, 24, 31, 34, 48, 55, 59, 64, 65, 71, 77, 80, 89, 91, 99, and 100 lead to intermediates which react exclusively and very rapidly with O<sub>2</sub> in the biosphere, and the overall reactions have been incorporated in one equation. Also, the primary intermediates formed in the following reactions rapidly decompose into smaller fragments, and for simplicity only the overall reaction was used in the calculations and is shown in Table III: 24 (HNO), 26 (HCOO<sub>2</sub>NO), 28 (CH<sub>3</sub>COO<sub>2</sub>NO), 31 (C<sub>4</sub>H<sub>8</sub>[OH][O]), 32 (C<sub>2</sub>H<sub>4</sub>[OH][O]), 34 (C<sub>4</sub>H<sub>8</sub>[CH<sub>3</sub>O][O]), 35 (C<sub>2</sub>H<sub>4</sub>[CH<sub>3</sub>O][O]), 37 (C<sub>4</sub>H<sub>7</sub>[O<sub>2</sub>][O]), and 93 (CH<sub>3</sub>CH[O<sub>2</sub>][O<sub>2</sub>]).

Reactions of singlet (<sup>1</sup>Σ<sup>+</sup><sub>g</sub>) and (<sup>1</sup>Δ<sub>g</sub>) oxygen molecules are not considered in this work, since their contribution to the overall chemistry is negligible (2). In Table III rate constants from ref. 15 are experimental values, while most data from ref. 2 are estimated. For some rate constants the room temperature values have been determined, and the Arrhenius pa-

**Table II. Conditions Chosen to Define Four Seasons**

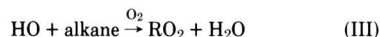
	Winter	Spring	Summer	Autumn
z <sup>a</sup>	80°	60°	40°	60°
α <sup>b</sup>	370	400	340	310
Temperature	-15°	5°	25°	5°
Relative humidity	75%	50%	50%	50%
a	0.5	0	0	0

<sup>a</sup> Solar zenith angle, average value from Figure 3, ref. 7. <sup>b</sup> Total ozone layer in Dobson units from Figure 1, ref. 20.

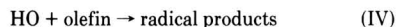
rameters had to be estimated, whereas for some other reactions in which more than one product channel is possible but only the overall reaction constant has been measured, an estimate of the relative importance of the channels had to be made. Such cases have been indicated by † and \*, respectively, in Table III.

### Results and Discussion

The composition of the system chosen to study the evolution of the described model is listed in Table IV. This type of mixture is an oversimplification of an actual air pollution situation, but contains representative quantities of compounds from the more important classes of reagents (4). In particular, the choice of a highly reactive olefin (*t*-2-butene) as a surrogate hydrocarbon for atmospheric reactive hydrocarbon mixes is commonly made (2, 4, 6) to simplify the calculations. It cannot be argued that more realistic models of polluted atmospheres should include contributions from several classes of hydrocarbons (21). Inclusion of a sizable amount of an alkane as starting material in our hypothetical pollution mixture would lead to a substantial increase in the total number of reactions and certainly change the overall reaction path, but in view of earlier tests by Demerjian et al. (2) and by Calvert and McQuigg (4), only minor changes in the evolution of the chemical system should be expected. The main reason for this is that the major alkane reaction



has a very low activation energy (22) and thus is nearly independent of temperature; similarly, the major olefin reaction



is assumed to be temperature independent in the present calculations (see Appendix).



The computer subroutine DIFSUB developed by Gear (23) was used for the integration of the set of differential equations. Since the rate constants and concentrations are expressed in ppm units (where ppm relates to atmospheric pressure), the concentrations were converted to their equivalent values at 25 °C for the calculations. The preexponential terms of the rate constants in Table III are also listed at 25°.

Figures 1 and 2 illustrate the now well-established patterns of concentration changes for some important species under

summer and winter conditions, respectively. Some major differences can be noticed. Under winter conditions the oxidation of NO to NO<sub>2</sub>, and consequently the formation of oxidants and peroxyacetyl nitrate (PAN), are much slower. Moreover, the final concentration of these species seems to reach lower limiting values. To elucidate the cause of these changes, the effects of variations in temperature and solar altitude were investigated separately.

Figure 3 shows the effect of different average solar altitudes

**Table III. Nonphotochemical Reactions and Their Rate Constants<sup>a</sup>**

No.	Reaction	Rate constant	Ref <sup>c</sup>
1	$O_3 + O \rightarrow 2O_2$	$2.8 \times 10^4 \exp(-2300/T)$	15
2	$O_3 + HO \rightarrow O_2 + HO_2$	$2.4 \times 10^3 \exp(-1000/T)$	15
3	$O_3 + HO_2 \rightarrow 2O_2 + HO$	$1.5 \times 10^2 \exp(-1250/T)$	15
4	$O_3 + NO \rightarrow O_2 + NO_2$	$5.1 \times 10^3 \exp(-1533/T)$	15
5	$O_3 + NO_2 \rightarrow O_2 + NO_3$	$1.8 \times 10^2 \exp(-2450/T)$	15
6	$O_3 + C_4H_8 \rightarrow C_4H_8O_3$	$1.1 \times 10^2 \exp(-1100/T)$	<sup>b</sup>
7	$O + O_2 + M \rightarrow O_3 + M$	$2.4 \times 10^{-6} \exp(510/T)$	15
8	$O + NO + M \rightarrow NO_2 + M$	$1.1 \times 10^{-4} \exp(940/T)$	15
9	$O + NO_2 \rightarrow O_2 + NO$	$2.5 \times 10^4 \exp(-300/T)$	15
10	$O + NO_2 \xrightarrow{M} NO_3$	$2.9 \times 10^4$ (2nd order limit)	15
11	$O + CH_2O \rightarrow HCO + HO$	$2.5 \times 10^4 \exp(-1400/T)$	2 <sup>++</sup>
12	$O + CH_3CHO \xrightarrow{O_2} CH_3COO_2 + HO$	$4.9 \times 10^4 \exp(-1400/T)$	2 <sup>++</sup>
13	$O + C_4H_8 \rightarrow C_4H_8O$ (epoxide)	$6.8 \times 10^3$	<sup>b*</sup>
14	$O + C_4H_8 \xrightarrow{O_2} C_4H_8O_3$	$2.7 \times 10^4$	<sup>b*</sup>
15	$O(^1D) + H_2O \rightarrow 2HO$	$5.1 \times 10^5$	15
16	$O(^1D) + M \rightarrow O + M$	$8.5 \times 10^4$	15
17	$2NO + O_2 \rightarrow 2NO_2$	$1.2 \times 10^{-10} \exp(530/T)$	15
18	$NO + NO_2 + H_2O \rightarrow 2HONO$	$2.2 \times 10^{-9}$	<sup>b†</sup>
19	$NO + NO_3 \rightarrow 2NO_2$	$1.3 \times 10^4$	15
20	$NO + HO \xrightarrow{M} HONO$	$8.2 \times 10^3$ (2nd order limit)	15
21	$NO + HO_2 \rightarrow NO_2 + HO$	$7.3 \times 10^4 \exp(-1200/T)$	<sup>b†</sup>
22	$NO + CH_3O_2 \rightarrow NO_2 + CH_3O$	$4.9 \times 10^3 \exp(-500/T)$	2*
23	$NO + CH_3O \rightarrow CH_3ONO$	$1 \times 10^2$	15
24	$NO + CH_3O \xrightarrow{O_2} NO + CH_2O + HO_2$	$1.7 \times 10^1$	15
25	$NO + HCOO_2 \rightarrow NO_2 + HCO_2$	$4.9 \times 10^3 \exp(-500/T)$	2
26	$NO + HCOO_2NO_2 \rightarrow 2NO_2 + HCO_2$	$4.9 \times 10^3 \exp(-3000/T)$	<sup>b</sup>
27	$NO + CH_3COO_2 \rightarrow NO_2 + CH_3CO_2$	$4.9 \times 10^3 \exp(-500/T)$	2
28	$NO + CH_3COO_2NO_2 \rightarrow 2NO_2 + CH_3CO_2$	$4.9 \times 10^3 \exp(-3000/T)$	<sup>b†</sup>
29	$NO + CH_2OO \rightarrow NO_2 + CH_2O$	$4.9 \times 10^3$	2
30	$NO + CH_3CHOO \rightarrow NO_2 + CH_3CHO$	$4.9 \times 10^3$	2
31	$NO + C_4H_8(OH)(O_2) \xrightarrow{O_2} NO_2 + C_2H_4(OH)(O_2) + CH_3CHO$	$2.4 \times 10^3 \exp(-500/T)$	2
32	$NO + C_2H_4(OH)(O_2) \rightarrow NO_2 + HCOOH + CH_3O_2$	$4.9 \times 10^3$	2
33	$NO + C_4H_8(HO_2)(O_2) \rightarrow NO_2 + C_4H_8(HO_2)(O)$	$2.4 \times 10^3 \exp(-500/T)$	2
34	$NO + C_4H_8(CH_3O)(O_2) \xrightarrow{O_2} NO_2 + C_2H_4(CH_3O)(O_2) + CH_3CHO$	$2.4 \times 10^3 \exp(-500/T)$	2
35	$NO + C_2H_4(CH_3O)(O_2) \rightarrow NO_2 + CH_3O + CH_3CHO$	$4.9 \times 10^3$	2
36	$NO + C_4H_8(CH_3O_2)(O_2) \rightarrow NO_2 + C_4H_8(CH_3O_2)(O)$	$2.4 \times 10^3 \exp(-500/T)$	2
37	$NO + C_4H_7(O_2)(O_2) \rightarrow NO_2 + C_4H_7(O_2)(O)$	$2.4 \times 10^3 \exp(-500/T)$	2
38	$NO_2 + NO_3 \rightarrow N_2O_5$	$5.6 \times 10^3$ (2nd order limit)	15
39	$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$	$3.4 \times 10^2 \exp(-1000/T)$	15
40	$NO_2 + HO \rightarrow HONO_2$	$1.2 \times 10^4$ (2nd order limit)	15
41	$NO_2 + HO_2 \rightarrow HONO + O_2$	$4.4 \times 10^1$	15
42	$NO_2 + CH_3O \rightarrow CH_3ONO_2$	$4.8 \times 10^2$	15, 2*
43	$NO_2 + CH_3O \rightarrow HONO + CH_2O$	$4.8 \times 10^1$	15, 2*
44	$NO_2 + HCOO_2 \rightarrow HCOO_2NO_2$	$4.8 \times 10^2$	2
45	$NO_2 + CH_3COO_2 \rightarrow CH_3COO_2NO_2$	$4.8 \times 10^2$	2

(Continued on page 804)

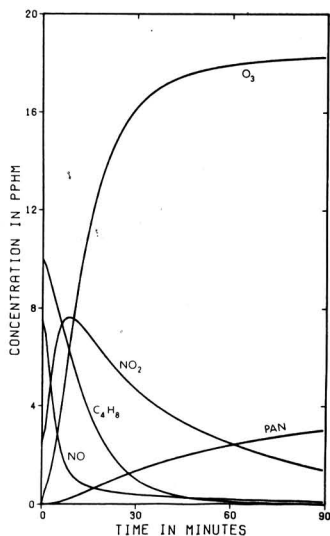
Table III. Continued

No.	Reaction	Rate constant	Ref <sup>c</sup>
46	$\text{NO}_3 + \text{HO}_2 \rightarrow \text{HONO}_2 + \text{O}_2$	$2.5 \times 10^3$	2
47	$\text{NO}_3 + \text{CH}_2\text{O} \rightarrow \text{HONO}_2 + \text{HCO}$	$2.4 \times 10^3 \exp(-2250/T)$	2
48	$\text{NO}_3 + \text{CH}_3\text{CHO} \xrightarrow{\text{O}_2} \text{HONO}_2 + \text{CH}_3\text{COO}_2$	$1.2 \times 10^3 \exp(-2250/T)$	2
49	$\text{NO}_3 + \text{C}_4\text{H}_8 \rightarrow \text{HONO}_2 + \text{C}_4\text{H}_7 \cdot$	$7.3 \times 10^3 \exp(-2250/T)$	2, <sup>b</sup>
50	$\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$	$3.4 \times 10^{16} \exp(-10600/T)$ (1st order limit)	15
51	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HONO}_2$	$2.5 \times 10^{-3}$	2 <sup>+</sup>
52	$\text{HONO}_2 + \text{HO} \rightarrow \text{NO}_3 + \text{H}_2\text{O}$	$8.8 \times 10^2 \exp(-400/T)$	15
53	$\text{HONO} + \text{HO} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	$3.1 \times 10^3$	15
54	$2\text{HONO} \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O}$	$3.5 \times 10^3 \exp(-4365/T)$	b <sup>1</sup>
55	$\text{CH}_4 + \text{HO} \xrightarrow{\text{O}_2} \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	$3.5 \times 10^3 \exp(-1710/T)$	15
56	$\text{CH}_2\text{O} + \text{HO} \rightarrow \text{HCO} + \text{H}_2\text{O}$	$2.1 \times 10^4$	15
57	$\text{CH}_2\text{O} + \text{HO}_2 \rightarrow \text{HCO} + \text{H}_2\text{O}_2$	$1.2 \times 10^3 \exp(-3250/T)$	2
58	$\text{CH}_3\text{CHO} + \text{HO} \xrightarrow{\text{O}_2} \text{CH}_3\text{COO}_2 + \text{H}_2\text{O}$	$2.2 \times 10^4$	2 <sup>+</sup>
59	$\text{CH}_3\text{CHO} + \text{HO}_2 \xrightarrow{\text{O}_2} \text{CH}_3\text{COO}_2 + \text{H}_2\text{O}_2$	$6.1 \times 10^2 \exp(-3250/T)$	2
60	$\text{H}_2\text{O}_2 + \text{HO} \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	$2.5 \times 10^4 \exp(-910/T)$	15
61	$\text{HO} + \text{HO} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$	$9.1 \times 10^{-3}$	15
62	$\text{HO} + \text{HO} \rightarrow \text{H}_2\text{O} + \text{O}$	$1.5 \times 10^4 \exp(-550/T)$	15
63	$\text{HO} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	$1.2 \times 10^5 \exp(-500/T)$	15
64	$\text{HO} + \text{CO} \xrightarrow{\text{O}_2} \text{CO}_2 + \text{HO}_2$	$2.1 \times 10^2$	15
65	$\text{HO} + \text{C}_4\text{H}_8 \xrightarrow{\text{O}_2} \text{C}_4\text{H}_8(\text{OH})(\text{O}_2)$	$9.8 \times 10^4$	b <sup>*</sup>
66	$\text{HO} + \text{C}_4\text{H}_8 \rightarrow \text{C}_4\text{H}_7 \cdot + \text{H}_2\text{O}$	$1.2 \times 10^4$	b <sup>*</sup>
67	$\text{HO}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O}_2\text{H} + \text{O}_2$	$1 \times 10^2$	2
68	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$4.4 \times 10^4 \exp(-500/T)$	15
69	$\text{HO}_2 + \text{HCOO}_2 \rightarrow \text{HCOO}_2\text{H} + \text{O}_2$	$2.1 \times 10^2 \exp(-500/T)$	2
70	$\text{HO}_2 + \text{CH}_3\text{COO}_2 \rightarrow \text{CH}_3\text{COO}_2\text{H} + \text{O}_2$	$2.1 \times 10^2 \exp(-500/T)$	2
71	$\text{HO}_2 + \text{C}_4\text{H}_8 \xrightarrow{\text{O}_2} \text{C}_4\text{H}_8(\text{HO}_2)(\text{O}_2)$	$1.2 \times 10^3 \exp(-1100/T)$	2, b
72	$\text{HO}_2 + \text{C}_4\text{H}_8 \rightarrow \text{C}_4\text{H}_7 \cdot + \text{H}_2\text{O}_2$	$3.8 \times 10^3 \exp(-2810/T)$	2, b
73	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow 2\text{CH}_3\text{O} + \text{O}_2$	$1 \times 10^2$	2, 15 <sup>*</sup>
74	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{O}_2\text{H} + \cdot\text{CH}_2\text{O}_2 \cdot$	$1 \times 10^2$	2, 15 <sup>*</sup>
75	$\text{CH}_3\text{O}_2 + \text{HCOO}_2 \rightarrow \text{CH}_3\text{O} + \text{HCO}_2 + \text{O}_2$	$3.9 \times 10^1$	2
76	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{COO}_2 \rightarrow \text{CH}_3\text{O} + \text{CH}_3\text{CO}_2 + \text{O}_2$	$3.9 \times 10^1$	2
77	$\text{CH}_3\text{O}_2 + \text{C}_4\text{H}_8 \xrightarrow{\text{O}_2} \text{C}_4\text{H}_8(\text{CH}_3\text{O}_2)(\text{O}_2)$	$7.8 \times 10^2 \exp(-1050/T)$	2, b
78	$\text{CH}_3\text{O}_2 + \text{C}_4\text{H}_8 \rightarrow \text{C}_4\text{H}_7 \cdot + \text{CH}_3\text{O}_2\text{H}$	$7.8 \times 10^2 \exp(-3000/T)$	2, b
79	$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	$2.4 \times 10^2 \exp(-3300/T)$	15
80	$\text{CH}_3\text{O} + \text{C}_4\text{H}_8 \xrightarrow{\text{O}_2} \text{C}_4\text{H}_8(\text{CH}_3\text{O})(\text{O}_2)$	$4.9 \times 10^2 \exp(-550/T)$	2, b
81	$\text{CH}_3\text{O} + \text{C}_4\text{H}_8 \rightarrow \text{C}_4\text{H}_7 \cdot + \text{CH}_3\text{OH}$	$7.6 \times 10^2 \exp(-2430/T)$	2, b
82	$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	$8.4 \times 10^3$	15
83	$\text{HCO} + \text{O}_2 \rightarrow \text{HCOO}_2$	$1 \times 10^2$	2
84	$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{HCO}_2 + \text{HO}_2$	$6.1 \times 10^2 \exp(-2040/T)$	2
85	$\text{CH}_3\text{CHO} + \text{O}_2 \rightarrow \text{CH}_3\text{CO}_2 + \text{HO}_2$	$6.1 \times 10^2 \exp(-2040/T)$	2
86	$\text{HCOO}_2 + \text{HCOO}_2 \rightarrow 2\text{HCO}_2 + \text{O}_2$	3.8	2
87	$\text{CH}_3\text{COO}_2 + \text{CH}_3\text{COO}_2 \rightarrow 2\text{CH}_3\text{CO}_2 + \text{O}_2$	3.8	2
88	$\text{HCOO}_2 + \text{CH}_3\text{COO}_2 \rightarrow \text{HCO}_2 + \text{CH}_3\text{CO}_2 + \text{O}_2$	3.8	2
89	$\text{HCO}_2 \xrightarrow{\text{O}_2} \text{HO}_2 + \text{CO}_2$	$1.9 \times 10^{15} \exp(-3500/T)$	2
90	$\text{HCOO}_2\text{NO}_2 \rightarrow \text{HONO}_2 + \text{CO}_2$	$1.9 \times 10^{13} \exp(-2500/T)$	2
91	$\text{CH}_3\text{CO}_2 \xrightarrow{\text{O}_2} \text{CH}_3\text{O}_2 + \text{CO}_2$	$6 \times 10^{15} \exp(-2500/T)$	2
92	$\text{C}_4\text{H}_8\text{O}_3 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\dot{\text{C}}\text{H}(\text{O}_2) \cdot$	$1.9 \times 10^{16} \exp(-7500/T)$	2
93	$\text{CH}_3\dot{\text{C}}\text{H}(\text{O}_2) \cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{O}_2$	$1 \times 10^4$	2
94	$\text{CH}_3\dot{\text{C}}\text{H}(\text{O}_2) \cdot + \text{O}_2 \rightarrow \text{O}_3 + \text{CH}_3\text{CHO}$	$2.4 \times 10^3 \exp(-500/T)$	2
95	$\cdot\text{CH}_2\text{O}_2 \cdot + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{O}_2$	$1 \times 10^4$	2
96	$\cdot\text{CH}_2\text{O}_2 \cdot + \text{O}_2 \rightarrow \text{O}_3 + \text{CH}_2\text{O}$	$2.4 \times 10^3 \exp(-500/T)$	2
97	$\text{C}_4\text{H}_8(\text{HO}_2)(\text{O}) \rightarrow \text{HO} + 2\text{CH}_3\text{CHO}$	$1.9 \times 10^{16} \exp(-7500/T)$	2
98	$\text{C}_4\text{H}_8(\text{CH}_3\text{O}_2)(\text{O}) \rightarrow \text{CH}_3\text{O} + 2\text{CH}_3\text{CHO}$	$1.9 \times 10^{16} \exp(-7500/T)$	2
99	$\text{C}_4\text{H}_7 \xrightarrow{2\text{O}_2} \text{C}_4\text{H}_7[\text{O}_2][\text{O}_2]$	$3.2 \times 10^{11} \exp(-5500/T)$	2
100	$\text{C}_4\text{H}_7[\text{O}_2][\text{O}] \rightarrow \text{HCO} + \text{CH}_2\text{O} + \text{CH}_3\text{CHO}$	$1.9 \times 10^{14} \exp(-2500/T)$	2

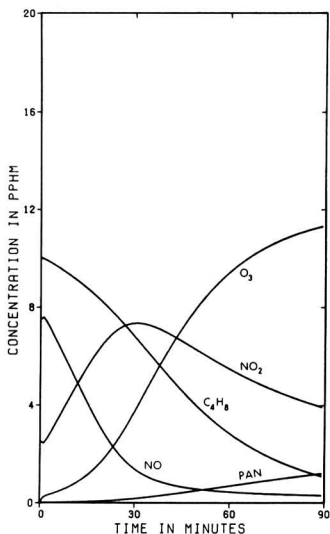
<sup>a</sup> In units  $\text{min}^{-1}$  (1st order),  $\text{ppm}^{-1} \text{min}^{-1}$  (2nd order),  $\text{ppm}^{-2} \text{min}^{-1}$  (3rd order); preexponential factors tabulated at 25 °C. <sup>b</sup> See Appendix. <sup>c</sup> All rate constants from ref. 2 are estimated values, except where indicated by superscripts <sup>+</sup>, <sup>\*</sup>: The partition between two reaction routes is estimated, but the overall rate constant is known. <sup>†</sup>: The rate constant is only known at one temperature; Arrhenius parameters are estimated.

**Table IV. Composition of Test Reaction Mixture**

	ppm
Air	10 <sup>6</sup>
Oxygen	2 × 10 <sup>5</sup>
Methane	1.5
NO	0.075
NO <sub>2</sub>	0.025
CO	10
CH <sub>2</sub> O	0.1
CH <sub>3</sub> CHO	0.06
<i>trans</i> -2-Butene	0.1



**Figure 1.** Temporal variations in O<sub>3</sub>, NO<sub>2</sub>, PAN, C<sub>4</sub>H<sub>8</sub>, and NO concentrations at 25 °C



**Figure 2.** Temporal variations in O<sub>3</sub>, NO<sub>2</sub>, PAN, C<sub>4</sub>H<sub>8</sub>, and NO concentrations at -15 °C

on the concentration changes of NO<sub>2</sub> and O<sub>3</sub> at a constant temperature of 25 °C. The specific absorption rates listed in Table I were used in these calculations. It is evident that the lower rates of product formation under winter conditions (Figure 2) are to a very large extent due to the change in solar altitude.

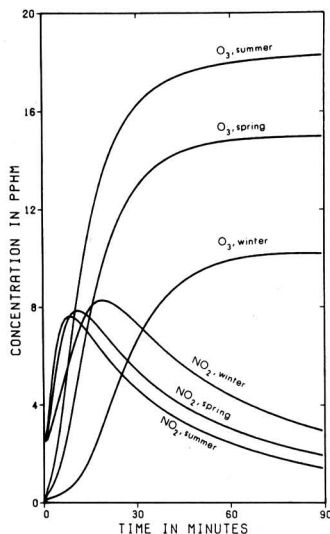
The effect of temperature on the temporal variation of NO<sub>2</sub> and O<sub>3</sub> at constant solar altitude is illustrated in Figure 4, using the specific absorption rates established for summer conditions listed in Table I. For comparison, the calculated total effect of temperature and solar altitude under winter conditions is also shown in Figure 4 where a quite substantial lowering in temperature, as can be expected during winter, has small effects on the chemical evolution of the reaction mixture and the final levels of oxidants. Some of the results from the calculations used for Figures 3 and 4 are assembled in Table V.

Experimental smog chamber experiments on temperature effects are very sparse. Jeffries et al. (24), using an outdoor smog chamber, reported that the maximum O<sub>3</sub> concentration decreases substantially with decreasing (presumably average daily) temperature provided the midday temperature is less than ~70 °F. These results, however, cannot be compared with the predictions of our calculations since they are compounded by effects of diurnal changes in temperature and photolytic radiation. Note, moreover, that only purely homogeneous gas-phase reactions were incorporated into our model; heterogeneous effects play an important role in smog chamber reactions, and it is not inconceivable that strong temperature effects may originate from such factors.

An interesting comparison can be made with regard to the ultimate ozone concentration in such mixtures. Temperature and solar altitude exert opposing effects. According to the well-established photostationary state between NO, NO<sub>2</sub>, and O<sub>3</sub> (25, 26), the O<sub>3</sub> concentration can be established from the relation:

$$[O_3] \approx \frac{k_{P1}[NO_2]}{k_4[NO]} \quad (V)$$

Due to the activation energy requirement of Reaction 4, *k*<sub>4</sub> is smaller at lower temperature; thus, an increase in O<sub>3</sub> con-



**Figure 3.** Temporal variations in O<sub>3</sub> and NO<sub>2</sub> concentrations at solar zenith angles of 80° (winter), 60° (spring), and 40° (summer) and constant temperature of 5 °C

centration under equal NO<sub>x</sub> conditions might be expected under winter conditions. However,  $k_{P1}$  decreases by a factor of nearly 5 under winter conditions, and this accounts for the lower O<sub>3</sub> concentration:

$$\frac{k_{P1}}{k_4} (\text{summer}) = 1.6 \times 10^{-2} \text{ ppm;}$$

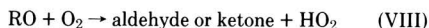
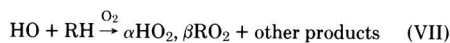
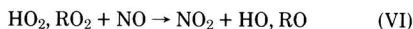
$$\frac{k_{P1}}{k_4} (\text{winter}) = 1.1 \times 10^{-2} \text{ ppm}$$

(In this calculation the albedo factor, 0.5 under winter conditions, has been taken into account.) Parallel to the expected decrease in ozone concentration, the data in Table V show that the slower rates of formation of PAN and other ultimate oxidation products are also related to the slower specific absorption rates during winter conditions.

It has been established in several studies (1, 4) that highly reactive small radicals (e.g., HO, HO<sub>2</sub>, and RO<sub>2</sub> where R = alkyl, acyl, etc.) are present in low concentrations in polluting mixtures and that they are the driving forces in the ongoing chemistry of these systems. The effectiveness of these small radicals is due to their participation in several chain reactions even though it has been suggested that the chain lengths might be actually rather short (4). It is interesting to investigate the influence of temperature and solar altitude on these chain reactions.

The chain lengths for the HO, HO<sub>2</sub>, and RO<sub>2</sub> radicals were calculated by the method outlined by Calvert and McQuigg (4) wherein the total rates of radical formation are divided by the primary rates. The temporal variations of the chain lengths of these radicals as functions of temperature and solar altitude are illustrated in Figures 5–7. In all cases, the chain lengths are initially long, but undergo a rapid decline to more or less constant values. In this leveling off region, 2–3 propagation cycles are involved in HO and HO<sub>2</sub> radical chains and approximately 5 in the RO<sub>2</sub> chains. It might appear that the initially long chains can be attributed to the fact that a sufficient radical concentration has to be built up before chain terminations can occur, as in Reactions 67–70. Time profiles of the radical concentrations, also shown in Figures 5–7, suggest that this could explain the initially long HO<sub>2</sub> and RO<sub>2</sub> radical chains but not that of the HO radical chain, since this radical is present almost instantaneously at a relatively high concentration of approximately 10<sup>-7</sup> ppm and the HO radical concentration actually decreases as the HO chain length approaches the leveling off region.

Close inspection of the total reaction mechanism indicates that many termination steps involve the NO<sub>2</sub> molecule via Reactions 40, 41, 44, and 45, and inspection of the rates of these reactions (Table III) shows that, together with Reaction 68, they constitute major termination reactions. During the initial stage of the reactions, characterized by the NO → NO<sub>2</sub> conversion, the major chain propagation occurs via the following reactions:



The present results show that initially the chains are long, but since these reactions deplete the chain propagating molecule NO and lead to the chain terminating molecule NO<sub>2</sub>, the chain lengths decrease and eventually become rather short. Moreover, the chain lengths of the HO<sub>2</sub> and RO<sub>2</sub> radicals become shorter as the radical concentration increases so that mutual termination Reactions 67–70, 73–76, and 86–88 can become important. This scheme also shows that the role of the

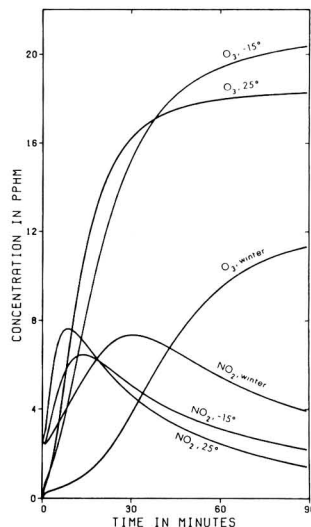


Figure 4. Temporal variations of O<sub>3</sub> and NO<sub>2</sub> at -15 °C and 25 °C at constant solar zenith angle of 40°

Table V. Concentration-Time Values for NO<sub>2</sub>, O<sub>3</sub>, and PAN under Varying Conditions of Temperature and Solar Altitude

	Summer	Winter	% Change
t <sub>[NO<sub>2</sub>]<sub>max</sub></sub> in min	A <sup>a</sup> 9	31	244
	B <sup>b</sup> 9	19	111
	C <sup>c</sup> 9	14	55
[O <sub>3</sub> ] at t = 120 min in ppm	A 0.18	0.12	-33
	B 0.18	0.10	-44
	C 0.18	0.21	+16
[PAN] at t = 120 min in ppm	A 0.035	0.016	-54
	B 0.035	0.018	-49
	C 0.035	0.035	0

<sup>a</sup> Calculated for conditions listed in Table II. <sup>b</sup> T = 25 °C, photochemical rates taken from Table I. <sup>c</sup> Temperatures from Table II; photochemical rates at a solar zenith angle of 40° (summer).

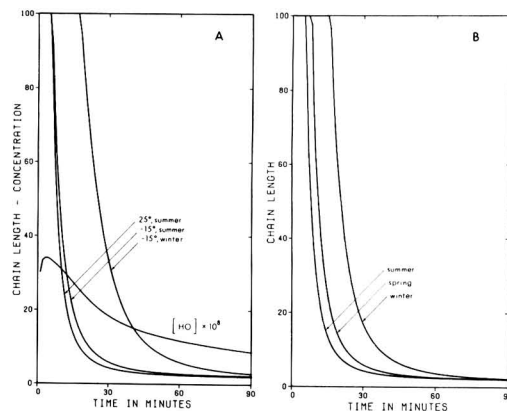
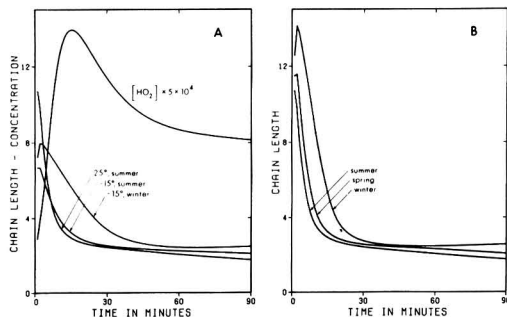


Figure 5. Temporal variation of chain length of HO radicals. A. Effect of temperature at constant solar zenith angle of 40°. Also shown is total effect of temperature and solar altitude and radical concentration in units of ppm under summer conditions. B. Effect of solar altitude at constant temperature of 25 °C

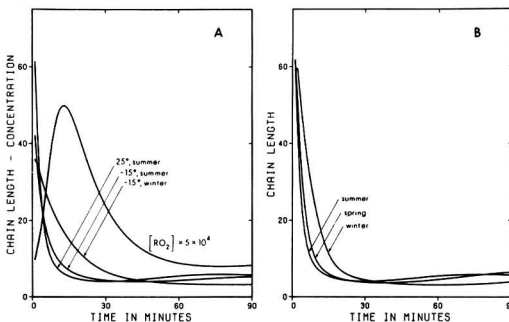
olefins is equally important, in that these molecules are necessary for propagation of the radical chains (4).

From Figures 5-7, only slight variations in the chain lengths of the major radicals are observed with decreasing temperature: Those of HO<sub>2</sub> and RO<sub>2</sub> are suppressed slightly, and that of HO is moderately enhanced. Since the rate of primary formation of these radicals is unaffected by temperature, the chain lengths depend mainly on the activation energies of the major reactions involved. Since these are generally small, only minor changes in the overall chemical evolution are predicted.

On the other hand, changes in solar altitude have a much larger influence. This should be expected since the primary source of all these radicals is principally photochemical in origin (HO is formed directly via Reactions P2 and P11 and indirectly via P1, P8, and P9; HO<sub>2</sub>, indirectly via P4-P9; and RO<sub>2</sub>, indirectly via P1 and P4-P9), and the rates of production of these radicals are considerably lower under winter conditions (cf. Table I). The lower production rates appear to be compensated for, in the case of the HO radical, by a substantial increase in the chain length. However, much less compensation is available to offset the slower rates of formation of RO<sub>2</sub> and especially HO<sub>2</sub> since mutual termination reactions maintain short chain lengths. It thus appears that the predicted retardation in the chemistry of an air pollution mixture under winter solar irradiation conditions is due mainly to the lowered rate of formation of the peroxy radicals HO<sub>2</sub> and RO<sub>2</sub>.



**Figure 6.** Temporal variation of chain length of HO<sub>2</sub> radical  
A. Effect of temperature at constant solar zenith angle of 40°. Also shown is total effect of temperature and solar altitude and radical concentration in units of ppm under summer conditions. B. Effect of solar altitude at constant temperature of 25 °C



**Figure 7.** Temporal variation of chain length of RO<sub>2</sub> radicals  
A. Effect of temperature at constant solar zenith angle of 40°. Also shown is total effect of temperature and solar altitude and radical concentration in units of ppm under summer conditions. B. Effect of solar altitude at constant temperature of 25 °C

## Appendix

**Estimation of Some Rate Parameters.** Reactions 18 and 54,  $NO + NO_2 + H_2O \rightleftharpoons 2HONO$ . The newly reported rate constant values (27) were combined with the procedure described by Demerjian et al. (2) to determine the temperature dependence of this reaction.

Reaction 21,  $NO + HO_2 \rightarrow NO_2 + HO$ . The activation energy for this reaction is taken as  $E_a = 2.4$  kcal from the data of Hack et al. (28). However, the extrapolated rate constant at 25°, using their preexponential factor, is much lower than that reported recently (29, 30). The preexponential factor was therefore set at  $7.3 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$  so that the calculated rate constant at 25° is the same as the more reliable value determined by Simonaitis and Heicklen (30). The latter authors claim that, contrary to Cox and Derwent's suggestion (29) the reaction i



does not occur, and this step was therefore neglected.

Reaction 26,  $NO + HCOO_2NO_2 \rightarrow HCO_2 + 2NO_2$ , and Reaction 28,  $NO + CH_3COO_2NO_2 \rightarrow CH_3CO_2 + 2NO_2$ . The rate constants for these reactions are based on the assumption that the A-factors are similar to those of the corresponding Reactions 25 and 27. The measured rate constant at 25° for Reaction 28 ( $0.16 \text{ ppm}^{-1} \text{ min}^{-1}$ ) (2) then leads to an activation energy of 6 kcal/mol. This seems reasonable since the reaction is almost thermoneutral. Reaction 26 has been assumed to have the same rate constant as Reaction 28.

Reaction 6,  $O_3 + C_4H_8 \rightarrow C_4H_8O_3$  (ozonide). The rate constant given in Table III is an average value from the data of Huie and Herron (31) and Becker et al. (32).

Reaction 13,  $O + C_4H_8 \rightarrow C_4H_8O$  (epoxide), and Reaction 14,  $O + C_4H_8 \xrightarrow{O_2} C_4H_8O_3$  (ozonide). These reactions feature very small or zero activation energies (33). The ratio  $k_{13}/k_{14}$  and the rate constants are taken from ref. 2.

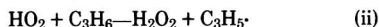
Reaction 49,  $NO_3 + C_4H_8 \rightarrow HONO_2 + C_4H_7$ . The rate constant was calculated using the procedure of Demerjian et al. (2). Recent results (34) seem to suggest that addition of NO<sub>3</sub> to an olefin could be an important reaction path. However, further experimental proof seems warranted, since on thermodynamic grounds addition is unfavorable compared to abstraction, and only Reaction 49 has therefore been considered in the overall scheme.

Reaction 65,  $HO + C_4H_8 \xrightarrow{O_2} C_4H_8(HO)(O_2)$ , and Reaction 66,  $HO + C_4H_8 \rightarrow H_2O + C_4H_7$ . The overall reaction (65 + 66) has recently been shown to feature a slightly negative activation energy (or, more likely, no activation energy but a temperature dependent A-factor) (35). The rate constant for Reaction 66 was estimated to be  $2.1 \times 10^4 \exp(-190/T)$  following Kerr and Parsonage (36). The rate constant for Reaction 65 was calculated from that measured for the overall reaction,  $1.7 \times 10^4 \exp(550/T)$ , and the calculated value for Reaction 66, taking 5 °C as an average temperature. Both reactions are for convenience assumed to be temperature independent over the studied temperature range, which is reasonable in view of the very small activation energies involved.

Reaction 71,  $HO_2 + C_4H_8 \xrightarrow{O_2} C_4H_8(HO_2)(O_2)$ , and Reaction 72,  $HO_2 + C_4H_8 \rightarrow H_2O_2 + C_4H_7$ . In the addition reactions of O(³P) and O<sub>3</sub> to olefins, the increase in the rate constant with increasing alkyl substitution is mainly reflected in the activation energy, and the A-factor remains nearly constant. The rate constant for the addition of HO<sub>2</sub> to ethylene has been suggested to be  $1.2 \times 10^3 \exp(-2500/T)$  (37), featuring the same activation energy as that for the addition of O<sub>3</sub> to ethylene. The rate constant for Reaction 71 has therefore been estimated to have an A-factor equal to that for the addition

of HO<sub>2</sub> to ethylene, with an activation energy equal to that of the O<sub>3</sub> and C<sub>4</sub>H<sub>8</sub> reaction.

For Reaction 72 the same procedure as outlined by Demerjian et al. (2) was used. Thus, assuming that the rate of Reaction 57 is equal to that of reaction ii



at 25° and that the A-factor of reaction ii is 2/3 A<sub>57</sub>, k<sub>ii</sub> is estimated to be 1.9 × 10<sup>3</sup> exp(-3370/T).

From the estimated rate constants for the reactions of HO, it can be calculated that at 25°,

$$\frac{k_{\text{add}}}{k_{\text{abstr}}} (\text{C}_3\text{H}_6) : \frac{k_{\text{add}}}{k_{\text{abstr}}} (\text{C}_4\text{H}_8) = 6:8$$

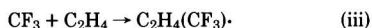
Assuming the same ratio applies in this case and with the additional assumption

$$A_{\text{abstr}}^{\text{C}_4\text{H}_8} = 2 A_{\text{abstr}}^{\text{C}_3\text{H}_6}$$

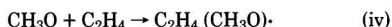
k<sub>abstr</sub><sup>C<sub>4</sub>H<sub>8</sub></sup> can be calculated.

Reaction 77, CH<sub>3</sub>O<sub>2</sub> + C<sub>4</sub>H<sub>8</sub>  $\xrightarrow{\text{O}_2}$  C<sub>4</sub>H<sub>8</sub>(CH<sub>3</sub>O<sub>2</sub>)(O<sub>2</sub>), and Reaction 78, CH<sub>3</sub>O<sub>2</sub> + C<sub>4</sub>H<sub>8</sub> → CH<sub>3</sub>O<sub>2</sub>H + C<sub>4</sub>H<sub>7</sub>. Since the exothermicity of Reaction 77 is almost equal to that of Reaction 71, the same activation energy is assumed. The A-factor used for Reaction 77 is that suggested by Benson (38). The rate parameters used for Reaction 78 are also those suggested by Benson.

Reaction 80, CH<sub>3</sub>O + C<sub>4</sub>H<sub>8</sub>  $\xrightarrow{\text{O}_2}$  C<sub>4</sub>H<sub>8</sub>(CH<sub>3</sub>O)(O<sub>2</sub>), and Reaction 81, CH<sub>3</sub>O + C<sub>4</sub>H<sub>8</sub> → CH<sub>3</sub>OH + C<sub>4</sub>H<sub>7</sub>. Demerjian et al. (2) compared Reaction 80 with CF<sub>3</sub> addition reactions. Thus, from Reaction iii



the rate constant for Reaction iv



is estimated to be 4.9 × 10<sup>2</sup> exp(-1000/T). Again, assuming that the change in the rate constant for addition to C<sub>4</sub>H<sub>8</sub> is a consequence of the activation energy term only, and with k<sup>C<sub>4</sub>H<sub>8</sub></sup>/k<sup>C<sub>2</sub>H<sub>4</sub></sup> = 4.7 at 25°, the activation energy for Reaction 80 is calculated from:

$$4.7 = \exp[(-E_a^{\text{C}_4\text{H}_8} + 2000)/298 R] \text{ or } E_a = 1.1 \text{ kcal}$$

The rate constant for Reaction 81 is determined in the same fashion as for 66 and 72. Thus k<sub>abstr</sub><sup>C<sub>4</sub>H<sub>8</sub></sup> = 3.8 × 10<sup>2</sup> exp(-2000/T), based by comparison with Reaction v:



k<sub>abstr</sub><sup>C<sub>4</sub>H<sub>8</sub></sup> is then calculated from the ratio k<sub>add</sub>/k<sub>abstr</sub> (C<sub>4</sub>H<sub>8</sub>): k<sub>add</sub>/k<sub>abstr</sub> (C<sub>3</sub>H<sub>6</sub>) and A<sub>abstr</sub><sup>C<sub>4</sub>H<sub>8</sub></sup> = 2 A<sub>abstr</sub><sup>C<sub>3</sub>H<sub>6</sub></sup>.

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# Stability Constants of Copper-Organic Chelates in Aquatic Samples

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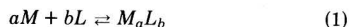
■ A procedure similar to an amperometric titration of a ligand with copper was used to determine the conditional formation constants of copper-organic chelates in several fresh water samples at controlled pH. The titration curve was constructed using anodic stripping voltammetry to detect unreacted copper. An equation for this curve was developed and revealed that both the stoichiometry and the formation constant of the complex formed during the titration could be obtained. The ligand in the water samples responsible for copper binding was characteristic of a conjugate base of a weak acid, the acid being almost entirely ionized at neutral pH. Estimates of the conditional formation constants for these complexes ranged in value from  $0.32 \times 10^5$  to  $5.2 \times 10^5$  at pH 6.5.

Matson (1) introduced an electrochemical method consisting of a complexometric titration combined with anodic stripping voltammetry (ASV) for estimating the concentration of organic ligands in natural waters. This method and additional procedures were used by Matson to estimate formation constants of metal-organic complexes found in natural waters (1, 2). Shuman and Woodward (3) described a similar titration from which the formation constants for 1:1 complexes could be calculated directly. The work reported here extends the usefulness of the latter method to include any stoichiometry and applies it to several natural water samples.

## Theory and Procedure

The procedure is similar to an amperometric titration of a ligand with metal, but in this case, ASV is used to gain sensitivity for application to very dilute solutions. Serial additions of a concentrated metal solution are made to a sample containing titratable ligands held in a three-electrode electrochemical cell. Figure 1 is a pictorial representation of the procedure where for simplicity a buret represents the micro-pipet actually used for additions and a beaker represents the electrochemical cell.

With each addition of metal there is a reaction between the metal  $M$  and the ligand  $L$  to form  $M_aL_b$  according to



The concentration of metal not bound to  $L$ , designated  $M'$ , and which is in equilibrium with  $M_aL_b$  is determined by ASV after each addition and gives an ASV response  $i_s = \kappa[M']$ , where  $i_s$  is the peak current of the stripping curve, and  $\kappa$  is a proportionality constant. The titration curve has two regions, a lower region where the ligand is titrated and the ASV response is low because most of the metal has reacted with  $L$ , and an upper region after the endpoint, where there is normal ASV response to the increasing concentration of uncomplexed metal. The shape of this curve is similar to a conductometric or colorimetric titration in which the product of the titration does not produce a response. The endpoint of the titration is the point at which the analytical concentration of added metal,  $C_M$ , is equal to  $(a/b) C_L$ , where  $C_L$  is the analytical concentration of ligand. This point is determined by extrapolation of data points in the two regions to a point of intersection using guidelines suggested by Rosenthal et al. (4).

Several assumptions are made about this titration. First, it is assumed that the complex,  $M_aL_b$ , does not contribute to

the anodic stripping current,  $i_s$ . Second, it is assumed that  $i_s = \kappa\{[M] + [ML] + [ML_2] \dots + [ML_N]\}$  where  $L_N$  represents ligands other than the ligand of interest, and where  $\kappa$  is the ASV response to all soluble forms of the metal not bonded to the ligand of interest. The numerical value of  $\kappa$  is obtained from the slope of the upper region of the titration curve. A third assumption is that at any point along the titration curve, the concentration of titratable ligand remaining is  $[L'] = [L] + [HL] + [H_2L] \dots + [H_nL] + [M_1L] + [M_2L] \dots + [M_NL]$  where  $M_N$  are metals more weakly bound than the titrant metal and therefore displaced by the titrant metal and where  $n$  is the number of displaceable protons associated with the ligand.

Other assumptions are that the ligand is in excess of titrant metal present in the solution prior to metal addition, and that  $M_aL_b$  does not kinetically dissociate appreciably during the period of metal accumulation at the mercury electrode. With regard to natural waters and the nature of the ASV experiment, these assumptions are reasonable. It is likely that the predominant organic ligands encountered in natural waters would be either polypeptides or humic materials which form large multidentate complexes with metals. Reduction of these complexes, if it takes place at all within the range of the potentials available to the mercury electrode, is irreversible and the dissociation rate of such complexes is slow (5). This means that a potential can be selected that will not be in the range that reduces the metal complex. On the other hand, simple inorganic and bidentate organic complexes are much more easily reduced and their contribution to the stripping current, except for slight differences brought about by their diffusion coefficients in solution, is the same as would be expected if all the metal existed as the simple aquated ion. In any event, the sensitivity of the ASV experiment to all these simpler forms is accessible in the slope  $\kappa$ .

With regard to the large organic molecules to be encountered in natural waters, the quantity  $C_L$  is interpreted as the concentration of individual functional groups acting independently as ligands and is not necessarily the concentration of individual molecules. Because of the complexity of these molecules, the functional groups may include a variety of

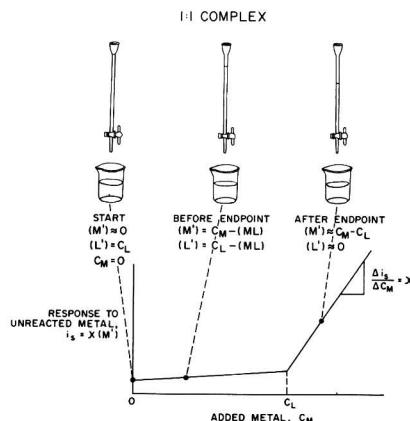


Figure 1. Procedure for titration of ligand with metal

configurations and molecular weights. This simplifying assumption is common to other studies in which bonding of copper to large multifunctional molecules such as polypeptides and proteins is investigated (6).

With reference to Reaction 1, a conditional formation constant can be written

$$K' = \frac{[M_a L_b]}{[M']^a [L']^b} \quad (2)$$

and since  $[M'] = i_s/\kappa$ ,  $C_M = [M'] + a[M_a L_b]$  and  $C_L = [L'] + b[M_a L_b]$ , the conditional formation constant expressed in terms of the experimental parameters is

$$K' = \frac{\frac{1}{a} (C_M - \frac{i_s}{\kappa})}{\left(\frac{i_s}{\kappa}\right)^a \left\{ C_L - \frac{b}{a} (C_M - \frac{i_s}{\kappa}) \right\}^b} \quad (3)$$

This can be rearranged into a polynomial in  $i_s$  and the substitution  $C_M = (a/b) g C_L$  made so that

$$\left(\frac{i_s}{\kappa}\right)^{a+b} + \left(\frac{i_s}{\kappa}\right)^a \left(\frac{a}{b}\right)^b C_L^b (1 - g)^b + i_s \left(\frac{a^{b-1}}{\kappa K' b^{b+1}}\right) - \left(\frac{g C_L a^b}{K' b^{b+1}}\right) = 0 \quad (4)$$

where  $g$  is the fraction of the stoichiometric quantity of titrant. For the important case of  $a = b = 1$ , this equation is a quadratic with the solution

$$\frac{i_s}{i_{\max}} = \frac{1}{2} \{ [g - 1 - (K'_{ML} C_L)^{-1}] + [(1 - g + (K'_{ML} C_L)^{-1})^2 + 4g(K'_{ML} C_L)^{-1}]^{1/2} \} \quad (5)$$

where the term  $i_{\max} = \kappa C_L$  is introduced to make the equation dimensionless. From this equation, the titration of a 1:1 complex depends only on the product  $K'_{ML} C_L$  where  $K'_{ML}$  is the conditional constant for the 1:1 complex.

Theoretical titration curves calculated from Equation 5 for three values of  $K'_{ML} C_L$  are shown in Figure 2 and indicate that considerable dissociation occurs if  $K'_{ML} C_L$  is small. Lines drawn in the figure represent the extrapolation to the endpoint at  $g = 1.0$ . For a "break" in the titration to be easily observed,  $K'_{ML} C_L$  must be greater than unity.

Values for the conditional constants could be obtained by comparing experimental with theoretical curves. However, a simplified method for analyzing the data is available. During the first additions of titrant and for reasonably large formation constants,  $[M'] = i_s/\kappa \ll C_M$  so that for a 1:1 complex, Equation 2 can be approximated by

$$K' \approx \frac{C_M}{\left(\frac{i_s}{\kappa}\right) (C_L - C_M)} \quad (6)$$

and rearranging

$$i_s \approx \frac{\kappa C_M}{K' (C_L - C_M)} \quad (7)$$

Therefore, a plot of  $i_s$  vs.  $[C_M/(C_L - C_M)]$  has a slope  $\kappa/K'$ . Since  $C_M$  is known from the amount of metal added,  $C_L$  is known from the endpoint and  $\kappa$  is obtained from the upper region of the titration curve, all the data necessary to calculate  $K'$  are available from the titration curve alone. Similarly, for any  $a:b$  complex

$$i_s \approx \left(\frac{\kappa}{K'}\right)^{1/a} \frac{\left(\frac{C_M}{a}\right)^{1/a}}{\left(C_L - \frac{b}{a} C_M\right)^{b/a}} \quad (8)$$

For the case of a 1:2 complex, for instance, a plot of  $i_s$  vs.  $[C_M/(C_L - 2C_M)^2]$  has a slope  $\kappa/K'$ . Therefore, it is possible to distinguish stoichiometry as well as to estimate conditional formation constants from this procedure. Errors expected in estimating  $K'$  using this approximation were discussed by Shuman and Woodward (3) for 1:1 stoichiometry. The procedure was applied by those authors to a model system of EDTA titrated with cadmium, and a diagnostic was developed to test the validity of the assumption that no kinetic dissociation of complex takes place during accumulation.

### Experimental

The electronic potentiostat used in this work was described previously (7). The three-electrode electrochemical cell held 50 mL of sample and was constructed of Vycor glass (Corning Glass Works). The micrometer syringe hanging mercury drop electrode (Metrohm Ltd.) had a volume of  $9.3 \times 10^{-4} \text{ cm}^3$ . The ASV accumulation step carried out at  $-0.700 \text{ V}$  vs. SCE for 5 min was followed by an anodic potential sweep at a rate of 43 mV/s. This potential was selected after preliminary studies with the natural water samples showed that at pH 6.0, the stripping current was independent of potential from 0.2 to 0.9 V vs. SCE. Additions of copper titrant were made with Eppendorf micropipets, and equilibration with deaeration following these additions was typically 10 min. The titrant solution was prepared from copper wire dissolved in Ultrex (J. T. Baker Chemical Co.) nitric acid and diluted with ultra-high-purity deionized water supplied by IBM Laboratories, Research Triangle Park, N.C. The pH was controlled by purging the cell with a mixture of Seaford Grade  $\text{N}_2$  (National Welders) and 5%  $\text{CO}_2/95\% \text{ N}_2$  (Matheson Gas Products). Flow rate of each gas was controlled independently with Lab-Crest Century Series 100 flow meters (Fisher & Porter). Samples were collected directly into acid-leached polyethylene jerricans and filtered through acid-leached 0.45- $\mu\text{m}$  Millipore type HA filters.

### Results and Discussion

Several questions were addressed in this work: Does chelation with organic ligands occur when metal is added to a sample of natural water? What is the formation constant of the metal complex formed with this addition? What is the acid-base character of the ligand? Does the ligand concentration correlate with any commonly measured water quality parameter? Before the procedure could be applied to natural water samples, the experimental design had to be carefully considered, especially as it pertained to the ASV technique. First, of the metals readily determined by ASV (Zn, Cu, Cd, and Pb), copper was selected because it generally forms the

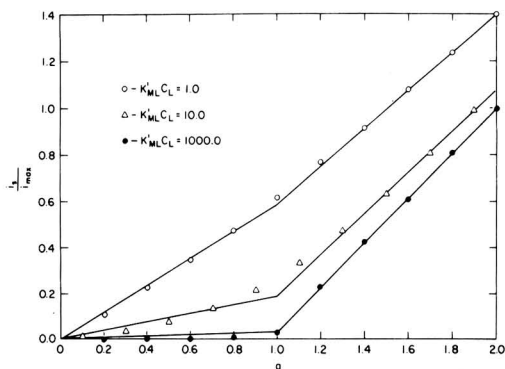


Figure 2. Theoretical titration curves calculated from Equation 5



most stable complexes with organic ligands and is the most easily reduced. This ease of reduction allows more than a 1.0-V overpotential to be applied for the accumulation step of ASV. Therefore, reduction of simple copper solution species (inorganic and simple organic complexes) can be carried out in a region where the stripping current is independent of potential. This consideration can be very important, particularly if Cu and Zn reductions are compared.

The reduction potential of inorganic Zn as carbonate and hydroxide species (which might form in natural waters) is of course a function of pH. Since a large overvoltage cannot be applied for Zn reduction before H<sub>2</sub> evolution commences at mercury, the ASV current sensitivity to Zn may be altered in an unpredictable way when the reduction potential of the major species shifts with a change in solution pH. If the reduction potential of the major Zn species is close to the potential applied for the ASV accumulation, that is, if the accumulation potential is selected in a region where the amount of Zn reduced is a function of the applied potential, then the observed stripping current may be as much an artifact of the potential selected as it is a result of any change in species, and erroneous conclusions concerning metal speciation could be drawn from the results. Each applied potential would give a unique set of observations, each requiring a separate interpretation with regard to speciation.

The study of Zn speciation in seawater by Piro et al. (8) in which the pH was varied from 1.4 to 8.0 and the solution electrolyzed at -1.25 V vs. SCE is open to this criticism. The half-wave potential of zinc hydroxide at pH 8 is about -1.20 V vs. SCE (9), and the half-wave potential of zinc carbonate in 10<sup>-3</sup> M carbonate solutions is about -1.30 V vs. SCE (10). These are two Zn species likely to be present in the higher pH region (11); therefore, it is possible that Piro under the conditions of his experiment was not electrolyzing Zn in the potential independent portion of the polarographic wave and that his current sensitivity to Zn increased as the half-wave potential shifted toward positive potentials with decreasing pH. In other words, the increase in current he observed with decreasing pH could have been as much due to a shift in the potential of the Zn reduction as it was to a change in Zn species.

It would seem best, before any interpretation is made of ASV data, to first establish the current sensitivity for the metal at the selected accumulation potential and at each set of solution conditions (such as pH and alkalinity) to reveal a possible change in current sensitivity. There are two ways in which this can be done, either by obtaining a "pseudopolarogram" of stripping current vs. applied accumulation potential or by carrying out the titration described above. Since the theory for pseudopolarograms for irreversible and quasireversible electrochemical reactions is not available, the titration is preferred. The data in the upper region of the titration curve establish the current sensitivity of the ASV experiment for the solution conditions and for the accumulation potential selected for the experiment. Only by carrying out one of these two procedures will metal speciation be separated from the possible artifacts brought about by an incautious selection of potential.

A second experimental decision was the selection of the hanging mercury drop electrode (HMDE) and a linear potential scan for ASV. Several workers have employed a thin mercury film electrode for analyzing natural waters by ASV, but there have been objections to its use because of intermetallic compound formation (12, 13), because of anomalies from surface "aging" whenever the mercury film is not replated frequently (14), and because of the occasional appearance of uninterpretable "double peaks" (15). The linear scan method was used because of its sound theoretical base (16). Also with linear scan and a fresh HMDE for each experiment, the

morphology of the current potential curve can reveal both reversibility and electrode adsorption processes (16, 17). This combination of HMDE and linear scan was chosen because it has the best theoretical development.

Several fresh water samples were titrated, and endpoints were obtained between  $2.0 \times 10^{-5}$  and  $12.6 \times 10^{-5}$  M. A sample of pond water collected near Chapel Hill, N.C., was the one most extensively studied, and its titration at pH 6.0 and at 6.5 is shown in Figure 3. The pH was controlled during titration by bubbling a mixture of CO<sub>2</sub> and N<sub>2</sub> through the sample. The accumulation potential of -0.700 V vs. SCE was in a range where the ASV current was independent of potential as judged from a pseudopolarogram. Reduction of the copper-organic complex was not observed. This could be expected since, in general, reduction of copper complex containing very large ligand molecules such as the proteins in serum albumin (18) or transfusion gelatin (19) does not take place at the mercury electrode. Difficulty in reducing these large complexes is most likely the result of steric hindrance to close approach at the electrode surface (5). Figure 3 was plotted on the same scale as the theoretical titration curves of Figure 2, and direct comparison reveals that the values of  $K'C_L$  are smaller than 10.0. The lines in Figure 3 represent extrapolations to the endpoint and include data off the scale to the right of the figure.

Several features of the experimental curves can be noted. First of all, the lower pH value has higher currents indicating greater concentrations of unassociated copper. Since the endpoint is independent of pH, the conditional constant is seen to be a function of pH, decreasing with decreasing pH. Secondly, the current sensitivity at pH 6.0 is somewhat greater than that at pH 6.5 as can be judged by comparing slopes in the upper region of the titration curves.

Two other observations can be mentioned. When the sample was titrated at pH 4.8, no "break" was observed, presumably because  $K'C_L$  was very small at this pH, and a line approximately the same slope as the upper region of pH 6.0 was obtained. Also, when the sample was irradiated in quartz containers with  $6 \times 10^6$  rads of gamma radiation from Cs<sup>137</sup>, the endpoint decreased to approximately 60% of the unirradiated samples, indicating a decrease in ligand concentration. This lends weight to the argument that the ligand titrated is organic material. Other arguments for the involvement of organic ligands and against the involvement of inorganic species come from considering the reactivity of complexes at

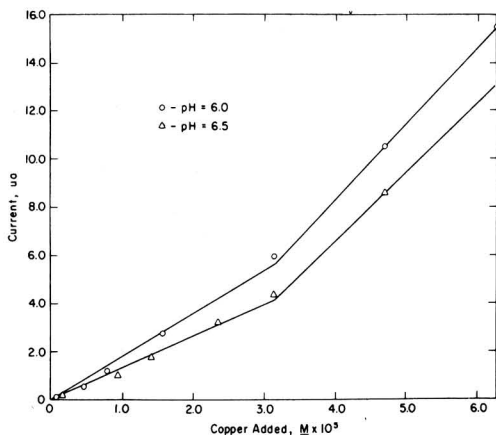


Figure 3. Titration of Chapel Hill sample with copper at pH 6.0 and 6.5

the HMDE during pre-electrolysis and the morphology of the individual stripping curves and of the titration curve itself.

First, as mentioned under Theory and Procedure above, most complexes with inorganic and bidentate organic ligands give an ASV current response almost identical to the aquated ion. Therefore, all inorganic Cu species that one can think of forming in natural waters in this pH range such as  $\text{Cu}(\text{OH})_2^+$ ,  $\text{CuO}$ ,  $\text{CuCO}_3^+$ ,  $\text{CuHCO}_3^+$ ,  $\text{CuOH}^+$ , etc. (11, 20), if they are soluble, are chemically labile to chemical substitution and could be expected to be polarographically reversible and therefore readily accessible and reactive to the electrode at the potential selected here. Inorganic copper complexes, ion pairs, and associated compounds are all labile to ligand substitution (21), so that as far as the electrode is concerned, availability of these complexes for reduction is identical to the simple aquated ion and the electrode current does not distinguish these species (5). If any voltammetric wave for the metal is seen at all, it includes the current due to all labile inorganic species. The only possible influence on the current could result from irreversibility of the electrode reaction. If the ligand releases or takes up protons at the electrode surface during reduction of the complex and if the solution is inadequately buffered, a local pH change could take place and contribute to irreversibility (5). This possibility with the reduction of copper from dilute carbonate solutions has been recently investigated and will be discussed in a future report (22).

A second argument, and perhaps this is too obvious to mention, is to point out that  $\text{OH}^-$  is in abundant supply (about 50 M) from  $\text{H}_2\text{O}$  equilibrium (rapid, of course) as is  $\text{CO}_3^{2-}$ , either from the fact of carbonate alkalinity, or as in these experiments, from  $\text{CO}_2$ -carbonate equilibrium used to control pH, so that  $\text{OH}^-$  or  $\text{CO}_3^{2-}$  cannot be "titrated" by adding  $3 \times 10^{-5}$  M copper, or even 100 $\times$  that amount of Cu(II) for that matter. Thus, if hydroxide and carbonate copper species were the only ones being formed upon addition of copper, one would not observe a titration curve as described above but instead would observe a constant slope for stripping current vs. copper added. A similar argument can be made against the suggestion that the added Cu(II) is here precipitating all the  $\text{OH}^-$  or  $\text{CO}_3^{2-}$ . Of course, if the titration is carried out to high enough Cu(II) concentration, insoluble or colloidal species which are inactive at the electrode will form as copper solubility is exceeded. But if this were an insoluble species with one of the abundant anions such as  $\text{OH}^-$ , the slope of the current-concentration curve should be seen to decrease with increasing excess copper added, and this is not at all like a titration curve. Such a decrease in slope was observed but far into the upper region of the titration curve after the endpoint. The possibility that the walls of the electrochemical cell are being "titrated" by adsorption of inorganic species upon them can be dismissed for these titrations since it was observed that the endpoint is independent of cell size and volume.

As far as adsorption of species on the electrode is concerned, the stripping peaks that have been observed have a morphology that agrees much more closely to that theoretically expected for a diffusion process (16) than it does to an adsorption process (17) so that adsorption of Cu(II) species does not seem to be very important. Besides, if Cu(II) species were adsorbing and consequently blocking either oxidation (stripping) or reduction (accumulation), this blocking should increase with increased copper concentration and produce a curve that was concave downward. Therefore, it is anticipated that the current-concentration curve would not look like titration curves if adsorption were taking place.

To determine whether chelate dissociation contributes to copper accumulation during pre-electrolysis, the dissociation rate constant at pH 6.5 was estimated using a rotating disk electrode (23) and a procedure described elsewhere (24). A rate constant of  $2 \text{ s}^{-1}$  was obtained and was used as in ref. 3

to calculate the fraction of the total copper flux attributable to complex dissociation. The fraction, about 0.2, suggests that estimates of the conditional formation constants are low by about 20%. Although correction of  $K'_{ML}$  values for kinetic dissociation could be made, it does not seem justified in light of the precision of the titration and the approximate manner with which the kinetic contribution was estimated.

Analysis of the titration data as a 1:1 complex is shown in Figure 4 for the Chapel Hill sample and four pH values. The

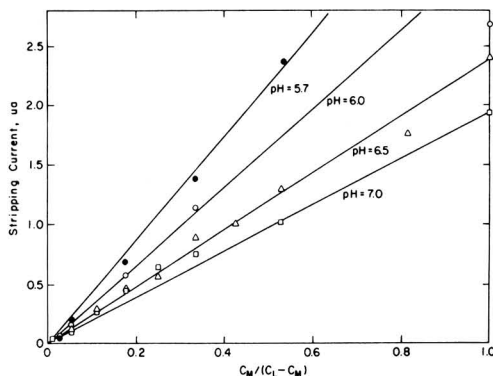


Figure 4. Analysis of titrations at pH 5.7-7.0 as 1:1 complex

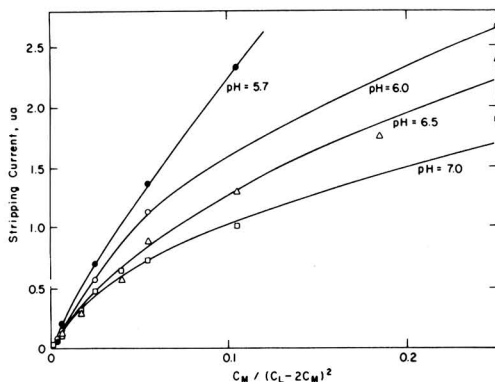


Figure 5. Analysis of titrations at pH 5.7-7.0 as 1:2 complex

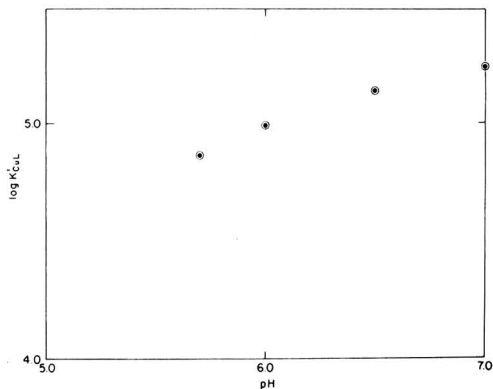


Figure 6. Conditional constant of copper complex vs. pH

**Table I. Results from Titrated Samples**

Sample	$C_L$	Fe	DOC, mg/L	Alk, meq/L	$K'_{ML}$
Swains Mill	$2.0 \times 10^{-5}$ M	$7.1 \times 10^{-6}$ M	14	...	$5.2 \times 10^5$ (pH 6.5)
Chapel Hill	$3.1 \times 10^{-5}$ M	$2.9 \times 10^{-6}$ M	32	0.46	$0.74 \times 10^5$ (pH 5.7) $0.98 \times 10^5$ (pH 6.0) $1.4 \times 10^5$ (pH 6.5) $1.6 \times 10^5$ (pH 7.0)
Lake Waccamaw	$9.1 \times 10^{-5}$ M	$<0.02 \times 10^{-6}$ M	23	0.16	$0.32 \times 10^5$ (pH 6.5)
Black Lake	$12.6 \times 10^{-5}$ M	$14 \times 10^{-6}$ M	39	0.20	$0.64 \times 10^5$ (pH 6.5)

regression line decreases in slope with increasing pH, indicating that the conditional formation constants increase with pH. An analysis of the data as a 1:2 complex is shown in Figure 5, where a line drawn arbitrarily through the points appears to deviate substantially from a straight line. These data suggest that the chelation involves a 1:1 complex.

The calculated conditional formation constants are plotted vs. pH in Figure 6, and the manner in which they increase with pH indicates that the ligand is the conjugate base of a weak acid that is nearly completely ionized in this pH range. As mentioned above, any variation in ASV sensitivity due to a change in the reversibility of Cu(II) reduction as may take place when pH is altered is reflected in  $\kappa$ . All inorganic species are lumped together and indistinguishable in  $[M']$  of Equation 2. Therefore, the change in the observed conditional constant with pH reflects only the change in  $[L']$  (shifts in concentration of protonated and unprotonated ligands and protonated and unprotonated complexes containing L) and the change in  $[ML]$  with pH.

Finally, all fresh water samples that were titrated are compared in Table I. Here,  $C_L$ , along with the iron content, dissolved organic carbon,  $K'_{ML}$ , and alkalinity of the sample, is presented. No correlations are evident in this small sampling.

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# Fractionation and Concentration from Water of Volatiles and Organics on High Vacuum System: Examination of Sanitary Landfill Leachate

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■ A high vacuum system developed to isolate, fractionate, and concentrate trace components from aquatic environments is applied to examine sanitary landfill leachate and other waters. Water samples are connected to a high vacuum system ( $10^{-6}$  mm), and the complex mixture of vapors (water, organics, inorganics, and gases) is pumped through a series of traps, maintained at successively low temperatures in the range from 0 to  $-268.6$  °C. The vapor pressures drop to negligible values at the various low temperatures, resulting in fractionation and trapping of volatiles. The volatiles on IR, GC, MS, and GC-MS analysis give a series of organic compounds and gases. The nonvolatile fraction is examined for metals, organic carbon, and substances of possible use as nutrients for microorganisms.

In the characterization of dissolved trace volatiles and nutrients, both organic and inorganic, their isolation or concentration from the bulk of water is usually accomplished by one of the several frequently applied methods or their combinations prior to instrumental analysis (1-4). These methods may result in loss of the highly volatile components found in some waters, e.g., hydrogen and methane, or in their contamination by air or by chemicals during analytical manipulations; furthermore, some of these processes may alter the composition of molecules as they exist in natural water and may yield a complex mixture of varied classes of closely related but different compounds, thereby making difficult the interpretation of analytical data for identification of individual molecules (5-10). Although a particular technique may be very effective in concentration for a certain class of compounds, it may be of little value for another set of pollutants, i.e., it is difficult to follow the wide spectrum of possible volatile trace components of water by a single procedure.

We have developed a method for water samples that is particularly useful in the separation, concentration, and measurement of volatiles and which eliminates or minimizes some of the difficulties associated with other methods. It employs a high vacuum system with a series of traps for fractionation of volatiles at successively low temperatures where their vapor pressures are reduced to negligible values (11, 12). Infrared spectroscopy, gas chromatography, mass spectrometry, and combined gas chromatography-mass spectrometry are used for the identification and quantification of individual components in each fraction. The nonvolatiles, high-molecular-weight organics, salts, and metals remaining as residue may be examined by usual methods of analysis (13). The vacuum procedure herein described has been used for the examination of leachate from a small-town sanitary landfill in New York State and for other types of ground waters.

The sanitary landfill is a common means for the disposal of solid waste and is often associated with pollution of ground and surface water, bad odors, and heavy metal deposition (14, 15). The environmental hazards and the chemical and microbiological activities in leachates are functions of a combination of factors including quality of landfill soil; temperature of air and ground; amount of rain, snow, and solar radiation falling on the surface; and, of course, the nature of the wastes and the age of refuse. With a few exceptions the gross organic carbon contents generally have been determined in such wa-

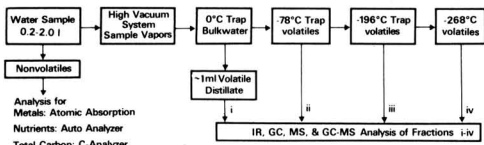
ters (16-19); however, more specific identification and quantification of pollutants or microbial nutrients, both organic and inorganic, are desirable to assess more exactly the impact of leachates on water and on air quality and as possible health hazards. Many of the organic compounds found in decomposing organic matter and leachates are volatile and are susceptible to vacuum fractionation. There has already been some work on toxic materials in leachates (20). It is hoped that further, more detailed information about the wide spectrum of possible microbial nutrients in leachates, seeps, and other ground waters will help to understand some of the problems associated with bacterial growth and its control.

## Experimental

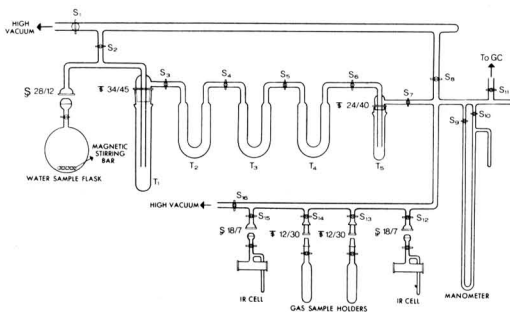
### Sampling and Fractionation of Volatiles from Water.

The schematic diagram of the analytical procedure is shown in Figure 1. The all-glass, high vacuum system is pumped down to less than  $10^{-6}$  mm pressure with the help of a mechanical fore pump and a mercury diffusion pump. The schematic diagram of the construction of the vacuum line is shown in Figure 2. The construction can be modified by simplification or in complexity to accommodate specific needs. The system illustrated is connected directly to the gas chromatograph via a six-port gas sampling valve for quantitative injection directly onto the column of volatiles fractionated from water. The water samples, collected in preevacuated flasks containing magnetic stirring bars, are attached to the high vacuum system. The mixture of water vapor and volatiles is gradually pumped through a series of traps,  $T_1$ - $T_5$  which are separated from each other and the vacuum manifold, manometer, outlets, and gas chromatograph by high vacuum stopcocks (Figure 2). These traps are maintained at low temperatures in the range from 0 to  $-268$  °C. The water sample is stirred continuously to facilitate vaporization. The mixture is fractionated as the vapor pressures of the volatile components drop to negligible values in successively colder traps. Thus, the bulk of the water is retained at 0 °C, and only a trace amount passes below  $-78$  °C.

The first trap also retains organics which have vapor pressures comparable to water or lower, but which are high enough to permit escape from the sample. The first trap should be large enough to retain a significant fraction of the sample, and be detachable, to remove the bulk of the trapped water. Almost all of the organics and gases are trapped by the time they reach  $-196$  °C except for the most volatile (hydrogen and methane) which are trapped at  $-268$  °C. The traps are maintained at ice-water (0 °C), dry ice-acetone ( $-78.5$  °C), liquid nitrogen ( $-195.8$  °C), and liquid helium ( $-268.6$  °C) temperatures. The capacity of the traps to retain volatiles is very large at these temperatures, thus eliminating the possibility of overloading. The vacuum line has provisions for fractionating further the condensed mixtures in each trap to simpler components by using appropriate low-temperature slush baths between 0 and  $-196$  °C. The evaporation of the sample is continued until most of it is transferred to different traps or until the evolution of volatiles ceases, as can be seen from the constantly stirred sample. As each of the low-temperature baths is finally removed from the traps, one at a time, starting from the lowest temperature, the trapped materials are allowed to expand into a precalibrated volume of the vacuum line which includes the manometer with side arm, the



**Figure 1.** Schematic diagram of analytical approach for fractionation of trace components in water



**Figure 2.** Schematic diagram of high vacuum system for fractionation (preconcentration) and measurement of volatiles in water  
S<sub>1</sub>-S<sub>16</sub>, high vacuum stopcocks; S, standard ball and socket joints; S, standard taper joints; T<sub>1</sub>-T<sub>5</sub>, traps maintained at low temperatures

detachable IR gas cells with side arm, and the gas sample holders (Figure 2). The volatiles, at measured pressures and volumes, are trapped by transferring the low-temperature baths from the trap in question to either the side arm of the IR cell or the lower part of the gas sample holder.

Alternatively, it is possible to cut off vacuum pumping before opening the water sample to the preevacuated system. The mixture of water vapor and dissolved volatiles passes through traps (T<sub>1</sub>-T<sub>5</sub>) maintained at temperatures from 0 to -196 °C, where the vapor pressures are reduced to negligible values, sustaining thereby the vacuum and thus the evaporation of sample. However, the most volatile fraction (hydrogen, methane, etc.) has significant vapor pressure at -196 °C which is measured on the manometer along with the volume. A part of this fraction is removed as such in a preevacuated, IR gas cell for the instrumental analysis and the balance pumped out. It is desirable, however, to use liquid helium to trap completely this fraction in cases when only a small volume is present. Thus, the handling of liquid helium can be either eliminated or reduced to a short time during the fractionation-trapping process.

The organics remaining in the bulk of water in 0 and -78 °C traps are recovered for analysis by distilling them on the vacuum line into the detachable trap T<sub>5</sub> (Figure 2) and collecting the initial 1 mL (approximately) most volatile distillate (21, 22). The nonvolatiles remaining in the original sample bulb consist of high-molecular-weight organics, metals, and nutrients or salts and are analyzed by the usual methods.

**Instrumental Analysis of Fractions.** The volatile fractions collected at -268, -196, and -78 °C and the aqueous distillate are examined for individual component molecules using the infrared spectrophotometer (Perkin-Elmer 621 and 727 and Beckman IR-10), the mass spectrometer, (AEI MS 902), the gas chromatograph (Varian aerograph 1800 with Varian 440 electronic integrator, Victor Digit-matic data printer, and Varian A-25 recorder), and the combined gas chromatograph-mass spectrometer (Finnigan 3300 with System Industries System 150 data system). Several gas

chromatographic columns have been used for the analyses and are listed below along with their operating conditions.

**Column No. 1.** 12 ft × 1/8 in. o.d. coiled stainless steel tube packed with GP carbopak B/4% carbowax 20 M + 0.8% KOH (Supelco, Inc.). Column temperature, 100 °C for 45 min, then 4 °C/min to 160 °C; detector, 195 °C; injector, 160 °C; N<sub>2</sub> carrier gas, 23 mL/min.

**Column No. 2.** 12 ft × 1/8 in. o.d. coiled stainless steel tube packed with GP 20% SP-2100/0.1% carbowax 1500 on 100/120 Supelcoport (Supelco, Inc.). Column temperature, 100 °C; detector, 195 °C; injector, 160 °C; N<sub>2</sub> carrier gas, 20 mL/min.

**Column No. 3.** 12 ft × 1/8 in. o.d. coiled stainless steel tube packed with 150-200 mesh porapak Q (Water Associates). Column temperature, 165 °C; detector, 240 °C; injector, 205 °C; N<sub>2</sub> carrier gas, 23 mL/min.

**Column No. 4.** 10 ft × 1/8 in. o.d. coiled stainless steel tube packed with GP carbopak B/3% carbowax 20 M/0.5% H<sub>3</sub>PO<sub>4</sub> (Supelco, Inc.). Column temperature, 100 °C for 10 min, then 4 °C/min to 180 °C; detector, 200 °C; injector, 185 °C; N<sub>2</sub> carrier gas, 45 mL/min.

**Column No. 5.** 12 ft × 1/8 in. o.d. stainless tube packed with 10% 1,2,3-tris(2-cyanoethoxy) propane on 80/100 chromosorb P AW (Supelco, Inc.). Column temperature, 60 °C; detector, 200 °C; injector, 175 °C; N<sub>2</sub> carrier gas, 20 mL/min.

The nonvolatile fraction remaining in the original sample bulb is used for estimation of metals by an atomic absorption spectrophotometer (Jarrell-Ash 82-6000 and PE 303), nitrogenous compounds and phosphates by the Autoanalyzer (Technicon-1), total organic carbon by the carbon analyzer (Envirotech), and sulfate and chloride by using the standard analytical procedures.

## Results and Discussion

In one of the experiments, a mixture of 265.2 μL of known organic compounds equivalent to 61.7 mL vapor at standard temperature and pressure was added to 200 mL deionized, redistilled water (Table I). The vapor volume of organics re-

**Table I. Organic Compounds Added to Redistilled Water for Recovery Studies**

Compound	Vapor pressure <sup>a</sup> at 20 °C, mm <sup>b</sup>	Vapor pressure <sup>a</sup> at -23 °C, mm <sup>b</sup>	Vol added, μL	Vol as vapor, mL
Methanol	91.6	5.74	8.0	4.40
Ethanol	41.0	2.36	12.0	4.58
2-Propanol	12.4	0.44	15.0	4.51
2-Methyl-2-butanol	1.80	0.05	4.0	0.80
1-Butanol	5.64	0.22	5.0	1.22
2-Methyl-1-butanol	3.90	0.11	9.2	1.90
1-Pentanol	4.32	0.12	10.4	2.14
1-Hexanol	0.78	0.02	21.7	3.88
Acetone	160.5	16.80	9.8	2.96
2-Butanone	76.2	6.86	13.6	3.40
2-Pentanone	11.7	0.43	20.3	4.29
Mesityl oxide	6.99	0.35	36.2	7.15
3-Methyl-2-butanone	11.2	0.41	16.4	3.43
3,3-Dimethyl-2-butanone	2.67	0.07	17.7	3.17
4-Methyl-2-pentanone	5.07	0.21	11.5	2.06
Cyclohexanone	3.43	0.18	54.4	11.80

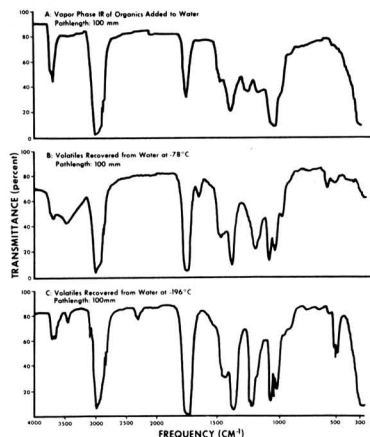
<sup>a</sup> Weast, R. C., Selby, S. M., Eds., "Handbook of Chemistry and Physics", Chemical Rubber Co., Cleveland, Ohio, 1973. <sup>b</sup> Approximate values only calculated from the data in reference above.

covered at  $-76$  and  $-196$  °C, respectively, was 11.3 and 21.7 mL. Under similar conditions using redistilled water only, 200 mL gave 4.6 mL volatiles. Thus, a recovery of approximately 50% is obtained in the two traps at  $-196$  and  $-78$  °C. The lower recovery is due to the fact that organics with vapor pressures comparable to water or lower remain in the first trap maintained at  $-23$  °C (carbon tetrachloride-dry ice slush bath), and those having significant vapor pressures at  $-196$  °C are pumped out and lost. The percentage accounted for is enhanced to more than 80 when these losses in the first trap are approximated in recovery calculations by excluding the volumes of the organics having vapor pressures less than about 0.2 mm at  $-23$  °C (Table I).

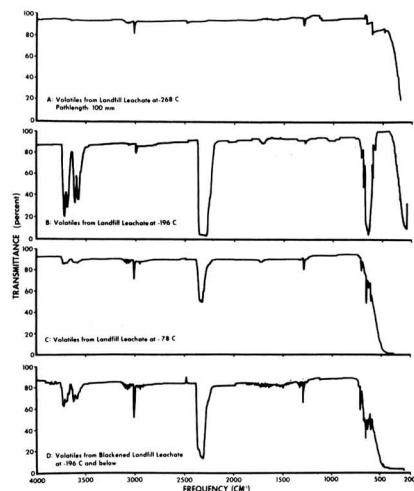
In subsequent experiments these losses were reduced further by using liquid helium in the last trap or by cutting off the pumping during the fractionation-trapping process and accounting for the organics in the bulk of water in the first trap ( $-23$  °C) by concentrating them to approximately 1 mL most volatile aqueous distillate (19, 20). No attempt was made to identify and quantitate individual compounds added to water except for the measurement of their gross volumes for recovery calculations. However, the infrared spectrum of volatiles at  $-78$  and  $-196$  °C compared well with the vapor-phase mixture of pure compounds except for the additional carbon dioxide in the recovered fractions originating probably from the water (Figure 3).

**Sanitary Landfill Leachate.** The leachate sample was collected at the site directly in preevacuated, 1-L sample flasks (Figure 2). The temperatures of the air and leachate were  $-7.6$  and  $1$  °C, respectively. The pH of sample in the field was 6.8, and it contained some dissolved oxygen. It was clear, straw colored, and had a pronounced bad odor. The sample, examined under a microscope, contained many bacteria, some motile, and living protozoa. A total of 221.8 mL of gaseous products at standard temperature and pressure was obtained in the traps from a liter of the leachate, and about 20% of the water was transferred to the  $0$  °C trap; however, the evolution of volatiles ceased when only about 5–10% of the sample had been transferred to the first trap as water. The amounts of volatiles trapped at  $-268$ ,  $-196$ , and  $-78$  °C were, respectively, 34.5, 139.2, and 48.0 mL. About 1 mL of the most volatile aqueous distillate was collected from the water in 0 and  $-78$  °C traps. The remainder of the leachate, enclosed in the sample bulb, turned black within days on standing at room temperature. The blackening was probably due to removal of oxygen and to precipitation of sulfides by sulfate-reducing bacteria under anaerobic conditions. The blackened leachate when subjected to further fractionation gave 18.4-mL volatiles having significant vapor pressure at  $-196$  °C (untrapped) and 84.1-mL volatiles with negligible vapor pressures at this temperature (trapped).

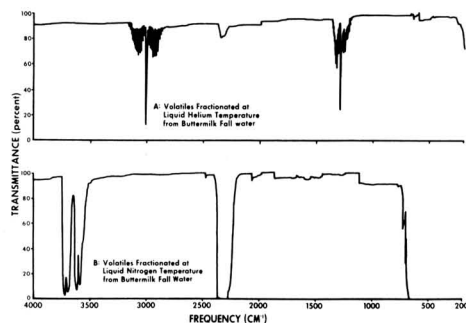
**Analysis of Volatiles.** The infrared spectra of the volatile fractions are shown in Figure 4. It is evident that the  $-268$  °C fraction shows absorption bands for methane only, whereas the fractions at  $-196$  and  $-78$  °C show mostly carbon dioxide and some methane (23). Methane was present in these fractions (Figure 4, B and C) because during this run, liquid helium was not used to trap completely the volatiles having significant vapor pressure at  $-196$  °C nor was the excess of this fraction pumped out. With complete removal by liquid helium, clean separation of methane from less volatile components is possible as shown in Figure 5 for another sample of water from a different source. The amount of methane and carbon dioxide calculated from the IR absorption data was, respectively, 35 and 45 mg/L of leachate, corresponding to only 22 and 10% of the total volume of volatiles fractionated. The remainder of the volatile sample may have consisted of such gases as hydrogen, nitrogen, and oxygen, having no infrared absorption, or of organics below their limits of detection under



**Figure 3.** Vapor-phase infrared spectrum of organics before adding to distilled water (A) and of fractions recovered from water on high vacuum system at  $-78$  °C (B) and  $-196$  °C (C)



**Figure 4.** Infrared spectrum of volatiles recovered from leachate at  $-268$  °C (A),  $-196$  °C (B), and  $-78$  °C (C) and from blackened leachate below  $-196$  °C (D)



**Figure 5.** Infrared spectrum of volatiles fractionated from water of Buttermilk Falls, N.Y., site at  $-268$  °C (A) and  $-196$  °C (B)

our analytical conditions. The volatiles from blackened leachates trapped at  $-196^{\circ}\text{C}$  and below gave, on infrared analysis, methane (3 mg/L) and carbon dioxide (28.8 mg/L), respectively, corresponding to only 4 and 14% of the total volume (102.5 mL) of the volatiles fractionated (Figure 4, D).

The mass spectra of the fraction collected at  $-196^{\circ}\text{C}$  and below confirm the presence of methane and also indicate a trace amount of hydrogen (Figure 6). The ability to detect the presence of methane and hydrogen is useful because of their possible use as carbon and energy sources in the course of microbial activities.

The gas chromatographic analysis with the flame ionization detector of the volatile aqueous distillate and  $-196^{\circ}\text{C}$  fraction on several columns gave a series of amines (Column No. 1), solvents (Column No. 2, 3), acids (Column No. 3, 4), hydrocarbons (Column No. 3, 5), and other organic compounds (Column No. 3). A large number of compounds were identified by matching under identical gas chromatographic conditions, retention times of the known standards with the unknown fractions. The identified compounds are listed in Table II. There were several peaks which were not identified by this method. Some of these have since been identified or confirmed by GC-MS. The GC-MS reconstructed chromatogram and the identified peaks for the volatile aqueous distillate are shown in Figures 7 and 8 on Columns 1 and 2, respectively. The mass spectral data in the literature (24, 25) or stored on the computer (26) are used in their interpretation.

**Analysis of Nonvolatiles.** The leachate sample gave 767  $\mu\text{g/mL}$  total carbon and 695  $\mu\text{g/mL}$  organic carbon on analysis by the carbon analyzer. The inorganic carbon, estimated by difference, 72  $\mu\text{g/mL}$ , was higher than the amount of carbon dioxide, 45  $\mu\text{g/mL}$ , fractionated on the vacuum line. It appears that most of the inorganic carbon in the leachate under our sampling conditions and analysis existed as carbon dioxide, and only a small fraction may have been combined with metals and nonmetals as carbonates and bicarbonates. The higher value of inorganic carbon, which includes carbon dioxide, on analysis with the carbon analyzer may also have been due to the fact that these analyses were made a few days later on the sample stored at  $4^{\circ}\text{C}$  in contrast to high vacuum fractionation which was started within hours of sample collection. The blackened leachate and the unused sample stored at  $4^{\circ}\text{C}$  showed on periodic infrared analysis production of carbon dioxide and methane supporting this possibility (Figure 9).

Keeping in mind that the sample in question was collected in late winter at freezing temperature, refrigerator temperature ( $4^{\circ}\text{C}$ ) was not effective in suppressing microbial activity. It is critical, therefore, that samples, especially winter samples, be analyzed as soon after collection as possible to avoid changes due to microbial transformations. The high vacuum line is thus feasible for following certain chemical changes in the biological system in the sample flask. With modification it would be usable to detect and identify volatile microbial metabolic products.

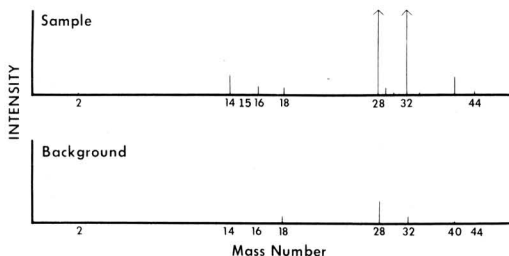


Figure 6. Mass spectrum of volatiles recovered from leachate at  $-196^{\circ}\text{C}$  and below

The analysis of the sample for nitrogenous compounds, phosphate, sulfate, and chloride is done by standard methods and for the metals by atomic absorption spectrophotometry. The quantitative results for these parameters are presented in Table III. These results are generally in the lower range of the values reported for some of these parameters from simulated landfill leachate (17, 18).

It is evident, therefore, that a variety of compounds both organic (hydrocarbons, amines, acids, alcohols, solvents) and inorganic (salts, nutrients, and metals) are present in seepage water from a sanitary landfill. Some of these classes of compounds are potential health hazards and have been reported

Table II. Organics and Volatiles Identified in Landfill Leachate

Compound	Identification method <sup>a</sup>
Methane (35 mg/L) <sup>b</sup>	GC (3), MS, IR
Ethane	GC (3)
Ethylene	GC (3)
1-Pentene	GC (3), GC (5)
Hexane	GC (5)
Heptane	GC (5)
Nonane	GC (5)
Decane	GC (5)
Dodecane	GC (5)
4-Methyl-1-hexene	GC-MS (2)
Acetone	GC (2), GC (3), GC-MS (2)
2-Butanone	GC-MS (2)
Chloroform	GC (2), GC (3)
Carbon tetrachloride	GC (2), GC (3)
Benzene	GC (2), GC (3), GC (5)
Toluene	GC (5)
Xylene	GC (2), GC (5)
Methanol	GC (2), GC (3), GC-MS (1)
Ethanol	GC (2), GC (3), GC-MS (1)
Propanol	GC (2), GC (3), GC-MS (1)
2-Butanol	GC (2), GC-MS (1), GC-MS (2)
2-Pentanol	GC-MS (1), GC-MS (2)
2-Hexanol	GC-MS (1), GC-MS (2)
4-Methyl-2-pentanol	GC-MS (1), GC-MS (2)
2-Heptanol	GC-MS (2)
2-Octanol	GC-MS (2)
Acetic acid	GC (3), GC (4)
Propionic acid	GC (4)
Butyric acid	GC (4)
Propanamide	GC-MS (2)
2-Methylethylenimine	GC-MS (1)
Methylamine	GC (1)
Methylamine hydrochloride	GC-MS (1)
Dimethylamine	GC (1), GC-MS (1)
<i>n</i> -Propylamine	GC (1)
Diethylamine	GC (1)
<i>n</i> -Butylamine	GC (1)
Di- <i>n</i> -propylamine	GC (1)
Di- <i>n</i> -butylamine	GC (1)
<i>n</i> -Hexylamine	GC (1)
Carbon dioxide (45 mg/L) <sup>b</sup>	IR, MS, GC-MS (2)
Hydrogen	MS
Nitrogen	MS
Oxygen	MS
Argon	MS

<sup>a</sup> IR, infrared spectroscopy; MS, mass spectrometry; GC, gas chromatography (1, 2, 3, 4, and 5 refer to column numbers described in text); GC-MS, combined gas chromatograph-mass spectrometer (1 and 2 refer to the column numbers).

<sup>b</sup> Quantitative values from IR data.

(phthalates, insecticides, heavy metals) (20). Forty-five distinct volatile organics and gases were separated and identified from the landfill leachate (Table II). Many of them were completely reduced aliphatic and aromatic compounds such as might be derived from petroleum derivatives. Many of the other partially reduced (or partially oxidized) organics probably originated to some extent from the anaerobic decomposition of organics by bacteria and partly as discarded waste. Methane is the commonly found completely reduced end product of anaerobic decomposition. The amines and short chain carboxylic acids (acetic, propionic, butyric) are also characteristic malodorous products resulting from the anaerobic conditions that characterize a water-logged landfill. With a few exceptions, the organics of the leachate are susceptible to further oxidative microbial degradation when the leachate becomes exposed to oxygen and a mixed microbial flora. When these materials enter aerobic surface or ground waters, stimulation of microbial growth with oxygen depletion and fouling of submerged surfaces is likely to ensue. The chlorinated hydrocarbons can travel further to contaminate surface or ground waters. Volatile sulfur compounds were present among the fractions but have not yet been specifically identified.

The high vacuum technique is useful for isolating and fractionating (preconcentrating) the wide spectrum of trace components in water from most volatile and lowest in molecular weight, hydrogen and methane, to nonvolatile high-molecular-weight organics, inorganics, and salts in a single sample. The quantitative values of the volatiles fractionated at low temperatures can be used further to quantitate individual component molecules in each fraction from the analytical data. We have used only IR absorption values (Figure 4) for quantifying methane and carbon dioxide. The identification of individual molecules in various low-temperature traps, though easier because of fewer components in each fraction is, however, ultimately limited by the sensitivity of the instruments utilized for their detection. The volume of the sample for examination can, however, be increased or decreased depending on the concentrations of components to provide significant amounts for instrumental analysis. It is desirable, in case of gas chromatographic analysis of volatiles, to use several detectors (electron capture, flame photometric) and columns to identify different classes of compounds (halogen and sulfur-containing compounds) and in the case of nonvolatile organics, to use liquid chromatography or high-resolution ion-exchange chromatography to obtain information about individual high-molecular-weight components (27). The method, though here applied to landfill leachate, may also be used for other types of samples such as air, relatively clean waters, and some biological materials.

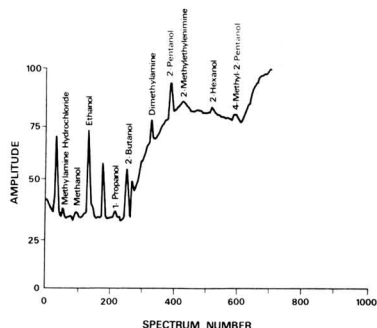


Figure 7. Reconstructed GC-MS chromatogram of volatile aqueous concentrate recovered from leachate on Column 1

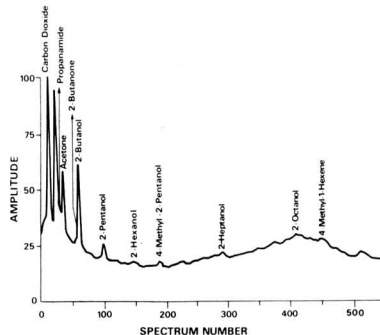


Figure 8. Reconstructed GC-MS chromatogram of volatile aqueous concentrate recovered from leachate on Column 2

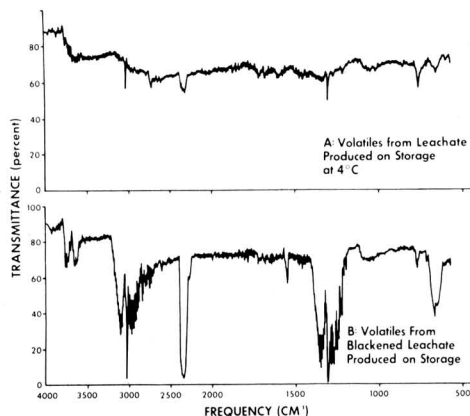


Figure 9. Infrared spectrum after prolonged storage of volatiles from untreated leachate stored at 4 °C (A) and blackened leachate stored at room temperature (B)

Table III. Nonvolatiles in Landfill Leachate

Metals and nutrients	Concn, mg/L
Sodium	136.0
Magnesium	66.0
Aluminum	0.13
Potassium	66.0
Calcium	272.0
Manganese	10.85
Iron	0.81
Copper	<0.01
Zinc	0.09
Cadmium	<0.01
Lead	0.03
Total carbon	767.0
Organic carbon	695.0
Inorganic carbon	72.0
Total nitrogen (Kjeldahl)	52.0
Ammonia-N	50.0
Nitrite-N	0.040
Nitrate-N	0.061
Total soluble phosphate-P	0.152
Phosphate-P	0.010
Sulfate-S	39.0
Chloride	205.0



### Acknowledgment

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### NOTES

## Copper and Other Heavy Metal Contamination in Sediments from New Bedford Harbor, Massachusetts: A Preliminary Note

Peter Stoffers<sup>1</sup>, Colin Summerhayes<sup>2</sup>, Ulrich Förstner<sup>1</sup>, and Sambasiva R. Patchineelam<sup>1</sup>

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■ The clay fraction of bottom sediments near the head of New Bedford Harbor, Massachusetts, contains more than 1% of Cu, Cr, and Zn combined. These and other heavy metals are industrial wastes that were discharged into the harbor over the past 80 years or so. They are located mainly in the clay fraction of the sediments, and their concentration warrants consideration of their recycling potential. Metal concentrations decrease exponentially seaward into Buzzards Bay, where surface sediments contain three times as much Cu (the main contaminant) as buried sediments. Clearly, the harbor is a leaky sink for contaminants. The effect on marine life of this widespread metal contamination is not yet known.

Marine sediments from bays and estuaries near large industrial and urban areas are typically contaminated with heavy metals like Cu, Pb, Zn, Cr, and Cd, which may be present in amounts 5-10 times higher than they were 50-100 years ago (1-5). Most of this recent concentration of metal is

due to discharge of industrial wastes into the sea. During a study of sediment dispersal in the Massachusetts coastal zone, we have found that the bottom sediments of New Bedford Harbor, on the estuary of the River Acushnet, contain large amounts of heavy metals, and it appears that these have an industrial source. A detailed report of this study is currently being prepared (6).

In Figure 1 we show the distribution of Cu in the clay-sized (smaller than 2  $\mu\text{m}$ ) fraction of surface sediments collected from the seabed by grab (92 samples) and gravity core (20 samples). We deliberately focused on the clay-sized fraction to eliminate chemical variations that may have been caused by variations in the grain size of the sediments (7). Copper concentration gradually decreases seaward from values of more than 6000 ppm near the head of the harbor to less than 100 ppm at the edge of Buzzards Bay.

We used 19 short gravity cores to study the history of metal contamination in the area (6). Samples were taken at 2-cm intervals in the top 10 cm of each core and at 20-cm intervals below that. In Table I we compare the metal concentrations in the upper 5-20 cm of three selected cores with the background metal concentrations that we measured near the bottoms of the cores: core locations are given in Figure 1. Maximum amounts of metal enrichment are  $\times 150$  for Cu,

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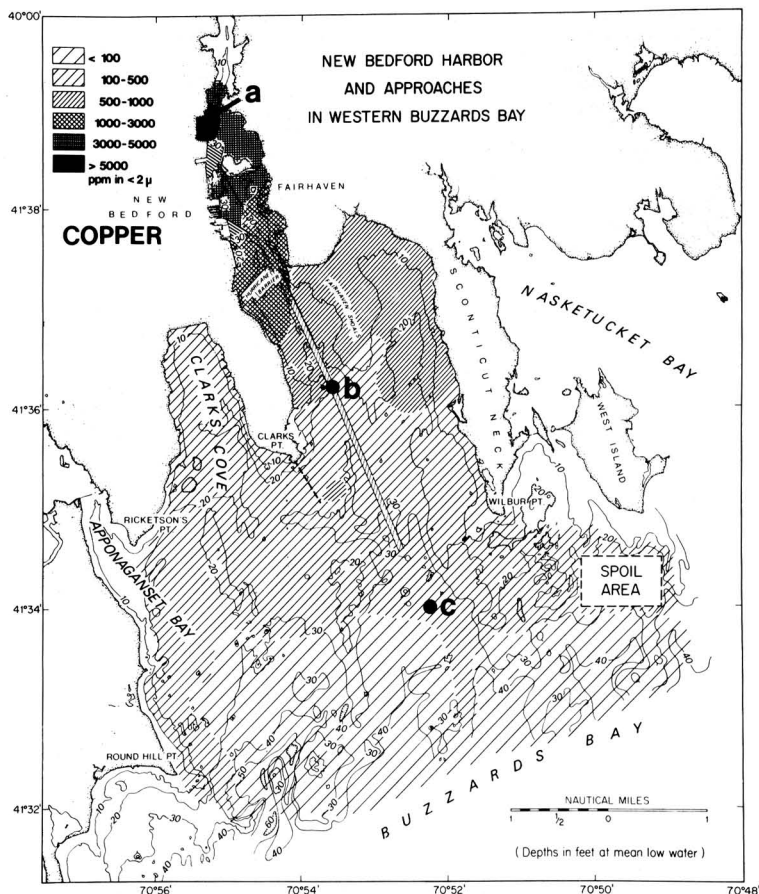
×100 for Cd, ×30 for Pb and Cr, and ×10 for Zn (Table I). Marked increases in the concentration of metal above background levels occur at burial depths of 60–80 cm in core A, at 40–60 cm in core B, and at about 10 cm in core C. The sediments are organically enriched black silts that smell of hydrogen sulfide; therefore, it seems highly unlikely that a significant amount of the metal found near surface results from diagenetic processes operating within the sediment column.

By analyzing different grain size fractions, we are able to show that the metals are associated with fine-grained particles. The largest amounts of Ag, Cd, Cr, Cu, Pb, and Zn were measured in the clay fraction smaller than 2 μm, and Cu reached 8500 ppm (or 0.85%) in the very fine clay fraction smaller than 0.63 μm. Almost 40% of Cu and Zn were located in the leachate-resistant fraction that consists largely of insoluble mineral detritus (Table II). We do not know yet in what mineral form these metals occur. About 20% of these same elements were located in authigenic phases that were leachable with an acid-reducing agent solution (Table II); in the highly reducing sediments from this area, iron sulfides are the main authigenic minerals (8). The remainder of the Cu and Zn was associated with the organic fraction of the sediment (Table II), probably because of the sorption of dissolved

Cu and Zn onto organic phases. Chromium showed a different distributional pattern, most (85%) being located in the authigenic fraction, or in the leachate-resistant fraction (8%) (Table II). We suspect that Cr may have entered the harbor mainly as chromate anions rather than in solid form.

Our data suggest that the source of metals is in the harbor, where rates of sediment and metal accumulation have been highest (6). Here four of our samples contain more than 1% of Cr + Cu + Zn in the clay fraction, and away from the harbor there is an exponential seaward decrease both in absolute metal concentration and in the thickness of the contaminated surface layer of sediments. Seaward diffusion of metalliferous waste therefore appears to have been very limited, although even the surface sediments at the seaward edge of the study area, and in Buzzards Bay, appear to be slightly contaminated, having Cu levels of more than 60 ppm that are three times higher than the background Cu levels of subsurface sediments in the same locality.

Inspection of publicly available EPA records suggests that industrial discharge of Cu-rich waste is concentrated close to the Cu maximum shown in Figure 1, and that Cu discharge may have reached 200 lb/day in recent years. Knowing the history of maintenance dredging in the harbor and the



**Figure 1.** New Bedford Harbor and its approaches in western Buzzards Bay, southeastern Massachusetts, showing distribution of Cu in the smaller than 2-μm fraction of bottom sediments

Letters a, b, and c refer to coring sites for which data are given in Table I. Map also shows location of dredged navigation channel leading to harbor, and of areas of recent dredging within harbor (diagonal hatching). Sample locations on which this map is based are given by Summerhayes et al. (6)

**Table I. Mean Abundances of Different Metals in ppm in Clay Fraction (Smaller than 2  $\mu\text{m}$ ) of Sediments from Tops of Three Representative Cores ( $n$  = Number of Samples Analyzed), Compared with Mean Abundances of Metals in Uncontaminated Sediments (Background) Found at Bottoms of Cores (Core Locations Given in Figure 1)**

	Cu	Cd	Pb	Cr	Zn
Core A					
0-20 cm ( $n = 6$ )	3136	52	616	2146	1550
Core B					
0-10 cm ( $n = 5$ )	580	6.6	210	439	484
Core C					
0-5 cm ( $n = 3$ )	117	1.4	104	218	315
Background	20	0.4	20	100	150

**Table II. Distribution of Metals in Percentages in Different Fractions of Clay Fraction of Sample, as Determined by Different Chemical Leaching Techniques (S. Rao, Analyst). Method of Chester and Hughes (14) Used for Authigenic Mineral Extraction**

Leaching method	Cu	Cr	Zn
Bitumen extraction with 1:1 alcohol: benzene mix	6.29	0.21	8.06
Cation exchange with 0.2 N BaCl <sub>2</sub> triethanolamine	17.6	0.01	21.38
Humic acid extraction with 0.1 N NaOH	1.36	1.57	0.2
Fulvic acid extraction with 0.1 N NaOH + H <sub>2</sub> SO <sub>4</sub> (pH 3)	17.28	4.86	4.28
Authigenic mineral extraction with acid-reducing agent	18.27	85.04	27.66
Resistant mineral (residue after extractions completed)	39.2	8.32	38.42
Total concn of metal (ppm)	2500	1850	595

thickness of Cu-rich sediment (up to about 70 cm), Summerhayes and others (6) calculate that metal-rich mud has been accumulating at rates of about 3 cm/yr in the deepest parts, and at rates of about 4 mm/yr in the shallower parts of the harbor. The history of waste metal accumulation covers a period of about 80 years, which is in good agreement with the known history of Cu discharge from industrial plants in this area.

Contamination of bottom sediments by Cu and associated elements in amounts similar to those reported in the harbor is common for marine sediments in mining districts rather than industrial areas (9-12). The amounts of metal in the sediment are sufficiently high to raise the intriguing possibility that they may be extracted profitably by some recycling process. Calculations suggest that there are about 3500 metric tons of Cu + Cr + Zn in the harbor muds; the possible value

of this deposit, at current market values, is about \$5 million. Mining the muds, which are about 0.5 m thick on average, would not present any problem. Further work is needed to ascertain what difficulties might be encountered in extracting different metals from the sediment.

From the exponential seaward decrease in metal concentration away from the harbor, and the seaward thinning of surface sediment contaminated with metal waste, it appears that the estuary of the Acushnet does operate as a pollutant sink preventing the transfer of solid and adsorbed metal waste to the open ocean. This particular sink, however, appears to be slightly leaky, since the top 10-20 cm of sediments from the edge of the study area and from further seaward in the center of Buzzards Bay contain about three times as much Cu as buried uncontaminated sediment from this region. Further studies should take account of the possibility that some of the waste metals may accumulate in the aquatic food chain in Buzzards Bay by way of deposit and filter-feeding organisms (9). It should also be pointed out that, like nutrients (13), some of the metals in these waste deposits may be reintroduced into the water column by natural chemical, biological, and geological processes (as well as by dredging); further work is needed to establish the importance of these remobilization processes and their effects on food chains in this region.

#### Acknowledgment

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## INDUSTRY TRENDS

**Du Pont** announced that installation of 150 000 ft<sup>2</sup> of "3110" elasticized polyolefin sheeting will help Masonite Canada Ltd. (East River, N.S.) meet provincial industrial effluent requirements.

**Republic Steel Corp.** broke ground at Canton, Ohio, for a huge industrial water treatment plant that will cost about \$19 million. Much of the plant's 14.4 mgd will be recycled through steel plant melt shop and rolling mills.

**CEA\* Carter-Day Co.** (Minneapolis, Minn.) has received a \$1.3 million contract for air pollution control at a new 675-MW coal-fired power plant of Iowa Southern Utilities at Ottumwa, Iowa.

**Eastman Kodak Co.** announced that it has had "notable successes" on a worldwide front in its efforts to keep energy usage down during 1976.

**Northeast Utilities** said that February 1977 was the most productive month ever for nuclear generation on its system, with 1.2 billion kWh coming from nuclear units.

**Chemical Separations Corp.** (Oak Ridge, Tenn.) has received a patent for its system for preferential removal of ammonia and phosphates from wastewater streams.

**Marine Construction & Design Co.** (Seattle, Wash.) has received an order for a third oil spill recovery vessel from Alyeska Pipeline Service Co., to be delivered to Valdez.

**Syracuse Research Corp.** (Syracuse, N.Y.) has been awarded an EPA contract for the study of chemical methods for the degradation and detoxification of pesticides.

**American Air Filter Co., Inc.**, announced that the \$2 million air pollution control system it is building for St. Mary's Cement Co. (Canada) is nearing completion. It will handle dust loadings to 315 grains/ft<sup>3</sup>.

**The Electric Power Research Institute** (EPRI, Palo Alto, Calif.) expects fuel prices to increase until the year 2000. EPRI also believes that the deferral of the fast breeder reactor will cost the U.S. \$100 billion-\$3.5 trillion.

**The Gas Research Institute** (Chicago, Ill.) has budgeted research at \$30.1 million, and expects that figure to rise to \$93 million by the fifth year of its existence. The Institute was founded last July.

**Continental Oil Co.** (Stamford, Conn.) said that last year it spent \$36 million for environmental programs, and that surface-mined land reclamation ran 40¢-\$6.25/ft of coal mined.

**Entropy Environmentalists, Inc.** (Research Triangle Park, N.C.), a leading firm in source sampling, celebrated its fifth anniversary last month, and is diversifying into fields such as nuclear containment and continuous monitoring service.

**Titan Southeast** (Miami, Fla.), a part of Titan Group, Inc., has a contract worth almost \$23.7 million for the construction of an expanded wastewater treatment plant—to be one of the largest projects in the U.S., near Irving, Tex.

**Met-Pro Systems, Inc.**, a subsidiary of Met-Pro Corp., has recently placed a demonstration "React-O-Therm" sludge destructor in operation at the company's Harleysville, Pa. plant. Nominal capacity is 500 lbs/h of waste liquids, slurries, or sludges.

**Zurn Industries, Inc.**, has agreed to sell its fire protection products business to Fire-End and Croker (Elmsford, N.Y.), and Sierra Fire Equipment Co. (Los Angeles, Calif.).

**ICI United States Inc.** (Wilmington, Del.) has formed a new unit that will market DARCO activated carbons, and combine sales, technical service, and developmental activities.

**Xonics, Inc.** has received a \$500 000 letter contract from the EPA for operation and maintenance of EPA monitoring of CHAMP, which provides air quality information in support of epidemiological studies.

**Research-Cottrell Inc.'s** Hamon Cooling Tower Division will design and construct a 10-cell mechanical-draft cooling tower for utilities in Boone County, Ky. Cost is \$5 million, approximately.

**Betz Laboratories, Inc.**, announced that its four consulting engineering subsidiaries will be bought by Betz-Converse-Murdoch, Inc. (BCM). BCM was formed for that purpose, and is 100% owned by its management and employees.

**Camp Dresser & McKee** vice president Richard Woodward will receive the American Water Works Association Research Award.

**Engineering-Science** is constructing tertiary facilities and a breakpoint chlorination system for over \$11.2 million for Arlington County, Va. The facilities—eight 36 × 30 ft adsorption basins—will contain 15 ft of activated carbon.

**National Motors Corp.** (Lancaster, Pa.) is unveiling an internal combustion-electric hybrid automobile. The car is expected to provide excellent road handling and achieve an average of 75 mi/gal, and will be called Gemini II.

# NEW PRODUCTS

## H<sub>2</sub>O treatment control system

The control system uses a minicomputer to control all the process equipment of a water or wastewater treatment plant. The minicomputer stores the operating program and receives and transmits all operating signals to the process equipment. The Permutit Co. **101**

## Wastewater monitoring system

The system is an ultra-sonic open-channel flow measuring and sampling one for permanent installation in municipal and industrial waste-processing streams. It provides flow-proportioned wastewater samples and monitored data. In addition to sample collection, the unit offers the means to measure pH, dissolved oxygen, turbidity, conductivity and temperature. Crane **102**

## Gas dividers

These units generate 6-, 7- or 9-pt calibration curves for ambient air monitors, continuous stack-gas analyzers, process control instruments and vehicle exhaust emission-gas analyzers. Horiba Instruments **103**

## Steam booster

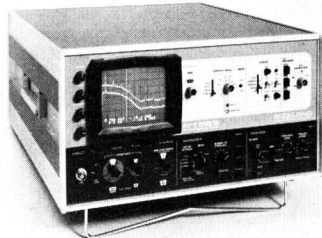
The unit, an insulated reciprocating compressor, takes low-pressure exhaust steam or steam from an existing steam boiler and compresses it to a higher pressure. Joy Manufacturing Co. **104**

## Floating barrier curtain

The curtain is designed to be used at refineries, power-generating stations and other sites requiring water containment or mixing areas. It prevents mixing of contaminated water with restricted or protected waters. The B. F. Goodrich Co. **105**

## Thermistor thermometer

The digital unit offers a -30 to +100 °C, with an instrument accuracy of ±0.2 °C. Temperature readings are updated 2.5 times/s to permit immediate display of temperature changes. Cole-Parmer **106**



## Spectrum analyzer

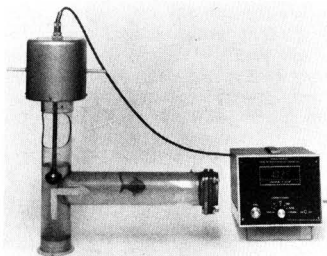
This real-time narrow-band analyzer covers the 0-100 kHz range, but it also provides tunable RMS voltage/power measurements and performs 1/3-octave and full-octave analysis. Rockland Systems Corp. **107**

## Water level recorder

The recorder is a float-operated instrument for strip-chart recording of water levels, precipitation or temperature. It operates unattended for months in remote locations. Leupold & Stevens **108**

## Turbidimeter

This portable unit is designed to meet the nephelometric method requirements of the EPA. The NTU ranges are 0-1.0, 0-10 and 0-100; the unit is linear over all three ranges. HF Instruments Ltd. (Ontario) **109**



## Viscometer

This stainless steel spherical sensor can continuously monitor the viscosity of seawater, brackish water, industrial effluents and sewage. The readout range is 10<sup>-1</sup>-10<sup>5</sup> centipoise. Nametre Rheodynamics **110**

## Filter holder

The open face 47 mm filter holder for air analysis features magnetic coupling that eliminates the use of clamps and threads. The effective filtration diameter is 35 mm. Gelman Instrument **111**

## Flocculant

Several grades of these waste treatment flocculants are available in bead form, in which storage life is extended and solubility is made more rapid. Allied Colloids **112**

## RO system

Reverse osmosis system demineralizes water for use as phosphating rinse water; inorganic and organic impurities are removed. At 77 °F the system produces 16 gpm. A built-in cleaning system permits monthly cleaning of the membranes. Osmonics **113**

## Turbidimeter improvement

A non-fouling, chemical-resistant window is now available as an option on the company's turbidimeters and suspended-solids monitors. The window makes it possible to make accurate measurements in sticky or corrosive streams. Monitor Technology **114**

## Oxygen analyzer

Direct reading of oxygen concentrations in sample gases in a range of 1-100% full

scale is possible with this paramagnetic sensing unit. No chemical reagents, batteries or sensor reactivation is needed for continuous monitoring of flue gases, stack gases, and hazardous environments. Environmental Tectonics **115**

## Filter/purifier system

Large-capacity purification chambers contain bulk granular carbon. Purification system is downstream of filter, and eliminates use of powdered carbon and pre-coated slurry tank. Fine carbon particles cannot migrate. SERFILCO **134**

## X-ray spectrometer

New, computer-controlled sequential x-ray spectrometer, Model SRS 200, uses x-ray fluorescence methods for non-destructive analysis. Solid, powder, and liquid samples can be analyzed for all elements from fluorine to uranium at concentrations of 0.0001-100%. Siemens **135**

## PBB detection

Automatic gas chromatograph has capability to detect polybrominated biphenyl (PBB) compounds in human blood serum samples. Varian **137**

## Colorimeter

Colorimeter is useful for municipal water monitoring, lake/stream studies, industrial water management, and other testing needs. More than 60 tests are possible with easy calibration, plus pH measurement. Works in field and laboratory. Hach Chemical **138**

## Heat exchanger

New heat exchanger improves heat-transfer efficiency for heating or cooling liquids in pipes. Permits reduction of cooling water to be used. Works through patented spiral system in pipes, which speeds cooling water through jacket. F.R. Gross Co. **139**

## Oil conservation

Device can be retrofitted on oil burners of conventional construction, even those more than 5 years old, and allow oil savings of up to 22% by more efficient burning. The Saab-Scania Group **140**

## Vacuum pumping fluids

New grades of perfluoropolyether fluids (Fomblin) are uniquely suited to vapor diffusion pumps. Can be used in direct contact with ozone, oxygen, fluorine gas, uranium hexafluoride. Fomblins are non-flammable, and can be exposed to air at up to 280 °C. Edwards High Vacuum **141**

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# NEW LITERATURE

- Heavy metal control.** Technical Data Bulletin 5885 describes Sulfex system for treatment of metal finishing and plating wastes, chemical/mining wastes, and cooling tower blowdown. System also handles problem of excess sulfide evolution. Permutit **151**
- Vent silencers.** Product Catalog No. 243 illustrates and describes a complete line of silencers for high-pressure vents and blowdowns. Internal silencer features are shown. Universal Silencer **152**
- Boiler problem solving.** Technical Paper 245 emphasizes engineering skills and personnel and treatment products for solving boiler problems. Case histories are given. Diagnostic ability is featured. BETZ **158**
- Air analysis.** Air Analysis Catalog lists full line of holders and filters for air analysis. Applications and specifications are listed. Gelman Instrument Co. **159**
- Gas analyzer.** Bulletin describes the new MA-3A Process Gas Analyzer, and lists applications, features, specifications, and typical data output. Rugged, parts-per-million range detectability. CVC Products, Inc. **160**
- Energy conservation.** Bulletin 9000 describes company services and products for energy conservation, environmental protection, equipment protection, and corrosion control. Dearborn Chemical (U.S.), Chemed Corp. **161**
- Steel chain.** Bulletin 7670 describes Rex welded steel chain, and explains advantages. One application is in water pollution control systems. Rexnord **162**
- Biomedical aids.** Expanded catalog lists isotopes and "labeled" compounds for analytical standards and diagnostic reagents. KOR ISOTOPES division of Eco-Control, Inc. **163**
- Recorders.** Catalog lists 2-, 4-, 6-, and 8-channel portable oscillographic recorders for many applications in data recording. Gulton Industries, Inc. **164**
- Analysis for OSHA.** CIRA Circular (Issue No. 7, March 1977) describes effectiveness of new CIRA 101 chromatographic infrared analyzer for separating and identifying air pollutants at OSHA concentration limits. Sadtler Research Laboratories, Inc. **165**
- Fiber glass pipe.** Brochure TRX-24A lists features and advantages of Permastran fiber glass pipe for water or fire main applications. Johns-Manville **166**
- Flow monitor.** Brochure describes non-contact flow monitor, the SF-15 Sensi-
- flow. Can monitor solid, liquid, sludge, or slurry, and has special advantages for measuring slow-moving materials. WESMAR Sensor Products Division **167**
- Chemical recovery.** Folder PCR-20 describes evaporative recovery systems in general, and the company's 20-gph recovery systems in particular. Special applications in recovering plating chemicals. Corning Glass Works **168**
- Laboratory instruments.** G77 Catalog lists measuring, control, and distillation instruments that can speed up laboratory procedure without sacrificing precision. Roger Gilmont Instruments, Inc. **169**
- Dust collectors.** Brochure describes "Swirl-A-Way" cyclonic dust collectors for cleaning 1760-144 000 cfm of gas. Operation and engineering are explained. Swemco, Inc. **170**
- Oil spill monitors.** Symposium paper reprint (1977 Oil Spill Conference, New Orleans, La.) lists current commercial applications of non-contract oil spill monitors in refineries and manufacturing plants. WRIGHT & WRIGHT, INC. **171**
- Labware.** 1977 Catalog lists full line of plastic laboratory ware, including new and improved products, and safety equipment. Nalge Co. **172**
- Chromatographic aid.** Technical brochure describes SD 3000 Spectrodensitometer for qualitative/quantitative analysis of chromatograms and other electrophoretic media. Schoeffel Instrument Corp. **173**
- Tape recorders.** Bulletin describes Series Eight-Four 4- and 8-channel tape recorders for many applications. Any combination of FM and direct data modules; voice interrupt may be provided. EMI Technology, Inc. **174**
- Hydrogen generator.** Late issue of UPDATE describes a new hydrogen generator that makes 99.9999% pure hydrogen from distilled water on the spot. Matheson **175**
- Precious metals.** Booklet lists 30 000 products including ores, minerals, abatement equipment, precious metals, and zirconium sponge. Some metals are used for catalysts. Engelhard **176**
- Sludge application.** Brochure describes new Wolverine Flotation Vehicle that has many diverse uses, including fertilizer and sludge application on land. Ward Commons Manufacturing Co., Inc. **177**
- Filters.** Bulletin F 126 describes facilities and equipment for forming, machining, making, and shipping steam condensers, filters, and filter/demineralizer systems. Quality assurance is featured. Delaval Turben Inc. **178**
- Titration.** Folder, "Digital Titration Is Here!", describes the Digital Titrator, Model 16999, for fast, accurate, inexpensive titrations in field and laboratory situations where quick determinations are required. Hach Chemical Co. **179**
- Boiler emission control.** Bulletin tells how the company offers to solve particulate/SO<sub>2</sub> removal problems for utility and industrial power boiler facilities. Lime/limestone, sodium, and other alternatives are listed. Air Pollution Industries, Inc. **192**
- Corrosion-resistant pumps.** Bulletin GP-2 details a complete line of corrosion-resistant pumps made of fiberglass. Applications at pulp/paper mills, waste treatment plants, and many others. Fybroc, Inc. **193**
- Detector.** Brochure describes photoionization detector with 10-50 times greater sensitivity than flame ionization detectors. Detector can measure organics, sulfur- and nitrogen-based compounds, and other trace undesirable substances. HNU Systems, Inc. **194**
- Flowmeter/sampler.** Brochure describes the 104 Controller, fully solidstate, which measures flow volume, and takes samples on a proportional-to-flow basis. Environmental Measurement Systems **195**
- Waste Usage.** "The Ultimate Resource", a new 16-mm film for free loan. Shows how waste recovery is done. Film made for Union Carbide Corp. Modern Talking Picture Service, 2323 New Hyde Park Rd., New Hyde Park, N.Y. 11040 (write direct).
- Composting.** Information on what types of composters can do a good job. J. C. Young Co., 5621 E. Calle del Paisano, Phoenix, Ariz. 85018 (write direct).
- SRM's.** The 1977 price list for Standard Reference Materials (SRM's) is available. Limited quantities. SRM's have many environmental analysis uses. Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234 (write direct).

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# BOOKS

**Environmental Law: A Guide to Information Sources.** Mortimer D. Schwartz, Ed. xiv + 191 pages. Gale Research Co., Book Tower, Detroit, Mich. 48226. 1977. \$18, hard cover.

This annotated bibliography covers three topics: the legal process, pollution control, and conservation of resources. The materials culled from are mainly English language books, government documents and proceedings of scientific conferences and symposia. Law libraries, environmental periodicals and environmental action groups are listed in appendices.

**Instrumentation for Monitoring Air Quality. Special Technical Publication 555.** 200 pages. American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103. 1977. \$15.25, hard cover.

In addition to discussions on the analysis and monitoring of sulfur and nitrogen oxides and hydrocarbons and ozone, this book covers recent developments in the methodology for measuring submicron aerosols. This volume should be useful to an environmental laboratory anticipating the purchase of new equipment.

**Survey of Instrumentation for Environmental Monitoring/Volume 2, Water.** Third Update. Lawrence Berkeley Laboratory, Technical Information Dept., University of California, Berkeley, Calif. 94720. 1976. \$10, looseleaf.

Among the topics covered in the original volume, published in 1973, are metals, nitrogen, halides, biological and physical parameters, pesticides and petrochemicals. This third update covers sampling and calibration techniques. This survey supplies critical comparisons among instrumentation methods now in use and recommends promising methods and new instruments.

**Energy: The Solar Prospect.** Worldwatch Institute, 1776 Massachusetts Ave., N.W., Washington, D.C. 20036. 1977. \$2, soft cover.

Solar energy, in all its myriad forms, is discussed in terms of existing and future technology and economics. The study concludes that given the alternatives, a solar future looks very bright.

**Fundamentals of Integrated GC-MS. Part III.** Benjamin J. Gudzinowicz, et al. vii + 603 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, N.Y. 10016. 1977. \$59.75, hard cover.

In pollution detection, toxicology, and many other fields requiring analysis, gas chromatograph-mass spectrometry (GC-MS) is an important tool, and has been since 1957. This book covers topics such as vacuum technology and the GC-MS interface, and optimization of

systems operational parameters. Data presentations aid the analyst in understanding the strengths and weaknesses of each particular method.

**Individual Onsite Wastewater Systems.** Nina McClelland, Ed. viii + 319 pages. Ann Arbor Science Publishers Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1977. \$22.50, hard cover.

In this work, leading U.S. and Canadian authorities look at rural wastewater problems, septic system repair, evapotranspiration systems, graywater and blackwater treatment for water conservation/reuse, land disposal, and many other pertinent topics. The book contains papers of the Third National Conference for Individual Onsite Wastewater Systems (Ann Arbor, Mich., November 1976).

**Textile Technology/Ecology Interface—1977.** iv + 93 pages. AATCC, P.O. Box 12215, Research Triangle Park, N.C. 27709. 1977. \$20 to AATCC members; \$40 to non-members, paper.

This book contains the papers presented at the Environmental Symposium given by the American Association of Textile Chemists and Colorists (AATCC) at Atlanta, Ga., in March. It discusses OSHA problems, use of ozone for textile waste treatment, 1977 effluent standards, heat recovery, air pollution control, water quality, and many other pertinent topics.

**Introduction to Wastewater Treatment Processes.** R. S. Ramalho. ix + 409 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1977. \$22.50, hard cover.

This book examines fundamental processes of wastewater treatment. It discusses a summary of the theory for each process; defines important design parameters for a process from laboratory scale or pilot plant equipment; and develops a synthetic design procedure. The text can be of help to students, engineers, and others in the wastewater field.

**Land Use Controls in the United States.** Elaine Moss, Ed. 362 pages. Natural Resources Defense Council, Inc., 15 W. 44th St., New York, N.Y. 10036. 1977. \$7.95, paper.

Use of land in the wrong way can harm the public in many cases. This book explains what legal recourse affected citizens may have, and defines the statutes and kinds of actions such citizens can take to make sure that the government does its job at protecting them. Case histories are presented, and strengths and weaknesses of laws are discussed.

**Stratigraphic Atlas of North and Central America.** T. D. Cook and A. W. Bally, Eds. 272 pages. Princeton University Press,

Princeton, N.J. 08540. 1977. \$50, cloth; \$15, spiral bound.

The locations of oil, coal, and mineral deposits are normally among the best-kept secrets of government and industry. Nevertheless, an atlas such as this one can impart a general idea of rock structures and the fuels or minerals they might contain. It was prepared by the exploration department of Shell Oil Co. (Houston, Tex.).

**Wastewater Conservation and Reuse.** Hillel I. Shuval, Ed. xiii + 463 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1977. \$29.50, hard cover.

This volume contains papers dealing with planned water recycling. It covers many technical aspects, and presents discussions of programs in many parts of the world. While the book is written on an advanced technical level, it is easily understood by non-specialists.

**Pesticides and Human Welfare.** D. L. Gunn and J. G. R. Stevens, Eds. xii + 278 pages. Oxford University Press, 200 Madison Ave., New York, N.Y. 10016. 1977. \$11, cloth; \$4, paper.

Pesticides play an important role in enhancing vegetable and meat production, and suppressing insect-vectored diseases, for example. But they have their disadvantages, too, and are often the target of antipesticide propaganda, well-founded or not. In this book, the editors seek to present a balanced view of the advantages and disadvantages of using pesticides.

**Methods Used in Establishing Permissible Levels in Occupational Exposure to Harmful Agents.** Technical Report Series 601. 68 pages. WHO Publications Center USA, 49 Sheridan Ave., Albany, N.Y. 12210. 1977. \$3.20, paper.

This report explains the basic principles on which evaluation of permissible levels depends, and what factors must be considered in order to reach decisions concerning these levels. What is being aimed at is a way to arrive at some workable international recommendations concerning permissible levels of harmful substances.

**Seagrass Ecosystems. Volume 4.** C. Peter McRoy and Carla Helfferich, Eds. xi + 314 pages. Marcel Dekker, Inc., 270 Madison Ave., New York, N.Y. 10016. 1977. \$29.75, hard cover.

Seagrass ecosystems have a unique quality. This book addresses their total ecosystems aspects, rather than biology alone. It covers productivity, physiology, system oceanography, systematics, decomposition, and consumers. Papers were presented at the International Seagrass Workshop, Leiden, The Netherlands.

# MEETING GUIDE

**August 18-19** Washington, D.C.  
**Energy Conservation in Industrial Plants.** New York University School of Continuing Education

*Write:* Ms. Heidi E. Kaplan, Information Services Manager, New York Management Center, Dept. 14NR, 360 Lexington Ave., New York, N.Y. 10017

**August 21** East Lansing, Mich.  
**Environmental Aspects of Industrial Fermentation Processes.** Society for Industrial Microbiology

*Write:* Ms. Ann Kulback, Society for Industrial Microbiology, c/o American Institute of Biological Sciences, 1401 Wilson Boulevard, Arlington, Va. 22209

**August 21-26** East Lansing, Mich.  
**Annual Meeting of the American Institute of Biological Sciences.** American Institute of Biological Science

Topics will include the ecological effects of power production, and biological control of pest organisms. *Write:* Ms. Carol H. Chisolm, coordinator of meetings, American Institute of Biological Sciences, 1401 Wilson Blvd., Arlington, Va. 22209

**August 22-24** Durham, N.H.  
**International Biannual Workshop on Nitrosamines.** University of New Hampshire

*Write:* Dr. Robert E. Lyle, Dept. of Chemistry, North Texas State University, Denton, Tex. 76203

**August 27-31** Boston, Mass.  
**Second Conference on Light Rail Transit.** Transportation Research Board

*Write:* W. Campbell Graebig, Engineer of Public Transportation, Transportation Research Board, 2101 Constitution Ave., N.W., Washington, D.C. 20418

**August 28-September 2** Chicago, Ill.  
**174th American Chemical Society National Meeting.** American Chemical Society

*Write:* A. T. Winstead, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036

**August 28-September 2** Washington, D.C.

**Twelfth Intersociety Energy Conversion Engineering Conference.** American Nuclear Society, American Chemical Society and others

*Write:* Glen A. Graves, general chairman, National Science Foundation, 1800 G St., N.W., Washington, D.C. 20550

**August 29-September 1** New Orleans, La.

**Second Symposium on Stationary Source Combustion.** U.S. Environmental Protection Agency/Industrial Environmental Research Laboratory-RTP

*Write:* Betty Farley, symposium coordinator, Acurex Corp./Aerotherm Division, 485 Clyde Ave., Mt. View, Calif. 94042

**August 31-September 2** South Lake Tahoe, Nev.

**15th Annual Seminar and Equipment Show.** Governmental Refuse Collection and Disposal Association

The exhibit will display a wide range of solid waste systems. *Write:* Bob Lawrence, City of San Leandro, 835 E. 14th St., San Leandro, Calif. 94577

**September 7-8** Gaithersburg, Md.  
**Seminar on Earthquake Design Criteria, Structural Performance and Strong Motion Records.** National Bureau of Standards and Earthquake Engineering Research Institute

*Write:* Richard N. Wright, B260, Building Research Building, National Bureau of Standards, Washington, D.C. 20234

**September 11-14** Washington, D.C.  
**12th Intersociety Energy Conversion Engineering Conference.** American Chemical Society's Divisions of Fuel Chemistry and Petroleum Chemistry

*Write:* G. Graves, National Science Foundation, 1800 G St., N.W., Washington, D.C. 20550

**September 11-14** San Francisco, Calif.

**1977 Mining Convention.** American Mining Congress

*Write:* American Mining Congress, 1100 Ring Building, Washington, D.C. 20036

**September 14-15** Asheville, N.C.  
**Southeastern Occupational Health Conference.** Southeastern Occupational Health Conference

*Write:* D. H. Robinson, M.D., Program Chairman, Southeastern Occupational Health Conference, Box 21372, Columbia, S.C. 29221

**September 18-22** Houston, Tex.  
**Energy Technology Conference and Exhibition.** The American Society of Mechanical Engineers (ASME)

*Write:* Gail Jannon, Manager, Industry Department, ASME, 345 E. 47th St., New York, N.Y. 10017

## Courses

**August 15-19** Madison, Wis.  
**Well Hydraulics.** University of Wisconsin-Extension

*Fee:* \$375. *Write:* Engineering Registration, The Wisconsin Center, 702 Langdon St., Madison, Wis. 53706

**August 15-19** Chicago, Ill.  
**The Application of Computer Programs in Preliminary Design of Wastewater Treatment Facilities.** Illinois Institute of Technology

*Fee:* \$250. *Write:* James W. Male, Pritzker Department of Environmental Engineering, Illinois Institute of Technology, Chicago, Ill. 60616

**August 22-25** Los Angeles, Calif.  
**Legal Aspects for Control Agency Decision Makers, Course No. 425.** Air Pollution Training Institute

*Fee:* \$77. *Write:* Registrar, Air Pollution Training Institute, MD-20, National Environmental Research Center, Research Triangle Park, N.C. 27711

**August 22-26** Research Triangle Park, N.C.

**Air Pollution Meteorology, Course No. 411.** Air Pollution Training Institute

*Fee:* \$99. *Write:* Registrar, Air Pollution Training Institute, MD-20, National Environmental Research Center, Research Triangle Park, N.C. 27711

**August 22-26** New York, N.Y.  
**Combustion Evaluation, Course No. 427.** Air Pollution Training Institute.

*Fee:* \$110. *Write:* Registrar, Air Pollution Training Institute, MD-20, National Environmental Research Center, Research Triangle Park, N.C. 27711

**August 29-31** Research Triangle Park, N.C.

**Source Sampling and Analysis for Gaseous Pollutants, Course No. 468.** Air Pollution Training Institute

*Fee:* \$105. *Write:* Registrar, Air Pollution Training Institute, MD-20, National Environmental Research Center, Research Triangle Park, N.C. 27711

**August 29-September 2** Madison, Wis.

**Solar Energy Thermal Processes.** University of Wisconsin-Extension

*Fee:* \$350. *Write:* C. W. Little, University of Wisconsin-Extension, Dept. of Engineering, 432 N. Lake St., Madison, Wis. 53706

**September 1** New Brunswick, N.J.  
**Recertification for Visual Emissions Evaluation.** Rutgers University

*Fee:* \$85. *Write:* Robert E. Hague, Instructor, Dept. of Environmental Science, Rutgers University, Cook College, P.O. Box 231, New Brunswick, N.J. 08903

**September 7-9** Davis, Calif.  
**Introduction to Environmental Planning, Course No. X421.4(4).** University of California, Davis/Extension

*Fee:* \$300. *Write:* Michael McCoy, University Extension, University of California, Davis, Calif. 95616



**September 8-9** Berkeley, Calif.  
**Solar Energy for Buildings, Houses and Pools.** University of California Extension

Fee: \$100. *Write:* Continuing Education in Engineering, UC Extension, 2223 Fulton St., Berkeley, Calif. 94720

**September 9-10** Madison, Wis.  
**Industrial Plant Boilers—Measuring and Improving Efficiency.** University of Wisconsin—Extension

Fee: \$145. *Write:* Charles E. Dorgan, Program Director, Dept. of Engineering, University of Wisconsin—Extension, 432 North Lake St., Madison, Wis. 53706

**September 12-16** New Brunswick, N.J.

**Stack Testing.** Rutgers University  
Fee: \$275. *Write:* Donald A. Deieso, Instructor, Dept. of Environmental Science, Rutgers University, Cook College, P.O. Box 231, New Brunswick, N.J. 08903

**September 12-16** Nashville, Tenn.  
**Control, Operation and Management of Biological Wastewater Treatment Plants.** Vanderbilt University

Fee: \$375. *Write:* Prof. W. W. Eckenfelder, Vanderbilt University, Box 6222, Sta. B, Nashville, Tenn. 37235

## International

**September 4-9** Reading, England  
**4th International Congress on Photo-synthesis.** Bookers, Boots, B.P. British Sugar, ICI, Monsanto, RHM, Shell, Tate & Lyle

Environmental issues will be discussed. *Write:* Dr. John F. Gibson, The Chemical Society, Burlington House, London, W1V 0BN, England

**September 5-8** London, England  
**Conference on New Process of Wastewater Treatment and Recovery.** Society of Chemical Industry

*Write:* Dr. D. H. Sharp, Society of Chemical Industry, 14 Belgrave Sq., London, SW 1X 8PS, England

**September 5-10** Dubrovnik, Yugoslavia  
**International Symposium on Sulfur in the Atmosphere.** EPA, ERDA, Electric Power Research Institute

*Write:* Rudolf B. Husar, Box 1185, Washington University, St. Louis, Mo. 63130

**September 6-8** Stockholm, Sweden  
**International Symposium on the Control of Air Pollution in the Working Environment.** Swedish Work Environment Fund and the International Labor Office

*Write:* ILO Symposium, c/o Reso Congress Service, S-105 24 Stockholm, Sweden

**September 12-16** Birmingham, England  
**International Reclamation and Disposal Exhibition.** Materials Reclamation Weekly

*Write:* Maclaren Publishers Ltd., P.O. Box 109, Davis House, 69-77 High St., Croydon CR9 1QH England

**September 26-28** Noordwijkerhout, The Netherlands

**2nd International Symposium on Aquatic Pollutants.** Commission of European Communities, U.S. EPA, U.S. NCI, Netherlands' Ministry of Public Health and Environmental Hygiene and others

*Write:* George L. Baughman, Environmental Research Laboratory, U.S. EPA, College Station Road, Athens, Ga. 30601

**September 26-30** St. John's, Newfoundland

**Fourth International Conference on Port and Ocean Engineering Under Arctic Conditions.** Memorial University of Newfoundland

*Write:* G. R. Peters, Chairman, POAC Organizing Committee, Faculty of Engineering and Applied Science, Memorial University, St. John's Newfoundland, Canada

## Call for Papers

**September 1 deadline**  
**1978 Offshore Technology Conference.** American Institute of Mining, Metallurgical, and Petroleum Engineers, and others

The meeting will be held May 8-11 at Houston, Texas. *Write:* Program Manager, Offshore Technology Conference, 6200 N. Central Expressway, Dallas, Tex. 75206

**September 1 deadline**  
**ASTM Symposium on Methodology for Biomass Determinations and Microbial Activities in Sediments.** American Society for Testing and Materials

The symposium will be held January 30-31 at Ft. Lauderdale, Fla. *Write:* Miss Jane B. Wheeler, ASTM, 1916 Race St., Philadelphia, Pa. 19103

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**INDEX TO THE ADVERTISERS IN THIS ISSUE**

**Carborundum/Water Management Division** ..... 743  
Ellis Singer & Webb Ltd. Advertising

**Fisher Scientific Company** .... OBC  
Tech-Ad Associates

**GCA/Technology** ..... 827  
Kenyon & Eckhardt Advertising Inc.

**Hach Chemical Company** ..... 743  
Wesley Day, Advertising

**Hydrolab** ..... 747  
Cooley & Shillinglaw, Inc.

**Martek Instruments, Inc.** ..... 771  
Tekmar Marketing Services

**Phlips Industries** ..... IBC  
C. J. Nicholl & Associates Ltd.

**Research Appliance Company** ..... IFC  
W. F. Minnick & Associates, Inc.

**Waters Associates** ..... 822  
Edward W. Fischer & Associates

**CLASSIFIED SECTION** ..... 830

**PROFESSIONAL CONSULTING SERVICES DIRECTORY** .. 828-829

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43	44	45	46	47	48	49	50	51	52	53	54	55	56
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143	144	145	146	147	148	149	150	151	152	153	154	155	156
157	158	159	160	161	162	163	164	165	166	167	168	169	170
171	172	173	174	175	176	177	178	179	180	181	182	183	184
185	186	187	188	189	190	191	192	193	194	195	196	197	198

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43	44	45	46	47	48	49	50	51	52	53	54	55	56
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115	116	117	118	119	120	121	122	123	124	125	126	127	128
129	130	131	132	133	134	135	136	137	138	139	140	141	142
143	144	145	146	147	148	149	150	151	152	153	154	155	156
157	158	159	160	161	162	163	164	165	166	167	168	169	170
171	172	173	174	175	176	177	178	179	180	181	182	183	184
185	186	187	188	189	190	191	192	193	194	195	196	197	198

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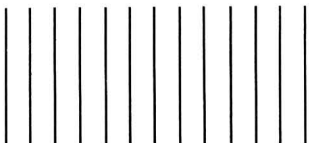
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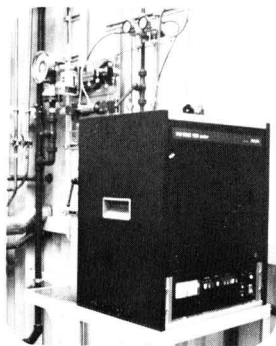


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