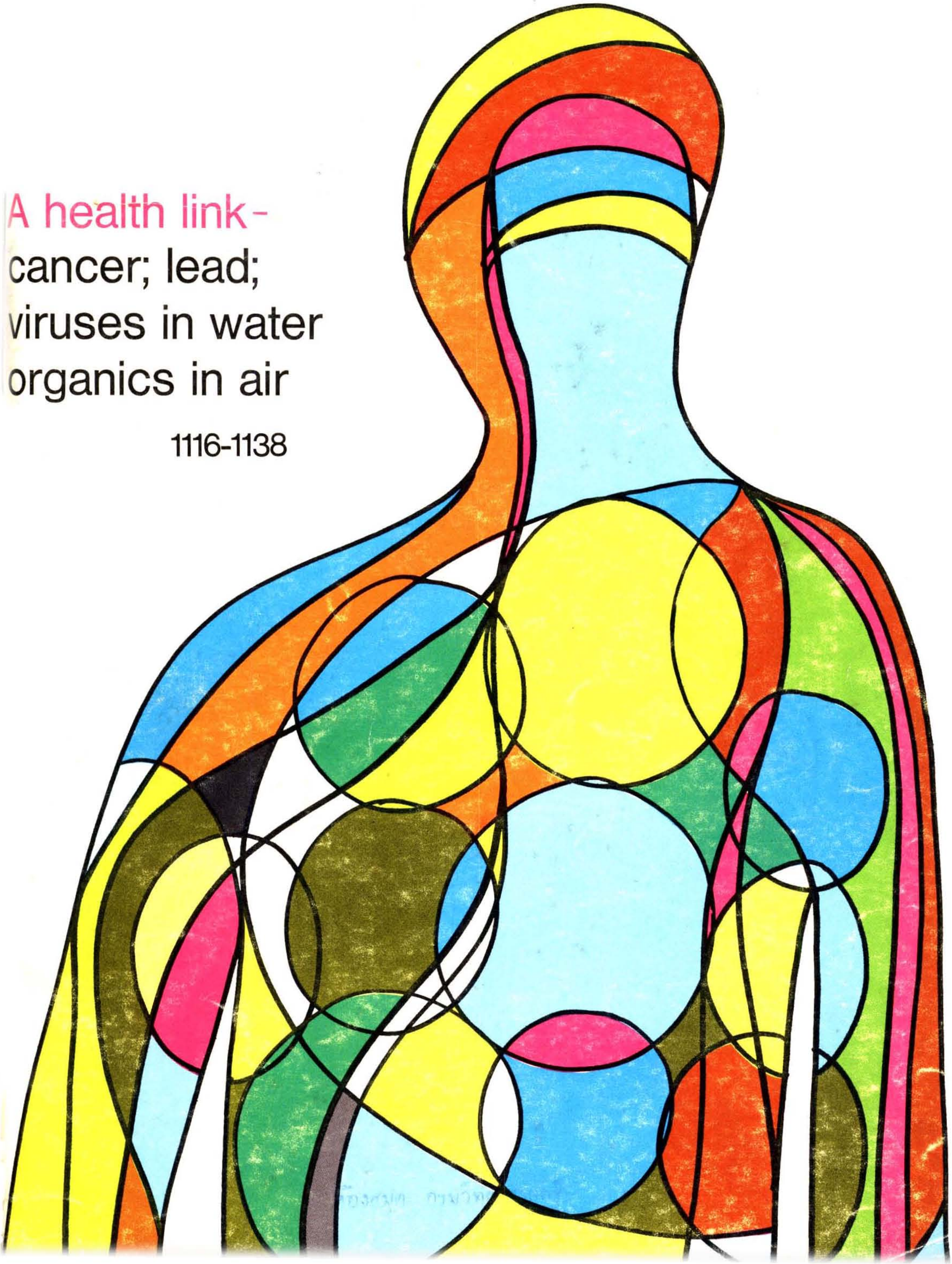
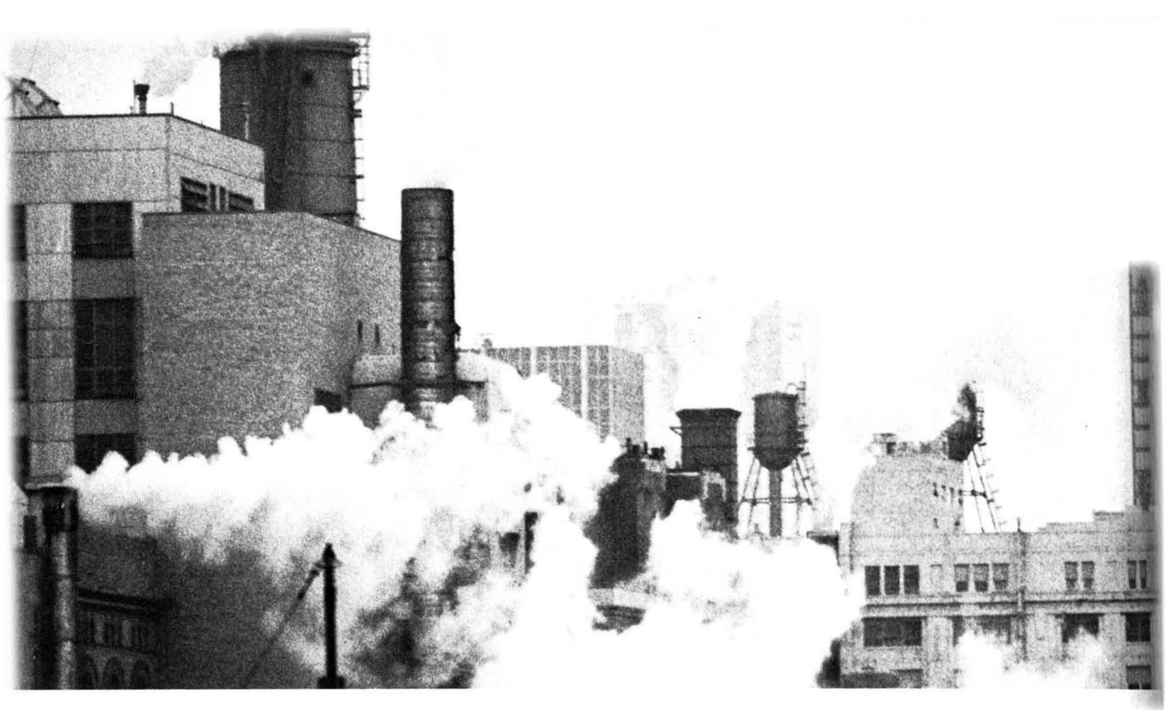
Environmental
Science & Technology

DECEMBER 1975



A health link-
cancer; lead;
viruses in water
organics in air

1116-1138



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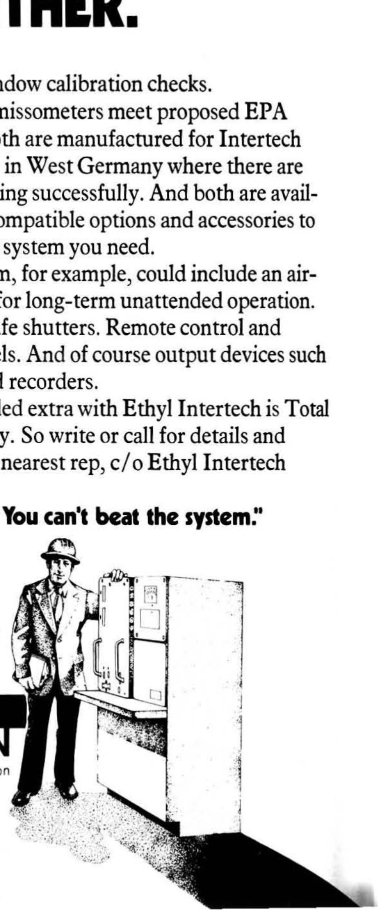

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CIRCLE 8 ON READER SERVICE CARD

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Volume 9, Number 13, December 1975

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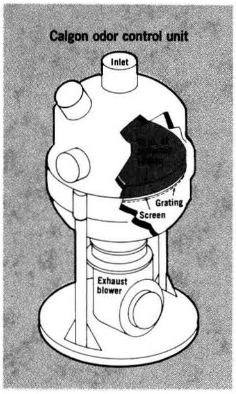

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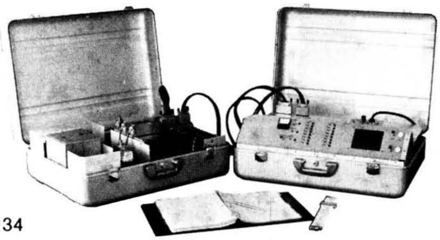

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CURRENT RESEARCH

Color removal by clays. Kinetic study of adsorption of cationic and anionic dyes 1139

V. V. Sethuraman and B. C. Raymahashay*

Kinetics of adsorption of anionic and cationic dyes by kaolinite and montmorillonite were studied. Control of ion-exchange capacities and nature of the exchange sites of the clays are discussed.

Particle size distributions of lead, bromine, and chlorine in urban-industrial aerosols 1141

J. J. Paciga, T. M. Roberts, and R. E. Jervis*

Distributions for atmospheric Pb, Br, and Cl were determined with respect to particle size at control sites and near lead refineries. The correlation between Pb and Br with automobile emissions allowed indirect estimates of nonautomotive lead near the refineries. Cl appeared derived from several sources.

Dynamics of 2,4,-D esters in surface waters. Hydrolysis, photolysis, and vaporization 1144

R. G. Zepp*, N. L. Wolfe, J. A. Gordon, and G. L. Baughman

The chemical action of 2,D esters in water was studied. Hydrolysis rates were dependent on position of the ester linkage, and can occur rapidly. Direct photolysis is slow and depends on various factors. Volatilization may be a significant path in the loss of hydrocarbon esters from water.

Elemental ratios along human hair as indicators of the exposure to environmental pollutants 1150

Vlado Valković*, Dubravko Rendić, and G. C. Phillips

Trace element concentrations along human hair were measured using proton-induced X-ray spectroscopy. It is shown that elements whose concentrations increase along the hair can be identified as pollutants in the area.

Synthesis gas from feedlot manure. Conceptual design study and economic analysis 1152

C. R. Engler, W. P. Walawender*, and Liang-tseng Fan

A process design was studied for the economic disposal, by pyrolysis, of feedlot residues. Plant size, residue moisture content, and transportation costs were considered. It was concluded that only large-scale processing under ideal conditions would be economically competitive.

Homogeneous gas phase chemiluminescence measurement of reactive hydrocarbon air pollutants by reaction with oxygen atoms 1157

Arthur Fontijn* and Roy Ellison

Reactivities in dilute hydrocarbon mixtures were determined by measuring the difference in emission intensities at 308.9 and 312.2 nm for O-atom/hydrocarbon reactions. Sensitivity to 0.2-ppm H_2C_4 equivalent and linear response to 1000 ppm are obtained.

Trace element composition in atmospheric particulates during 1973 and summer of 1974 at Chadron, Neb. 1164

A. W. Struempler

Particles filtered from air were analyzed for nine elements. Metals derived from soil could be differentiated from those from anthropogenic sources. These data will provide background levels for future particulate monitoring of the area.

Performance of charcoal tubes in the determination of vinyl chloride 1168

J. E. Cuddeback*, W. R. Burg, and S. R. Birch

Adsorption of low levels of airborne vinyl chloride on activated charcoal was studied. Breakthrough volumes and storage characteristics are presented. Methodology is described for 90% recovery of vinyl chloride after two weeks sample storage.

Comparison of manual and automated analysis methods for sulfur dioxide in manually impinged ambient air samples 1172

O. J. Logsdon II* and M. J. Carter

Data from analysis of SO_2 by two automated methods, both adaptations of the para-rosanaline method, and the EPA reference method were compared. Results were not significantly different from, and were more precise than the reference method.

Analysis of air pollutants using sampling tubes and gas chromatography 1175

J. W. Russell

Organic pollutants from air were concentrated using sampling tubes filled with gas chromatographic packings. Quantitative recovery, ppb sensitivity, and sampling convenience are advantages. Breakthrough volumes and recovery values were determined for various packings.

NOTES

Rate of evaporation of low-solubility contaminants from water bodies to atmosphere 1178

Donald Mackay* and P. J. Leinonen

Equations are presented that can be used to predict approximate rates of evaporative loss of low-solubility contaminants in an air–water system.

CORRESPONDENCE

New Orleans drinking water sources tested by gas chromatography–mass spectrometry

V. L. Snoeyink and J. L. Laseter 1180

Correction. J. L. Laseter 1174

---

* To whom correspondence should be addressed.
This issue contains no papers for which there is supplementary material in microform.

Credits: 1105, *C&EN* staff photo, Fred Zerkel; 1106, Boeing Aerospace Co.; 1114, UCC's O. K. McCallister

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For more information contact
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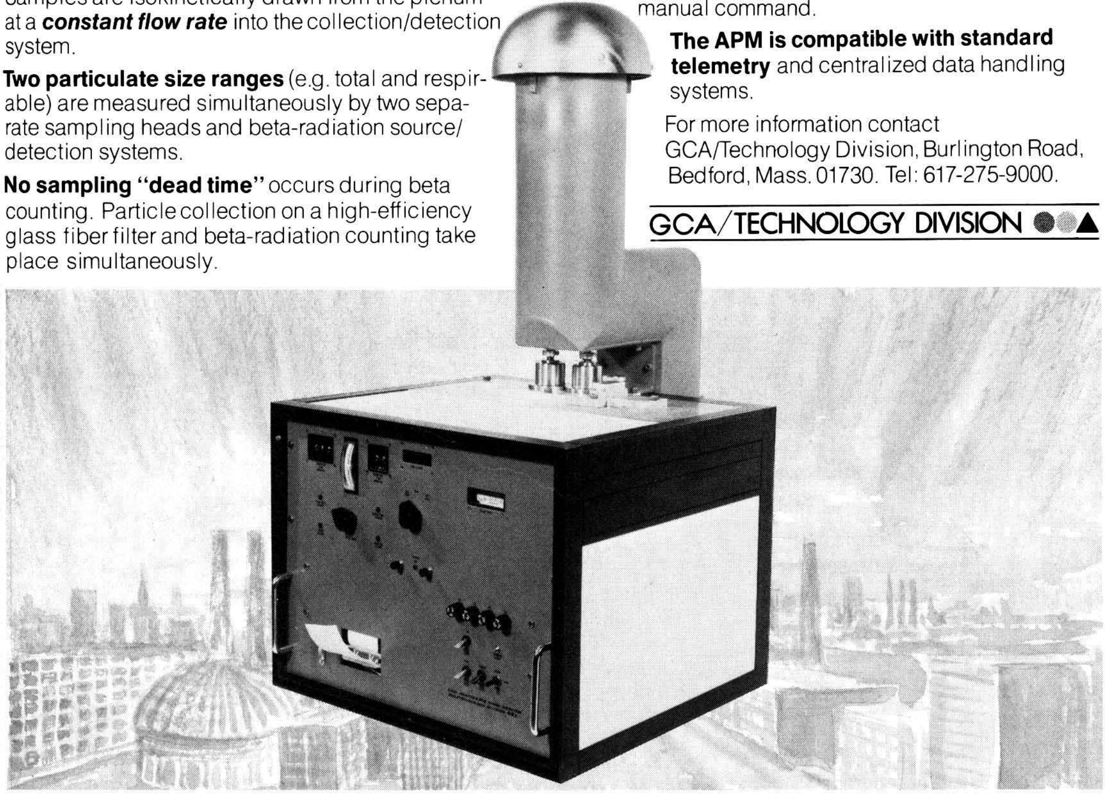

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CIRCLE 24 ON READER SERVICE CARD

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For author's guide and editorial policy, see June 1975 issue, page 547, or write Katherine I. Biggs, Manuscript Reviewing Office, *ES&T*

It's your health

The first half of this environmental decade was marked by tremendous legislative strides to protect the health and welfare of the U.S. citizenry. Since its formation on December 2, 1970, the Environmental Protection Agency has made inroads for clean air, clean water, less noise, safer pesticides while the Departments of Labor and HEW have attempted a safe work-a-day world for U.S. workers.

There has been no Donora, no Minamata. But in the absence of a toxic substances control act and judging from the health-related issues raised by *ES&T*'s Lois Ember in this month's special report, we have a considerable way to go.

As one announced presidential candidate reaffirmed at a meeting of the National Association of Environmental Professionals in Washington, D.C., one basic need for environmental legislation is the saving of human lives. Automotive air pollution kills 4000 Americans each year. Sulfur emissions from coal-powered plants will, if unchecked, kill 25,000 people in the next five years.

To be sure there are chemicals on the loose in the environment. For example, they are showing up in our drinking water and the uncertainty here is that health effects from exposure to such materials may not show up for long periods of time, perhaps 25–40 years. At the same time, the exposure to such materials is chronic and continuous, from conception to death. The risk to such exposures may never be fully evaluated, at least with any predictive capability. But a concept of no risk is an unworkable premise. All agree. There are risks in everyday life—driving, flying, skiing, rappelling, even crossing a busy intersection.

Some make a distinction between voluntary and involuntary risks. Others point out that you really do not know that you are taking a risk. For example, the nonworker living in a neighborhood near an industrial source of emissions simply may not know that exposure to these emissions may be injurious to health. What is surfacing is that he at least must be made consciously aware of a "potential" or "suspect" problem. The special report is must reading for all.

Stanton Miller

What's important for you in a water monitor?

Accuracy
How do you rate your data for accuracy?
What kind of accuracy do you expect from a field monitor?

Calibration
How often do you calibrate to insure accurate data?
Do you perform single, two-point or multi-point dynamic calibration?
Do you correct for variation in temperature of the sample—and also for variation in temperature between water sample and calibration solution?

Cleaning
How frequently do you clean your water sensor elements?
How much algae build-up can you tolerate on your sensors?
How long does it take before solids encrustation and sedimentation affect sensor reading?

Maintenance
How often do you have to send out field crews for monitor maintenance?
Can you *schedule* your maintenance?

Can it all add up to a cost-effective answer?

Accuracy
Your water pollution control strategy depends on the degree to which you can trust your data. Over treatment costs run high. Philips calibration techniques, plus ability to cross-correlate parameters through data reduction assure continuously accurate data.

Calibration
Unless sensors are calibrated at close regular intervals (daily, for example) changes in sensitivity and variations in temperature and ionic strength can produce erroneous readings. Philips 2-point dynamic calibration solves the problem through use of 2 calibration solutions to establish reference points bracketing the expected measuring range.

Cleaning
Solids encrustation and algal bloom alter sensor readings. Ultrasonic cleaning every 12 or 24 hours, as required, of basic chemical sensors (pH, redox, pCl, DO and temperature) minimize sedimentation of suspended solids and biological growth.

Maintenance
Many monitors require daily attention. Philips water station, which reports on a total of 7 parameters, requires cleaning only once a month.

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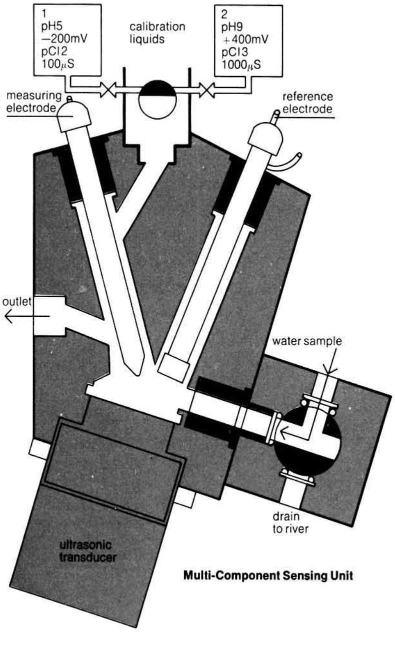

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LETTERS

Jobs, jobs, jobs

Dear Sir: In the article, "Where Will the Jobs Be?" (*ES&T,* September 1975, p 806) you mention on page 812 sources of information on graduate programs in Environmental Engineering. Another reference is the Register of Environmental Engineering Graduate Programs. It is available from: Dr. Joe Malina, Director of Environmental Health Eng., 305 Eng. Labs. Bldg., University of Texas, Austin, Tex. 78712.

A similar volume covering undergraduate programs is being edited now. For more information contact: Donald B. Aulenbach, Ph.D., Chairman, Subcommittee on Undergraduate Environmental Engineering Education, Rensselaer Polytechnic Institute, Troy, N.Y. 12181. [518-270-6553].

John H. Austin
Clemson University
Clemson, S.C. 29631

Car emissions & fuel economy

Dear Sir: We at the Environmental Activities Staff of General Motors were happy to see E. S. Starkman's article on automotive emission control and fuel economy (*ES&T,* September 1975, p 820). An error appeared, however, in Figure 6 on page 824 in which three of the curves charting HC emissions against spark advance are reversed. Although the careful reader can detect the presence of the error quite easily, he would not be able to tell how the curves should be placed.

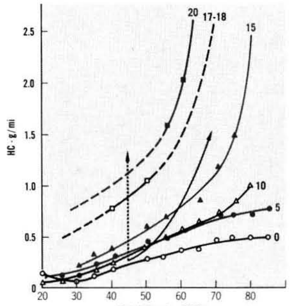
Fred W. Bowditch
General Motors Corp.
Warren, Mich. 48090

Ed: The corrected chart is reprinted below.

FIGURE 6

Emission and economy tradeoffs

at 55 mph road load condition
(Numbers on curves give percent EGR)



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The bold solid line shows the increasing spark advance required to maintain best fuel economy with increasing EGR rates, and the resulting detrimental effect on HC emissions. The dashed line superimposed shows the effect of increasing the EGR rate while maintaining a constant spark setting

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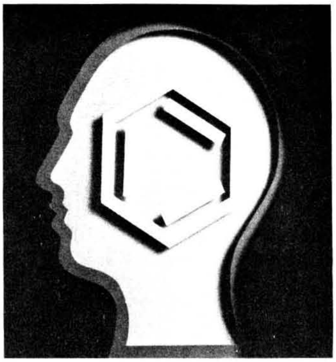

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INTERNATIONAL

If more than one heavy metal is polluting a water body, what are mutual effects? Jorma Miettinen, chairman of the University of Helsinki (Finland) radiochemistry department, is conducting studies of combined metal effects, sponsored by the International Atomic Energy Agency (Vienna, Austria), and the Academy of Finland. For example, in marine plankton, lead decreased cadmium's toxicity when the ratio Pb:Cd was high (above 10) but increased it when the ratio was low. In fish, zinc seemed to offer some protection against cadmium and mercury toxicity; protection against mercury was less. Citing the existence of sparse data, Miettinen is calling for more studies of "synergism effects" of more than one metal in water.

WASHINGTON

EPA will require pollution controls at gasoline pumps in eight U.S. cities to help reduce the smog problem by limiting the amount of gasoline vapors released to the air. The affected cities are Baltimore, Md., Washington, D.C., Newark, N.J., Boston, Mass., Denver, Colo., Los Angeles, Sacramento and the San Joaquin Valley, Calif. Requirements for some cities in Texas are to be released soon. Compliance is to begin in late 1976 and be completed by mid-1977.

The Third Resource Recovery and Waste Reduction report to Congress has been delivered. EPA's Office of Solid Waste Management Programs (OSWMP) found that the principal method of resource recovery to date is the separation of recyclable material at the waste source. Technology for resource recovery from mixed wastes is in the development stage, and the main obstacles to resource recovery are weak markets for secondary materials and institutional problems. EPA estimated that by 1985, waste reduction techniques, which involve redesigning of products or changes in patterns of consumption, could reduce waste generation by more than 20 million tons/year. In a related matter, OSWMP is offering a new injury reporting and information system to industry. Interested organizations should contact EPA's Washington office.

Rasmussen on reactor safety

The Nuclear Regulatory Commission (NRC) has released the final report on reactor safety. The $3–4 million, 3-yr study, directed by Norman C. Rasmussen of the Massachusetts Institute of Technology concluded that the risks attendant to the operation of present-day light water nuclear power plants are very low compared to other natural and manmade risks. For example, the study estimated the probability that a person living in the vicinity of a nuclear power plant will be fatally injured in a reactor accident as one in 5 billion per year; this compares to one in 4000 for a motor vehicle accident. The probability of latent health effects except for thyroid nodules was calculated to be a small percentage of the normal incidence rates and would be difficult to detect.

The Occupational Safety and Health Administration (OSHA) has recently released proposed health standards for toluene, lead, asbestos, and 11 other toxic substances including styrene, ethyl benzene and ozone. OSHA's latest proposed health standard is for trichloroethylene, and it has proposed reducing worker exposure limits for beryllium.

The Securities and Exchange Commission proposed regulations requiring corporate disclosure of the costs of environmental protection and compliance with pollution control laws. Acting under District Court order, the SEC said it was required to consider environmental protection under the National Environmental Policy Act of 1969. The SEC proposed rules would provide investors with information on the extent to which a public firm has failed to meet water and air standards. Public corporations would have to disclose reports showing noncompliance within the previous 12 months, and detail current and future spending for equipment and facilities necessary to meet environmental standards. Public comments will be received through Jan. 12.

President Ford signed into law P.L. 94-112, which amends the Water Resources Planning Act of 1965, P.L. 89-90 (see *ES&T,* October 1975, pp 924–928). The new law affects appropriations for the U.S. Water Resources Council, changes the membership in the Council and alters the amount paid to consultants. Authorization for state planning grants at a level of $5 million annually is extended for fiscal 1977 and 1978; operation of the Council is authorized at $1.5 million annually; and authorization for national assessments and coordination of River Basin plans at $10 million are extended for fiscal 1976 and 1977. The administrator of EPA, among others, is elevated to full membership on the Council. Consultants are to be compensated at the prevailing salary for GS-18 civil servants.

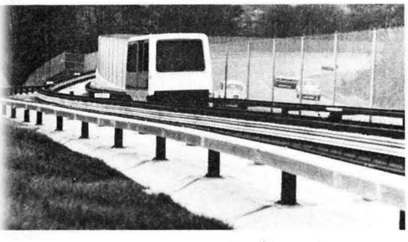
STATE

Recent findings indicate that cars alone are not the culprit in Washington, D.C.'s summer smog episodes. Manmade pollutants, arriving with the south-southwest winds, have been traced to Fredericksburg and Richmond, Va., 50–100 mi away. Douglas D. Davis, a chemist at the University of Maryland, under funding from the National Science Foundation's Research Applied to National Needs program, has been sampling air in a 12,000 mi^2 corridor from Washington to Richmond since 1973. Long distance transport of air pollutants is just being recognized as a national problem. EPA administrator Russell Train recently suggested that control measures, now restricted to urban areas, be extended to rural areas.

The "dirty dozen" states that have made the least progress in building waste water cleanup facilities under P.L. 92-500, according to the National Utility Contractors Association (NUCA) were: Hawaii, Florida, Delaware, Georgia, Wisconsin, West Virginia, Alabama, Mississippi, Indiana, Oklahoma, South Carolina and North Carolina. These states, ranked according to the dirtiest, spent an average of 3.8% of the funds allotted to them. They spent an average one fourth as much as the twelve best performing states: Oregon, Idaho, Washington, Montana, Alaska, Maine, South Dakota, North Dakota, Virginia, Iowa, New Hampshire and Colorado. According to the report, water pollution abatement projects could provide jobs for 120,000 workers in the construction industry nationwide.

Land use in a nine-county area around Cincinnati, Ohio, was surveyed by using NASA's LANDSAT-1 satellite. The survey, which produced a map of 225 drainage areas down to one-acre detail, was produced by the Bendix Corp. for the Ohio-Kentucky-Indiana Regional Council of Governments. The Council is developing a model to predict water quality in rivers and lakes under existing and potential land use policies. This inventory of present land use along with population projections for the area will form the basis for predicting future land use and for assessing its impact on water quality.

The Personal Rapid Transit system at Morgantown, W. Va., is now carrying passengers at full 13-hour-per-day service. This system, the first of its kind in an urban environment, consists of 45 electrically powered cars, three stations and 4.2 mi of guideway lanes. The system is fully automated and links the city's central business district with two campuses of W. Va. University. The University is now operating the system under an Urban Mass Transportation Administration grant, with operation and maintenance support from Boeing Aeorspace Co., the developers of the system. Extension plans call for a 50% increase in guideway lanes and the addition of two passenger stations.



A personal rapid transit

A bill restricting the use of fluorochlorocarbon compounds in aerosol spray cans has been passed by the N.Y. Legislature and signed by the Governor. The law directs the Commissioner of the Dept. of Environmental Conservation to promulgate labeling, restriction and distribution rules and regulations by Jan. 1, 1976, and to implement the restricted uses by Jan. 1, 1978. N.Y. is the second state to pass such a bill; Oregon was the first.

ASSOCIATION

The Occupational Health/Safety Programs Accreditation Commission (OHSPAC), a non-profit organization governed by eight professional societies including the American Conference of Governmental Industrial Hygienists, is contacting companies in the U.S. explaining the benefits of its accreditation process. Companies fill out document criteria that are evaluated by an OHSPAC review committee; the accreditation process reviews policies, programs, regulatory compliance, facilities and equipment among other things. Companies meeting all document requirements are then assigned a site inspection. If they meet all requirements they become accredited through OHSPAC for three years. OHSPAC headquarters are at Akron, Ohio.

MONITORING

Oak Ridge National Laboratory is conducting an inventory of biological monitoring programs in the U.S. The project is funded by the Council on Environmental Quality, ERDA and others. Information on the purpose, scope and availability of data from the various biological monitoring programs throughout the U.S. will be gathered and stored in a computer data bank. The data base is intended to be informative not evaluative, and to provide the basis for more unified decision-making regarding living natural resources. The participants in this inventory will receive a printed summary of the collected information.

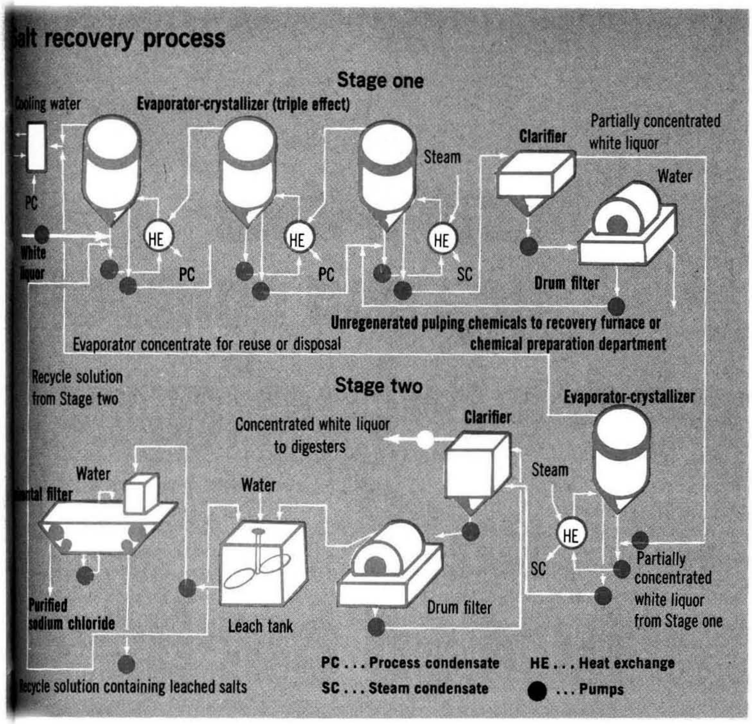
Better fuel economy could be achieved by monitoring the pressure of oxygen in fuel exhaust gases. According to John Logan, Chairman of UOP Inc., solid-state electrolytic sensors can be installed in a car's exhaust system, and can be replaced as quickly as a spark plug. They signal a minicomputer that would keep the carburetor "in tune", so that fuel is efficiently burned, and NO_x emissions are minimized. The sensors incorporate an electrolytic disc made with a mixture of zirconium and yttrium oxides onto which different forms of platinum are deposited as electrodes, one exposed to exhaust gas, the other to air. The disc is sealed into a ceramic tube against a conductive gasket.

TECHNOLOGY

Savings realized through recycling of water and chemicals could pay for the rental or lease of an evaporative recovery system that permits this recycling for metal finishing operations. This system, known as Wastesaver, is manufactured by Wastesaver Corp. (Bristol, Conn.) and is being used at more than 70 installations. According to J.T. MacDermid, Wastesaver president, the system eliminates any effluent from production lines on which it is used. He estimated that finishers starting pollution control with his company's system save enough on chemicals to pay for the system in one year, or even in as little as 30–60 days where precious metals are involved.

Costs of burning air pollutants are reduced with heat recovery systems. These systems use heat generated by burning solvent fumes to pre-heat new fumes prior to combustion, and to heat high-temperature hot water used in turn to heat platen presses. In the system, developed by CEA Combustion, Inc. (Stamford, Conn.), burning oxidizer exhaust gases heat incoming solvent fumes from 220° F to about 790° F, thereby providing oxidizer fuel cost savings of about 52%. Since part of the hot water needed for platen presses and ovens for industrial laminate manufacture in Germany and the U.S. is heated by recovered heat, generator fuel requirements are cut by about 80%, according to CEA. Exhaust gases have less than 50 ppm of hydrocarbons and 2 ppm of phenol, and there are no odors from the 23,540 scfm oxidizers.

Trapping gasoline vapors for recondensation and recycling is accomplished with a special hose developed by Goodyear (Akron, Ohio). The hose, known as Spiraflex 1400, is presently designed for use at bulk terminals and on tank trucks, as Phase I of an EPA gasoline vapor recovery program. Phase II is aimed at cutting vapor losses at the "gas" pump. At present, in an area like that of Washington, D.C., for example, vapor losses can account for more than 11,000 gpd of gasoline, and contribute to air pollution. In the first phase, trapped vapors will be taken in the tank truck back to the terminals where they will be reliquefied.



Can a kraft pulp mill have no wastewater treatment (wwt) facilities, and yet discharge no contaminated effluents? A patented salt recovery process (SRP), developed by Erco Envirotech Ltd. (Canada) brings such a situation about; the first full-scale installation of the SRP process will be at Great Lakes Paper Co. Ltd. (Thunder Bay, Ont.). This "closed cycle" process allows recovery and recycling of pulping and bleaching water and chemicals, thereby eliminating the need for wwt facilities. Only 4000 gal of fresh water are needed per ton of pulp, and net energy savings are put at 560,000 lbs of steam per ton of pulp. Very substantial capital and operating cost savings are foreseen.

Shellfish processing wastes could be good fertilizer for agricultural lands, E. Hugh Gardner of Oregon State University (OSU, Corvallis), said. These wastes, mainly from shrimp and crab, contain essential plant nutrients, such as calcium, nitrogen, phosphorus, potassium, and sulfur. However, it must be determined which crops will benefit most from shellfish wastes, Gardner pointed out, and that is why the OSU Sea Grant College Program has begun a two-year project to study the effects of shellfish wastes on agricultural lands. Another reason is that the Oregon Dept. of Environmental Quality will forbid estuarine discharge of these wastes after April 1976.

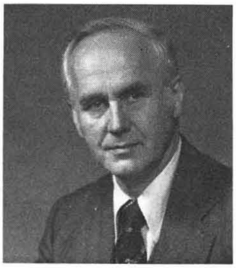
INDUSTRY

Mitsubishi Petrochemical Co. (Tokyo, Japan) has announced expansion of its environmental protection facilities. These facilities analyze air, water and industrial wastes, and examine food for purity and nutritional value. Mitsubishi's latest such expansion is at Yokkaichi (*ES&T,* June 1975, p 512), where it will provide full environmental,technical and advisory services in many aspects, not only for itself, but for other companies and municipalities. Mitsubishi also is the core of Japan's Reverzer Association, a nationwide network of companies using Mitsubishi's "Reverzer" system for recycling waste plastics and making new products.

Predicasts (Cleveland, Ohio) forecasts that water use will grow faster than population; water treatment faster than water use; and chemical treatment faster than other treatment. According to Predicasts, shipments of water treatment chemicals should approach 43 billion lbs by 1985, representing an annual growth rate of more than 11%/yr from 1974. Shipment value should increase at 14.5%/yr, to reach $3.4 billion by 1985. Predicasts sees more growth in polyelectrolytes than in inorganic coagulants; membranes more than filter media; ion exchange resins more than lime; oxygen more than air.

The National Association of Recycling Industries (NARI, New York, N.Y., *ES&T,* November 1975, p 1015), has taken action in the U.S. Court of Appeals (Washington, D.C.) to expand its suit against the Interstate Commerce Commission (ICC) and consolidate it into one major proceeding. Suits are against ICC's permission for rail freight rates to increase a total of 27% in a series of "hikes" that cost shippers over $75 million/yr. Especially odious to NARI is the ICC's 10% increase effective October 11. NARI has been charging that these rates discriminate against recyclables, and effectively subsidize railroads' losses on competing virgin materials shipments.

Con Edison (New York, N.Y.) and the Empire State Electric Energy Research Corp. announced a research project aimed at using solid waste and sewage sludge for production of electric power. Wright-Malta Corp. (Ballston Spa, N.Y.) will construct and operate a laboratory-scale model of equipment needed to use these materials. Essentially, the starting materials would be gasified. These materials could include not only sludge and municipal solid waste, but high-sulfur coal, residual oil, and many industrial wastes. Con Edison hopes that fossil fuel savings, together with solution of a serious municipal disposal problem, would be effected.



GM vice-president Kehrl

Howard Kehrl, executive vice president of General Motors, said that the catalytic converter is perhaps GM's most successful introduction of a major new automotive technology. Kehrl said that not only is the converter doing the emission control job it is supposed to do, but it has also had "an astonishing trouble-free record of reliability." He also said that the converter has been responsible for major improvements in new car fuel economy and driveability, and lower auto maintenance costs for owners. Kehrl cited GM research to determine future sulfate emissions under adverse weather and traffic conditions.

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The monitoring jackpot

A report from ICESA—the International Conference on Environmental Sensing and Assessment

Las Vegas, Nev., was the gathering place for 95% of the world's monitoring experts from 41 countries in mid-September for the first International Conference on Environmental Sensing and Assessment.

Pollutants—heavy metals, pesticides, organics, inorganics—in air, water, and land, and more specifically in such environmental samples as ground water and drinking water, were the subject of the more than 240 papers presented at the conference. It attracted more than 1000 attendees, 57 exhibitors, and 17 press registrants.

"There is virtually no subject in the area of environmental sensing and assessment that you have not covered in your daily sessions," Christian A. Herter, Jr., told the luncheon attendees. Herter, deputy assistant secretary of state in the Bureau of Oceans and International Environmental and Scientific Affairs, a position that was created by Congressional mandate about a year ago, referred to environmental affairs as the new dimension of U.S. foreign policy. The U.S. being perhaps the biggest polluter has the experience to help others with cleanup. "Because of our own history," Herter added, "we probably know as much about this subject as any other country . . . but we still do not know the big picture, even today. We can only speculate. This is why the conference . . . and the work that you are doing at home in this field is so relevant."

Earthwatching

Monitoring is a global need and the global view of the environment is the subject of Earthwatch (*ES&T*, March 1974, p 214). Earthwatch, the keystone of the United Nations Environment Program (UNEP), involves four aspects; monitoring is the first. It also includes research, data evaluation, and exchange of information about managing the state of the environment.

It is important to note that 90% of the environmental problems, particularly of industrialized countries, have to be dealt with on a national and local basis. Therefore, the Global Environmental Monitoring System (GEMS) will rely heavily on national and local monitoring activities.

"Over the next year or two there will be a series of meetings of highly expert country representatives to design pieces of the system in the seven program areas of GEMS" (see box), the spokesman from the Department of State noted. The first such meeting, on ocean monitoring, will take place early next year. Hopefully, shortly thereafter, there will be a meeting on global atmospheric pollution and its impact on climate.

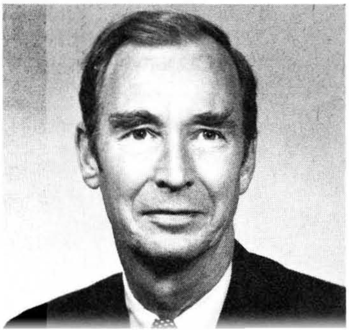
It is also important to point out that in the environmental field, there is no international enforcement machinery. Although Earthwatch, if successful, can provide basic information—from monitoring and research—it cannot provide a believable judgment and evaluation to the international community, Herter opines. But he is optimistic that UNEP could become the great intellectual force in environmental matters, utilizing and taking advantage of the best scientific brains in the international community.

At press time, no U.S. focal point had been announced for its monitoring activities although NOAA (the National Oceanic and Atmospheric Agency), which was created by a reorganization plan similar to another one that created the EPA, is perhaps the leading contender for that distinction.

Other UNEP business

The Information Referral Service (IRS) is another item of UNEP. UNEP asked each member country of its Governing Council to designate a lead agency as the IRS focal point. In the U.S., EPA was given this distinction and opened its facility in Washington, D.C., on October 6. The central computer for the IRS is located in Geneva, Switzerland. Data will not be exchanged in IRS. Rather, for example, if a country wants to know more about SO_2 controls or advanced municipal wastewater treatment, it will be referred to existing sources of information in various countries. Then, that country will have to establish direct communications with the sources.

Dept. of State's Herter
"Environmental affairs . . . new direction in U.S. foreign policy"



Another activity, under UNEP aegis, to be located in Europe, is the International Registry of Potentially Toxic Chemicals. Although it is being established now, a computer capability in this area probably will not exist for "two or three years," according to Herter's view.

New monitoring slant

What is becoming more obvious as we proceed down the monitoring path is the need for an integrated concept of monitoring. Rather than gathering more and more data on more and more pollutants in more and more environmental samples, the integrated monitoring concept tries to ascertain the total exposure to critical receptors; for example, the exposure of lead to an infant, SO_2 to a tree, or the pollutant burden to man from his food, air, and water. In other words, to add up all the exposures. It is also referred to as exposure monitoring—what the receptor, the newborn, the senior citizen, the emphysematic, and others are actually exposed to.

Then, perhaps for the first time one will be in a position to tell what the potential damage or harm might be. This concept has been pioneered by Dr. Delbert S. Barth, director of the EPA Environmental Monitoring and Support Laboratory (EMSL) in Las Vegas, Nevada, and general chairman of the conference.

Barth said, "This (ICESA) is the first major scientific conference to focus on monitoring pollutants of national and in-

GEMS—the Global Environmental Monitoring System

Its seven program goals:

- an expanded human health warning system
- an assessment of global atmospheric pollution and its impact on climate
- an assessment of the extent and distribution of contaminants in biological systems, particularly food chains
- an improved international disaster warning system
- an assessment of the state of ocean pollution and its impact on marine ecosystems
- an assessment of the response of terrestrial ecosystems to environmental pressures
- an assessment of critical problems arising from agricultural and land use practices.

ternational importance." He continued, "It is also the first major conference to look at health related or exposure monitoring, the kind of monitoring which determines a person's exposure to a pollutant from all routes including air, food, water, and skin combination. The World Health Organization is planning to implement a system for health related exposure monitoring on a global basis."

Also, in Washington, D.C., in October, a 3-day workshop session of the National Academy of Sciences and the Department of State discussed further aspects of monitoring activities including the seven monitoring items of the GEMS. This workshop is preparatory to the development of the U.S. position and the U.S. contribution to the GEMS. Delegates to that workshop included G. B. Morgan of the EPA Las Vegas EMSL, Ronald Engle (EPA Office of Research & Development, Washington, D.C.), Norman Glass (EPA Corvallis lab), and Ken Biglane of the EPA Office of Hazardous and Toxic Materials.

Other views

Dail Brown of NOAA mentioned that Earthwatch calls for the designation of establishment of three levels of assessment activities—world, regional, and national. A proposed framework calls for the designation of World Environmental Assessment Centers for each of the seven areas of the GEMS. Then, Regional Environmental Assessment Centers would support the world centers, which in turn would be supported by the national environmental assessment.

"The implementation of Earthwatch will call for the broadest international participation and cooperation," Brown said. "The months ahead will be critical to the future viability of Earthwatch, and the viability of Earthwatch may be critical to the future well-being of the Earth and its inhabitants."

Wilson Talley, EPA deputy assistant administrator, who represented EPA administrator Train at the ICESA, mentioned that the No. 1 priority in EPA R&D is effects research and noted that monitoring was part of it. He said that the EPA R&D effort amounts to about $250 million per year, of which $70 million goes for the support of 15 laboratories.

Noel Brown, chief of the UNEP liaison office (New York City), acknowledges that Earthwatch is both a showpiece and an index of viability of the UNEP. He refers to Earthwatch as "action planning at the global level." What is necessary in all this monitoring activity is the avoidance of discovery by accident—such as the depletion of the ozone layer. What is obviously needed is an early warning system, but not false alarms!

Looking ahead

The umbrella title of the Las Vegas meeting accounted for the fact that two meetings were combined to form the ICESA. The first was the International Symposium on Environmental Monitoring, with sponsors being the World Health Organization, EPA, and the University of Nevada, Las Vegas. The second meeting was the 3rd Joint Conference on Sensing of Environmental Pollutants with co-sponsors being nine organizations including the American Chemical Society (ACS) and the Institute of Electrical and Electronics Engineers (IEEE). The broad subject of the combined meeting was the dual theme of practical health-related monitoring and advanced technology for assessment of environmental pollutants.

In any event, the conference proceedings are being published by IEEE (New York City) in two volumes and should become available this month. Another such conference will more than likely be held in another two years. SSM

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CIRCLE 13 ON READER SERVICE CARD

The latest in wpc technology was not all that was exhibited and discussed. Fearless cleanup forecasts for the U.S. were made, and a Canadian view was presented

Water talk under the Florida sun

"In the domain of the environment, national frontiers do not exist. High standards in one country are useless if pollution exported by a neighboring country comes in and degrades water and air quality," the Hon. Jeanne Sauvé, Minister of Environment Canada, told *ES&T* on the occasion of the 48th Annual Conference of the Water Pollution Control Federation (WPCF, Washington, D.C.), held at Miami Beach, Fla., in October. Minister Sauvé emphasized that pollution does not respect manmade boundaries. Referring to the development of Canada's national effluent control requirements, she also told a luncheon session of the WPCF conference that the approach being used is a consultative one involving technical discussions with both industry and the provinces. "Canada's constitution has compelled us to take a cooperative, consultative approach to resolving water-use conflicts, pollution problems, control alternatives, and prevention of future water pollution," Minister Sauvé said.

One way to abate water pollution that might otherwise be exported is through improved control technology. Such technology, was discussed and exhibited at the conference, attended by over 8000, including about 575 exhibitors.


Environment Minister Sauvé
"Pollution respects no boundaries"


WPCF president Wagner
"Dollars are needed for innovation"

Carbon

One of the major problems associated with sewage treatment is odor control, especially where evil-smelling hydrogen sulfide (H_2S) and mercaptans are concerned. At the conference, Calgon Corp. (Pittsburgh, Pa.) introduced a new impregnated vapor phase (IVP) granular activated carbon (GAC) developed specifically to control these particularly obnoxious odors.

Raymond Poltorak, a development engineer with Calgon, told *ES&T* that an H_2S loading of 20–25% can be achieved with IVP carbon, as compared with the 9.5% loading possible with standard carbons. With methyl mercaptan, a 9.5% loading can be obtained with IVP, as compared to a 4.1% loading with a standard high-surface-area activated carbon. Poltorak added that an IVP system can safely handle a 100-ft/min space velocity and requires only a 1.5-ft carbon bed depth instead of the 3-ft bed depth normally required with standard carbons. In some cases, he said, IVP carbon can be chemically regenerated in place.

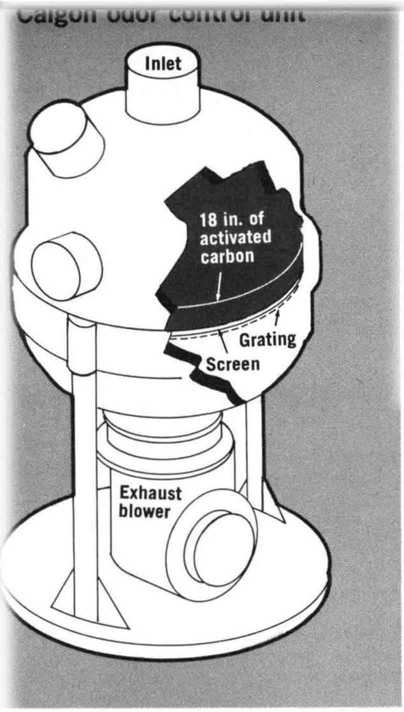
An illustration of IVP carbon's capacity can be derived from test data which showed that a 6-in. test bed installed on a vacuum filter exhaust was about one-third saturated after 700 hrs, and that the test bed was still removing the H_2S completely after 1000 hrs. Although H_2S concentration averaged 5 ppm during the test, actual levels varied from 1–40 ppm. At no time during these wide fluctuations in concentration was H_2S breakthrough observed.

Poltorak mentioned that 24 new IVP systems are now in various stages of design, development, or installation. He said that IVP carbon in conjunction with properly engineered hardware seems to offer more effective and economical control of sewage plant odors.

Measuring wastewater flow

One of the problems in the wastewater treatment area has been the development of flowmeters specially adapted to wastewater. At last year's conference in Denver, Colo., Envirotech Corp. (Menlo Park, Calif.) predicted that it would have such a meter by October 1975. At the Miami Beach conference, Frank Sebastian, senior vice president of Envirotech, announced that such flowmeters, which his company's Sparling Division developed, are now being marketed as Sparling "Series 500" obstructionless flowmeters. These meters have externally mounted electro-acoustic transducers that do not contact the fluid. Flow tubes range 4–24 in. System accuracy is within 1% or better of actual flow, and is unaffected by suspended solids, grease coatings, air bubbles, or changes in the physical properties of the flow streams, according to Envirotech.

Envirotech's National Sonics Division announced the development and availability of a sludge density meter. This device ultrasonically senses the density of sludges and slurries, including those from municipal sewage, water softening, industrial waste, and industrial processing. The meter provides continuous control, monitoring, and read-out, and also controls the density of suspended solids being pumped in any selected line. Envirotech says that calibration is



simple, and that the need for manual sludge sampling is eliminated.

Filtration

Two Massachusetts inventors, Roland E. Weber and Carl J. Zimmermann, announced that they are ready to offer a multi-stage system that can filter out more than 99.8% of suspended solids from raw sewage. Their company, Industrial Pollution Control Corp. (IPC, Ware, Mass.), offers a typical industrial system for approximately one-third of conventional system costs, and says that filtrate water would be so clean that it can be recycled into manufacturing processes. Indeed, IPC says that even bacteria can be removed, and that only "some chlorine" will take care of viruses to make it potable.

IPC has demonstrated its system by cleaning water from the Ware River, which is too heavily polluted for most fish or for any recreation. The filter unit demonstrated was a standard production model that processes 3000–12,000 gal/hr of water. Processed water was conducted to a swimming pool containing two dozen trout.

The firm says that its system is self-cleaning, and that the material taken out by the filters may be recovered for processing into useful products. For example, 1000 gal/hr units of the IPC system demonstrated the filtering of carborundum and granite powder from water at Barre, Vt., a granite quarry area. The recovered dehydrated waste can be used as a fine ball-bearing polish. Also, some filtered-out sanitary waste solids might be sold as fertilizer.

The IPC system design won for Weber and Zimmermann the Inventors Club of America's "Invention of the Year" award for 1974. In a recent proposal for a Massachusetts textile manufacturer, IPC predicted that by using a $150,000 system the company can save about $45,000/yr in water costs alone by recycling the filtered water back into the manufacturing process.

Water reuse

One of the ultimate objectives of water cleanup is wastewater reclamation, especially in relatively water-short areas, such as southern California. Toups Corp. (consulting sanitary engineers, Santa Ana, Calif.) evaluated reclaimed wastewater as an alternative water source for irrigation and ground water recharge for the south coast of Santa Barbara County, Calif. For that area and purpose, Toups estimated costs of $205/acre-ft for reclaimed wastewater, compared to $302/acre-ft for "imported" water from the California Water Project. For agricultural purposes, 4800 acre-ft/yr of reclaimed water could be supplied at a total project cost of less than $13 million. Side benefits would be nutrient reuse and fertilizer cost savings, as well as more water for agricultural expansion. However, reliability and controls must be emphasized if reclaimed water is to be used, according to Toups.

On the international scene, the Republic of Singapore (225 mi^2; population 2.25 million) has much incentive to reclaim wastewater, and has, in fact, been doing so since 1966. In that year, a wastewater reclamation plant that treats effluent from an activated sludge plant was completed; it supplies 5.4 mgd of process water to about 43 industries. The need for reuse is evident when one considers that most water around Singapore is that of the sea, and that catchment facilities for the 96-in. average annual rainfall are limited.

In 1972, Camp Dresser & McKee International (CDMI, Boston, Mass.) completed a study for a wastewater reclamation demonstration plant to provide a higher-quality effluent. In September 1974, a 100,000 gpd plant went into operation and has "excellent" effluent quality despite wide influent quality fluctuation, CDMI president Donald Cullivan told the conference. Treatment includes solids contact clarification; ammonia stripping; recarbonation; clarification; dual media pressure filtration; GAC; demineralization; and alternatives of chlorination and ozonation.

Needed: money

Addressing technological innovation for wpc, Victor Wagner, associated with Howard, Needles, Tammen and Bergendoff, and also 1975–1976 president of the WPCF, told a press conference, "We know how to do better, but we need the dollars." He pointed out that dollar commitments to wpc technology improvement have been declining in total dollars, and more so, in terms of constant dollars. For this and other reasons, including "gross underestimation" of costs of water cleanup, deadlines will not be met, Wagner said. This evaluation was also expressed by EPA administrator Russell Train who predicted that goals would be achieved, but that "we won't attain 1977 goals by 1977, or 1983 goals by 1983."

In fact, there is a means—known for centuries—of making very clean water from most types of dirty water, especially if energy and cost are no object. It entails distillation, as Wagner wryly reminded the press conference. However, perhaps with very few small-scale exceptions, distillation is not "in the cards"; thus, wpc technology continues its quest for other, more cost- and energy-effective means of counteracting water pollution. The feeling in Miami Beach during those sunny October days was that given reasonable time and deadlines, and somewhat more funding generosity, these more efficient techniques, even for nonpoint sources, hopefully, will evolve at a healthy rate.

JJ

When a load of chemicals spills...

... telephone wires crackle, and cleanup moves fast

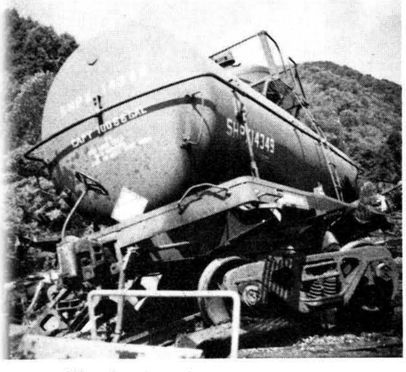
It was after 11 p.m. on July 22, when the plans Larry Lusher, HELP manager, had for a good night's rest were thwarted by the insistent ring of the telephone at his St. Albans, W.Va., home. The caller was Jerry Zook, dispatcher at the Penn Central Railroad's central office at Cincinnati, Ohio. Zook told Lusher that his switchman had smelled something pungent while switching a train that included six tank cars of liquefied petroleum gas (LPG) and one tank car of methyl isocyanate (MIC) toward Urbana, Ohio. He then asked Lusher, "What do you want me to do?"

Since LPG is explosive and MIC is highly toxic, Lusher had the train stopped two miles from Urbana. He then had all people from the train, as well as those in the surrounding four-mi^2 area evacuated, and the area totally sealed off by the state police. No sources of sparks, not even flashlights, were allowed in the area.

Lusher was ready to leave for the area, along with other HELP personnel, by helicopter, when he received another call telling him that a knowledgeable Penn Central road agent was on the scene and could assist. The agent had special safety-certified non-sparking monitors and flashlights, as well as self-contained breathing equipment. He checked the train for leaks that fortunately turned out to be nothing worse than ammonia; however, one can appreciate the need for strict precautions, for it could have been an LPG or MIC car that was leaking.

HELP

The hurry call came through the HELP (Hazardous Emergency Leaks Procedure) system that Union Carbide Corp. (UCC) maintains at its South Charleston, W.Va., plant. HELP was brought into being in 1964 because UCC's management felt that the company had a major business and moral commitment to safety in all phases of its involvement in the chemical industry, including transportation. Thus, the system, which to date has logged no fatalities, is set up to deal with chemical transportation emergencies, and is manned by trained operators. These operators know whom to contact seven days a week, 24 hours a day, and are at "hot-line" telephone 304-744-3487, for which Elva Mae Pridemore is supervisor. This number is to be used only to report a chemical transportation emergency.



Wreck. *In minutes, emergency team was on the scene at Marmet, W. Va.*

When an emergency call comes to that number, the operator will immediately contact one or more of six HELP coordinators who would be available, or Lusher. Information given to the HELP person should include

- specific location of the damaged container
- material involved
- type of container (drum, tank car, tank truck, other)
- name of caller and how to reach him
- description of conditions involved.

Once the information has gone to HELP, the coordinator will know which of 34 plant and 31 specialty contacts, including chemists, engineers, medical doctors, and other trained people, inside or outside UCC, may be called day or night for advice and assistance. These people are "patched" into the HELP system so that the emergency call becomes a conference call, if necessary. Safety, health, fire, and law enforcement officials are "patched" in as needed. Full instructions, including personnel safety and medical procedures go to the appropriate parties. In the event of telephone unavailability, or as otherwise needed, the system also works by radio. HELP applies principally to transportation of UCC products; however, in many cases, HELP will render emergency assistance where UCC products are not involved.

Chemtrec

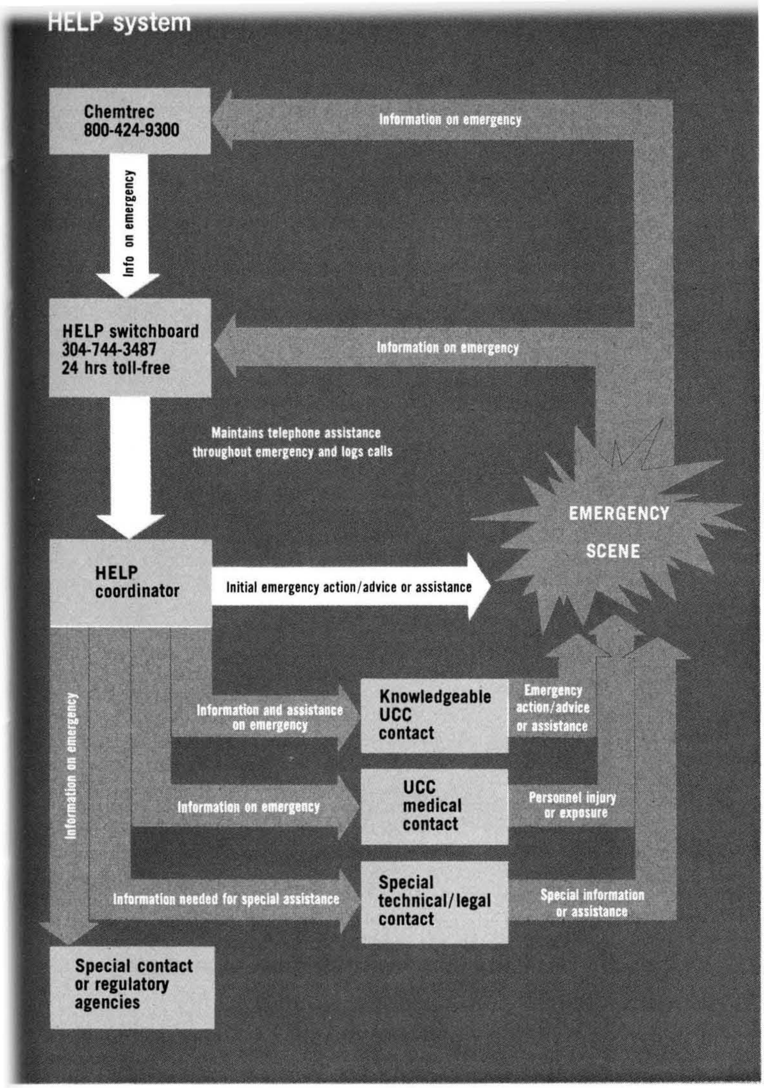
Founded in 1970, Chemtrec, the Chemical Transportation Emergency Center, is also manned at all times. It is a service of the Manufacturing Chemists Association (Washington, D.C.), organized and managed by John Zercher, and is reached, for emergencies only, by calling 800-424-9300, and giving the same type of information as is given to HELP (indeed, HELP is tied into Chemtrec. Chemtrec will provide immediate information on the nature of the product, and appropriate response data, and will then contact the shipper who makes his expertise available in order to solve the problem. Chemtrec will also contact the Bureau of Explosives, Chlorine Institute, National Agricultural Chemicals Association (NACA), or appropriate government agencies, as needed.

For example, one rainy night at Sharpsville, Pa., residents complained of skunk-like odors. The local fire chief found a leaking tank car on a siding; it was stenciled: "For Mercaptans Only." He called the Chemtrec "hot-line" and gave the tank car number, by which Chemtrec located the shipper. Chemtrec then had the shipper arrange for repair of the tank car; meanwhile, the fire chief was told that the odor could be reduced by flushing the spill area with household bleach.

Chemtrec keeps detailed files on chemical products, including trade names, and personnel contacts at manufacturers and shippers. Files are so organized that the Chemtrec representative on duty can readily find the necessary data to tell the caller how to handle the emergency, and to contact the shipper, or another system, such as HELP. The object is to initiate emergency countermeasures as soon as possible, because some escaping chemicals can be environmentally harmful, explosive, flammable, offensive, toxic, or some combination of these.

Other systems

Other "hot-line" systems are available. For instance, in Canada, there is the Transportation Emergency Assistance Plan, or TEAP system. TEAP ties into HELP, Chemtrec, and others. Since 1970, NACA (Washington, D.C.) has maintained a "hot-line" for Class B poison pesticide leaks or spillage, and has the services of 14 NACA member companies and more than 40 safety teams; the number is the same as Chemtrec's. If chlorine is a problem, one contacts CHLOREP (Chlorine Emergency Plan) of The Chlorine Institute (New York, N.Y.), through one's supplier, or Chemtrec. Also, under HELP, there is WEAP (Waterways Emergency Action Plan) at 304-747-0001, or at HELP's number.



Many other chemical and oil companies also have "hot-line" numbers under various acronyms.

Recently, Chemtrec called HELP for advice on what was first taken to be a chemical fire. Realizing that the "smoke" was a highly toxic pesticide, potentially fatal to the firemen under such concentrations, the HELP coordinator called the nearest NACA Union Carbide contact. HELP operators maintained a four-way "patch" between HELP, the NACA expert, the exposure site, and the treatment center, and staved off what could have been a lethal situation. Meanwhile, Chemtrec found the manufacturer who, incidentally, had stopped making the product five years previously.

HELP and WEAP became involved in early August, when a faulty rail on the "Chessie" System caused a 29-car train wreck at Marmet, W.Va., and a spill of huge quantities of glacial acetic acid into a stream that empties into the Kanawha River. Coordinators were on the scene almost an entire weekend; ironically, they had been returning from another emergency job when the wreck occurred—no rest for the weary! Fortunately, there were no significant environmental consequences of the acetic acid spill.

Computerizing

Lusher told *ES&T* that there are now plans for the HELP program to computerize the records of all transportation incidents. This computerized data bank should offer a number of benefits. For example, perhaps certain hazardous chemicals will show up in leaks and spills more often than others, and new methods of packing and shipping such chemicals may be developed. Also, the availability of leak or spill countermeasure instructions would be enhanced.

There are significant data on which to build this bank, and more come in all the time. Lusher said that emergency calls average about 15 per month within a general range of 6–25.

One emergency packing method that the data bank might further enhance is called "overpacking." Overpacking at UCC involves carefully sliding a leaking or damaged drum into a container of surgical-grade stainless steel—each such container costs $600. HELP people know at all times where each of these containers is. The bad drum sealed inside is returned to the nearest UCC plant, decontaminated, and scrapped. In some cases, the product is decontaminated and scrapped; in others, it is reclaimed.

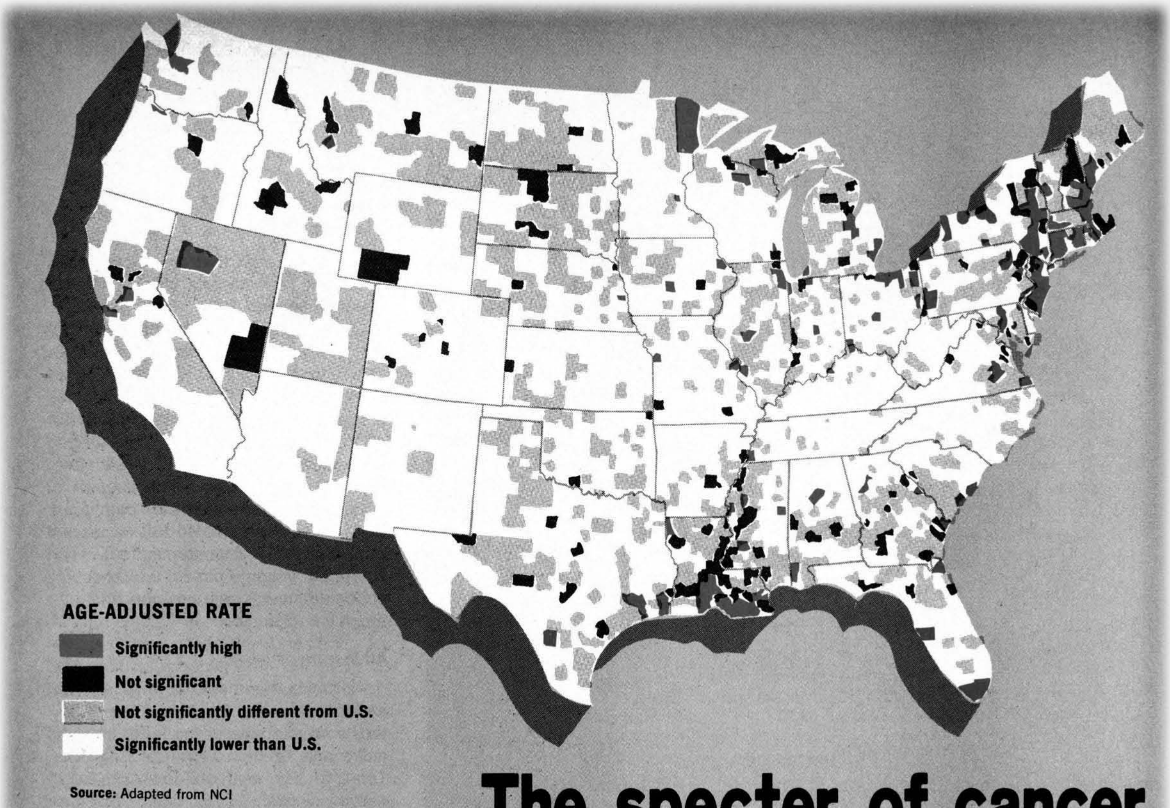
All in a day's work

An incident can involve anything from an innocuous dye to some "hairy" material. An example of the latter involved a fire at a chemical plant at Columbia, Tenn., in July; nearby stood tanks full of carbon disulfide (CS_2). Often, CS_2 can ignite spontaneously in air, and becomes CO_2 and SO_2. If the air is humid, as on that July day, extremely toxic hydrogen sulfide could also be produced through reaction with the air's moisture. Lusher advised evacuation of the plant and the area within one-half to one mile of the CS_2 tanks.

On the other hand, Chemtrec received a call from the London (England) Fire Brigade. A drum of chemical product from New Jersey, en route to Spain, was leaking at Heathrow Airport. The drum contained a harmless dye, but the Brigade needed to be assured.

On October 20, in the presence of an *ES&T* editor, Lusher was informed that HELP coordinator Jack Burgess received a call about a drum containing toluene diisocyanate (TDI), a polyester feedstock. TDI is quite toxic, adversely affecting skin, eyes, lungs, and mucous membranes. The TDI drum was punctured by a fork lift at Louisville, Ky. Burgess explained how to neutralize and clean up the spill, as well as how to patch the punctured drum. The TDI drum would then be overpacked and shipped to UCC's plant to Institute, W.Va., for reclamation.

That call came in at 11:38 a.m., when Burgess, who is also department head of drumming chemicals at UCC's South Charleston plant, telephoned Lusher to pass on information concerning the Louisville incident, and to obtain guidance, if needed. Oh, well, it's all in a day's work! JJ

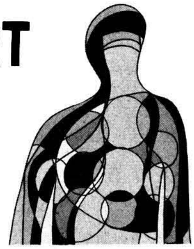


Source: Adapted from NCI

The specter of cancer

ES&T's Lois Ember finds that environmentally-caused diseases are definitely on the increase, that early warning systems to flag emerging problems are urgently needed, and that lower life forms are being considered in the design of screening systems

SPECIAL REPORT



This year 600,000 people in the U.S. contracted cancer, and more than 300,000 have died from it. From 60–90% of all human cancers are caused by environmental factors, including cigarette smoking. These figures do not include the debilitating effects and even deaths resulting from cardiovascular and respiratory diseases, also suspected of having environmental causes.

Technological man is rudely being persuaded that he cannot with impunity tamper with his environment. Whichever way he turns he is being bombarded with the deleterious effects of his vaunted technology. Like the mythical multiheaded Hydra, his problems seem to multiply with each solution he effects. Consider these:

- To protect himself from the noxious exhausts spewing from his automobile he designs the catalytic converter. An answer to hydrocarbon and carbon monoxide emissions is converted to a potential sulfuric acid problem.
- To generate electricity to drive his civilization, he burns fossil fuels. The sulfur oxides emitted pollute his air and fall to the earth as acid rain to pollute his crops and waters.
- To make his polluted waters drinkable, he disinfects them with chlorine. The chlorinated hydrocarbons formed are potentially cancer-inducing compounds.
- To propel hair sprays, deodorants and household cleaners he uses Freon in pressurized cans. This Freon is now suspected of destroying the stratospheric ozone layer. More ultraviolet rays may then strike the earth causing an increased incidence of skin cancer.
- To earn a living he unwittingly subjects himself to cancer-causing organic chemicals, asbestos, arsenic . . . and the list seems interminable.

Hercules killed his serpent by cauterizing the necks as he cut off the heads. The U.S. Congress has attempted to cauterize the nation's increasing pollution problems by passing the Clean Air Act and the Federal Water Pollution Control Act Amendments, the Occupational Safety and Health Act, and the Safe Drinking Water Act among others. The proposed Toxic Substances Control Act, introduced every year since 1973, will probably die again this legislative session.

How successful have these laws been in protecting the health and welfare of the American people? Not too successful if medical (epidemiological) evidence of rising rates of diseases such as cancer is considered.

Yet, there are some who will insist that if cancer, respiratory and cardiovascular illnesses are social diseases, the result of urbanization and industrialization, then the same technological genius that went into their cause can be harnessed for their prevention.

Cancer mapping

Analytical studies have shown that manmade chemicals, suspected or known to be carcinogenic (cancer-causing), are found in the air we breathe, the water we drink and the food we eat. Of the estimated 2+ million chemicals known, no more than 6000 have been tested to determine whether they cause cancer; only 1000 have been shown to possess any carcinogenic activity. And, probably only 500 of these 1000 compounds are potentially hazardous to man, according to John A. Cooper, II, deputy associate director for carcinogenesis, National Cancer Institute (NCI).

There is, at the moment, no systematic way to prescreen new substances before they enter the environment. After-the-fact testing is being conducted at NCI where, at any one time, some 450 compounds are assayed for their cancer-causing potential.

To date NCI lists only 32 compounds as substances known to be carcinogenic to man. Included in this list are vinyl chloride, asbestos, chromium (hexavalent), tobacco, β-naphthylamine, benzidine and the cattle-fattening hormone DES (diethyl stilbesterol). The Occupational Safety and Health Administration (OSHA) within the Dept. of Labor has set health standards for four of the above mentioned substances.

In an effort to unravel environmental and occupational factors in the cause of cancer, scientists in the epidemiology branch of NCI have turned to the computer to analyze and map cancer deaths. A 4-yr study, which covered the U.S. by counties for the period 1950–1969, has highlighted geographic clusters where the incidence of certain types of cancers is high.

When the NCI scientists correlated industrial activity with high-cancer-risk counties, they found that white male workers in the chemical industry had high rates of lung, liver and bladder cancers; these rates could not be explained by factors such as urbanization and socioeconomic class. High rates of bladder cancer were found in white males in counties clustered in areas where automobiles and two types of heavy machinery are manufactured.

Copper, lead and zinc smelter workers were found to have a high incidence of lung cancer. Since females in these same counties were also found to have above average rates of lung cancer, it was suggested that hazards of the workplace were being spread to the home and the surrounding community. An airborne by-product of the smelting operation, arsenic, a known human carcinogen, is the suspected cause. Another example of this invasive phenomenon, again with lung cancer, is found in asbestos workers, their families and in the community surrounding the factories.

The NCI group responsible for the mapping studies is now refining its data. In more detailed studies of the cancer hot spots, the researchers are examining the influences of urbanization, ethnicity, migration and constituents of the water supply on cancer rates.

The NCI scientists, T. J. Mason, F. W. McKay, R. Hoover, W. J. Blot and J. F. Fraumeni, Jr., caution that the maps only provide clues to factors that contribute to cancer causation; they emphasize that the maps should act to stimulate further studies.

Cancer interest at EPA

Taking up the NCI challenge, the U.S. EPA this July awarded an 18-month contract to System Sciences Inc. (Bethesda, Md.) to study the correlation of cancer mortality between 1968–1973 with the industrial structure of the U.S. in 1959. What is being sought is the relation of exposure of industrial effluents and emissions to the incidence of cancer. Edward Brooks, in EPA's Office of Toxic Substances, and project officer on this contract, told *ES&T* that the study may be expanded to include diseases other than cancer, such as respiratory and cardiovascular diseases.

Another group within EPA that has sensed an increased need to untangle the mysteries of cancers' causes is the Office of Health and Ecological Effects (HEE) within the recently reorganized Office of Research and Development. Under the direction of Roy E. Albert, acting deputy assistant administrator, HEE is charged with providing the necessary scientific information to support the promulgation or enforcement of standards and regulations. Long-term research programs are designed to gain a better understanding of the effects of environmental contaminants on living entities, including man, and on the ecosystems in which these entities exist.

Albert has been designated the coordinator for all cancer matters within EPA, which is now formulating a policy on carcinogens. He realizes that there are substances that cannot be eliminated from the environment and the problem is to "control them (carcinogens) to minimize the risk of cancer, and yet permit their use in a fashion which is not economically prohibitive."

Early warning systems

According to reliable estimates, more than 200,000 chemicals of commerce are available today, and hundreds more enter the marketplace yearly. The need to predict their potential hazards to man is imperative. Yet, neither the Clean Air Act nor the Federal Water Pollution Control Act Amendments contain provisions for the premarket or premanufacture review of health and safety data for chemicals. To date, no Toxic Substances Control Act exists. Because there is a lag period between the reduction of the release of contaminants to the environment and the resulting decrease in concentration in the environment, anticipatory actions and early warning systems are needed.

Chemicals carcinogenic to man

aflatoxin
2-aminobiphenyl[a]
arsenic[a]
asbestos[a]
auramine
benzene[a]
benzidine[a]
bis(chloromethyl)ether[a]
cadmium oxide and sulfate[a]
chromium compounds[a]
hematite[a]
2-naphthylamine[a]
nickel compounds[a]
n,n-bis(2-chloroethyl)2-naphthylamine[a]
soot and tars[a]
stilbestrol
vinyl chloride[a]

[a] found in the workplace
Source: International Agency for Research on Cancer

Conceptually, lower life forms could be used to monitor the environment for emerging hazards, and act as indicators of potential hazards to man. They could also be considered for use in the design of new, improved and more rapid in vitro screening systems for toxic substances.

An important component of an early warning system would be a specimen bank such as the Registry of Tumors in Lower Animals, tucked away in the labyrinth of the Smithsonian Institution. Invertebrate or cold-blooded vertebrate specimens with lesions, collected from natural habitats, zoological parks, aquaria and laboratory experiments, can be sent to the Registry to be preserved and studied. The specimen may be a slide, a bit of tissue, a head or the whole animal. A report of the findings is eventually sent to the contributor.

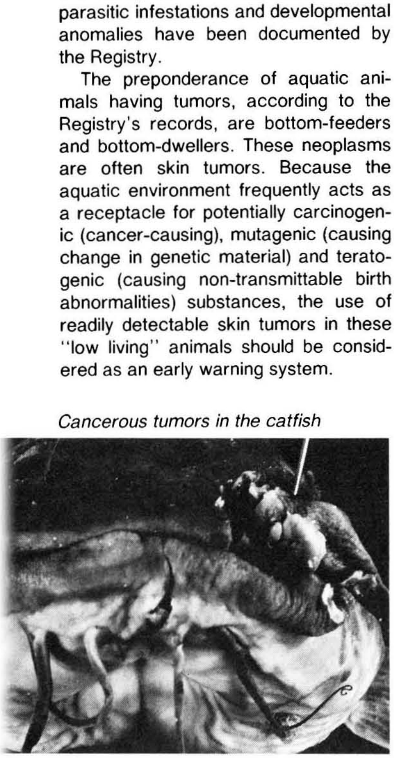
The idea for the Registry emerged within NCI in 1963 and received the blessings of the National Academy of Sciences-National Research Council that same year. Two years later, in 1965, the NCI approved the concept and awarded a contract to the Smithsonian the following year.

A collection of tumors

The Registry's collection now contains about 5000 specimens of which 55% have neoplasms (tumors). The highest percentage of tumors (60%) are found in bony fish, but substantial numbers are found in amphibians (16%) and mollusks (14%). Neoplastic lesions have even been documented in the fruit fly, the insect that has contributed so hugely to our knowledge of genetics. A variety of other disorders caused by viral or bacterial infections, parasitic infestations and developmental anomalies have been documented by the Registry.

The preponderance of aquatic animals having tumors, according to the Registry's records, are bottom-feeders and bottom-dwellers. These neoplasms are often skin tumors. Because the aquatic environment frequently acts as a receptacle for potentially carcinogenic (cancer-causing), mutagenic (causing change in genetic material) and teratogenic (causing non-transmittable birth abnormalities) substances, the use of readily detectable skin tumors in these "low living" animals should be considered as an early warning system.

Cancerous tumors in the catfish



In addition to analyzing specimens to determine lesion types and probable causative agents, the Registry's staff under the direction of John C. Harshbarger has also developed a computerized data bank of information collected from Registry records and published literature. The staff, often in conjunction with the specimen contributor, conducts experimental studies on the nature and cause of tumors in these lower life forms.

The Rainbow trout is often touted as the prime example for the use of tumors in fish as a reliable indicator for the presence of potential human carcinogens. These fish, raised in hatcheries, were found to have a high rate of liver tumors. The cause was traced to fish food contaminated with aflatoxins. Aflatoxins have since been found to be carcinogenic to certain mammals, and epidemiological evidence strongly suggests that they are carcinogenic to man. As a result of these studies, the Food and Drug Administration has established tolerance limits for aflatoxins in food.

The Rainbow trout emerged as an unwilling indicator for cancer, and was pressed into service as an experimental model. It may yet serve as the rallying point for increased use of lower animals in research directed to the cause and prevention of cancer in man. Harshbarger and his staff, buttressed by documented evidence from the Registry, offer strong arguments for their use.

Specimen banks

A more comprehensive specimen and data bank, a National Environmental Banking System, may yet come into being. Suggested as early as 1973 at a conference sponsored by the National Science Foundation (NSF), the feasibility of such a banking system is now being studied by the EPA with the cooperation and funding of the NSF and the National Bureau of Standards. The Human Effects Research Laboratory (Chapel Hill, N.C.) within EPA's Office of Health and Ecological Effects is spearheading this $300,000 project.

As ultimately envisioned, the banking system would preserve, store, catalog and selectively analyze specimens for pollutants. Samples of human, other animal and plant tissue as well as air, water, soil and food would comprise the specimens in this system. It is assumed that the data derived from the analyses would be useful in the early detection of problems, and in forecasting future problem areas. The storage of specimens would provide a flashback capability should new and unforeseen problems emerge.

A case for the use of marine animals in biomedical research was strongly made at a conference held earlier this year in Washington, D.C. Conferees emphasized that some marine organisms would make excellent model systems for study because they contain organs and even cell types similar enough to man's to manifest similar disease states—diabetes in the carp, arteriosclerosis in the Pacific salmon, and epilepsy-like convulsions induced in neurons of sea slugs.

Because these marine organisms are simpler life forms they can be more thoroughly probed to yield secrets of disease processes that have so far eluded investigators who have used the more common laboratory animals—rodents, cats, dogs and monkeys.

These lower life forms, particularly marine invertebrates, have been so little studied that the whole area of invertebrate biology is, as Paul Yevich, a scientist participating in the Marine Biomedicine Research conference said, "an exciting world of unknowns."

Hazards of the workplace

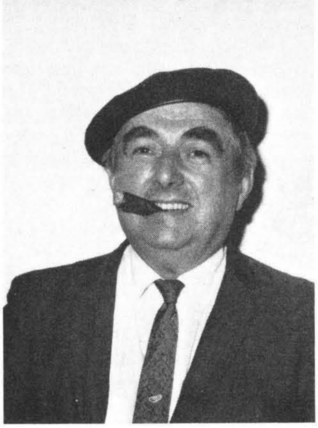
Heavy metals, minerals and organic chemicals are hazardous concomitants of industrialization. The early Romans recognized the dangers of mercury, and criminals sentenced to death were sent to work in the mercury mines. And 200 years ago, Percivall Pott reported cancer of the scrotum in chimney sweeps. But it is only recently, because of the long latency period between exposure and first evidence of clinical disease (the time-to-tumor incident) that arsenic, asbestos and synthetic chemicals of industry, introduced since World War II, are being identified as cancer-causing agents.

A research group headed by Dr. Lorenzo Tomatis of the International Agency for Research on Cancer (Lyon, France) studied about 200 commonly used chemicals and linked 17 to cancer in man. Of the 17 chemicals known to be carcinogenic in man, 14 are hazards of the workplace (see box material). Most of these hazards can be eliminated or reduced by changes in production processes and by using emissions control equipment.

Because of the astronomical number of chemicals synthesized yearly, and the long latency period before cancer becomes apparent, the backlog in testing for potential carcinogens simply increases. More rapid screening tests, using bacteria instead of animal systems, are being developed. But, until these bacterial systems are perfected, labor unions representing textile, chemical, atomic, and steel workers among others are beginning to work with medical doctors (epidemiologists) to set up studies and surveillance techniques to detect cancer and other diseases linked to occupational hazards.

An interesting, non-chemical occupational hazard—whole-body vibration—

Paul Yevich walks down the aisle on his way to the podium and your wandering mind snaps to attention. This is not the expected denizen of the staid scientific meeting. His short, ample figure is clothed in a dark boxy suit (rumpled? no, but your mind plays tricks). A green beret sits on his head, canted at a rakish angle. Protruding from his mouth, a stunted soggy black stogie. He begins to talk and you'll swear you hear "dems" and "doz" but it's just his strong Pennsylvania accent and your own mind supplying the necessary accoutrements to complete this Damon Runyonesque character.



But, strip away this facade and you'll find the patient scientist who has collected and dissected more than 50,000 marine specimens, and who has published more than 25 articles on studies undertaken at EPA's National Marine Water Quality Laboratory (NMWQL) at Narragansett, Rhode Island. Yevich, a research biologist studying diseases of marine invertebrates, was instrumental in the formation of the histopathology unit within the NMWQL when the EPA was known as the Federal Water Quality Administration. With the establishment of this unit came the need to adapt mammalian techniques, or devise new methods to prepare marine specimens for routine tissue examination. The methods that Yevich developed are now documented in the second edition of EPA's Biological Methods Manual.

With his limited staff, which consists of himself, a technician and "any part-time help we can get," Yevich has recently been studying, at the cellular level, the effects of oil pollutants on marine life. He has documented gonadal tumors in soft shell clams, a species in which cancer was not thought to exist. These clams have been collected since 1971 from an oil spill site at Long Cove, Searsport, Me. His control animals, collected in waters only 50 mi away, show no evidence of tumors.

Although the histologic anatomy of many marine species is negligible, knowledge of seasonal changes in the tissues of these life forms is even more meager. To fill this gap, Yevich and his staff have been collecting specimens from their native habitat once a week, every week of the year. They have found unusual cyclic morphological changes in the nervous, renal and digestive tissues of many of the invertebrates studied. They have also noted histologic differences between animals raised in captivity, and the same species collected from the field.

During the course of the research, Yevich's histopathology unit has collected a vast amount of information on marine species (ranging from protozoa to fish) that have been exposed to heavy metals, hydrocarbons and detergents. This information is being translated to a series of atlases on the comparative histology and histopathology of marine animals. The first atlas, on the comparative histology of commercially important bivalves, is now being compiled and will be published next year.

was studied by Thomas H. Milby, Robert C. Spear and Carl A. Keller at the University of California-Berkeley. Through the cooperation of Local No. 3 of the International Union of Operating Engineers, and under NIOSH funding, the scientists were able to study the diseases contracted by construction workers exposed to chronic, low-frequency, high-amplitude, whole-body vibration.

From the Union's health plan records covering a 20-month period, about 3900 claims for medical services were collected. The exposed group consisted of heavy machine operators, while the control group consisted of workers (such as oilers and soil testers) not subject to whole-body vibration but otherwise working on sites where machine operations are in progress.

In general, those construction workers exposed to whole-body vibration were more likely to file claims for medical services than workers in the control job classifications. Only with diseases of the male genital organs was a strong correlation with whole-body vibration apparent. But, a peaking phenomenon became evident. When heavy machine operators became afflicted with certain types of heart disease, a particular type of obesity, gout or diseases of the muscles or skeleton, the data suggested that they left the jobs that subjected them to whole-body vibration.

NIOSH/OSHA activities

The National Institute of Occupational Safety and Health (NIOSH) and OSHA have undertaken a joint 3-yr effort to accelerate the development of health standards. By late 1977, about 275–300 complete health standards will be promulgated.

In 1971, OSHA issued its first set of 500 threshold limit exposure standards for chemical substances. These standards were adopted in one full swoop from the American Conference of Government Industrial Hygienists. Four hundred of these 500 standards are to be expanded into complete health standards under the joint NIOSH/OSHA Standards Completion Project (SCP). A complete standard includes monitoring, medical surveillance, analytical methods, housekeeping and record keeping requirements.

OSHA's performance in the promulgation of health standards has not been sterling. To date, the Agency has promulgated complete health standards for 16 substances, and has proposed another 23 standards (see box material).

Under the 1970 Occupational Safety and Health Act that created NIOSH and OSHA, NIOSH was charged with developing criteria documents that are sent to OSHA for standards development. So far, 27 criteria documents have been sent to OSHA; from that number OSHA has promulgated one standard—for asbestos. By the end of this year, OSHA will receive seven more criteria documents from NIOSH, including one for oxides of nitrogen and another for hexavalent chromium compounds.

Don't drink the water

On November 7, 1974, the Environmental Defense Fund (EDF), a New York-based national environmental organization, released a report by Robert H. Harris, a water quality engineer. His report stated that the water that New Orleans, La., draws from the Mississippi River contains chemicals suspected of causing cancer in man. The report mentioned that NCI had found Orleans Parish, La., to be a cancer hot spot, and then went on to draw the implication that the river water may be a factor in the high incidence of cancer in certain Louisiana parishes.

After review of the EDF study the NCI concluded that the report "in no way implicates water as an explanation for the high cancer rates in the parishes of Louisiana which draw all or part of their water supplies from the Mississippi River." The NCI review further stated that undisciplined methods had been used to arrive at the conclusions in the EDF report.

The very next day, on November 8, 1974, the U.S. EPA released its report announcing that 66 trace organic chemicals had been found in New Orlean's drinking water supply. Administrator Russell Train, that same day, ordered a nationwide study of drinking water supplies of 80 major cities to determine the extent of chemical contamination. This survey found that 95% of the water tested contained small quantities of organic chemicals, some of which were under study at the NCI for their cancer-causing potential.

On December 17, 1974, President Gerald Ford signed into law P.L. 93-523, the Safe Drinking Water Act, which authorized the EPA to set national standards for drinking water, but left enforcement of the standards to state and local authorities. In March 1975, the EPA proposed draft standards that set limits for organic and inorganic chemicals and pesticides in drinking water supplies. The standards, some of which have already been modified, become effective in December 1976.

The concentrations of the suspected carcinogens found in the nation's drinking water supplies are very low, and probably went undetected for years because analytical methods were not yet sophisticated enough to detect them. Whether these low levels can be implicated in the etiology of cancer is a question that begs an answer.

Some scientists have called P.L. 93-523 an unnecessary response to the perceived crisis of the moment. A NCI report to the Surgeon General stated that "no level of exposure to a chemical carcinogen should be considered toxicologically insignificant for man." Whether a safe threshold for exposure to a carcinogen exists is a widely debated and as yet unanswerable question. With P.L. 93-523, the U.S. has chosen to err on the side of safety, at least until the ultimate goal—zero discharge of pollutants into the nation's waterways—of another federal water act, P.L. 92-500, becomes technologically and economically feasible.

A collision course

What does a one-industry town do when it discovers that the industry is polluting its sole source of drinking water with a suspected carcinogen? This is a question many small towns throughout the U.S. may be forced to answer in the very near future. It may take another Solomon, however, to solve the resulting repercussions when environmental considerations collide head-on with economics.

Case in point: Duluth, Minn., whose source of drinking water is Lake Superior. Fifty-five miles upshore of Duluth, in Silver Bay, Minn., The Reserve Mining Co. daily dumps about 67,000 tons of its powdered rock wastes, taconite tailings, into the Lake. Reserve has been dumping its wastes into the Lake since 1955. The tailings contain asbestos-like fibers.

The Lake's waters are so contaminated that a quart of unfiltered water taken from Duluth's water system contains about 50 million asbestos-like fibers, according to an EPA scientist.

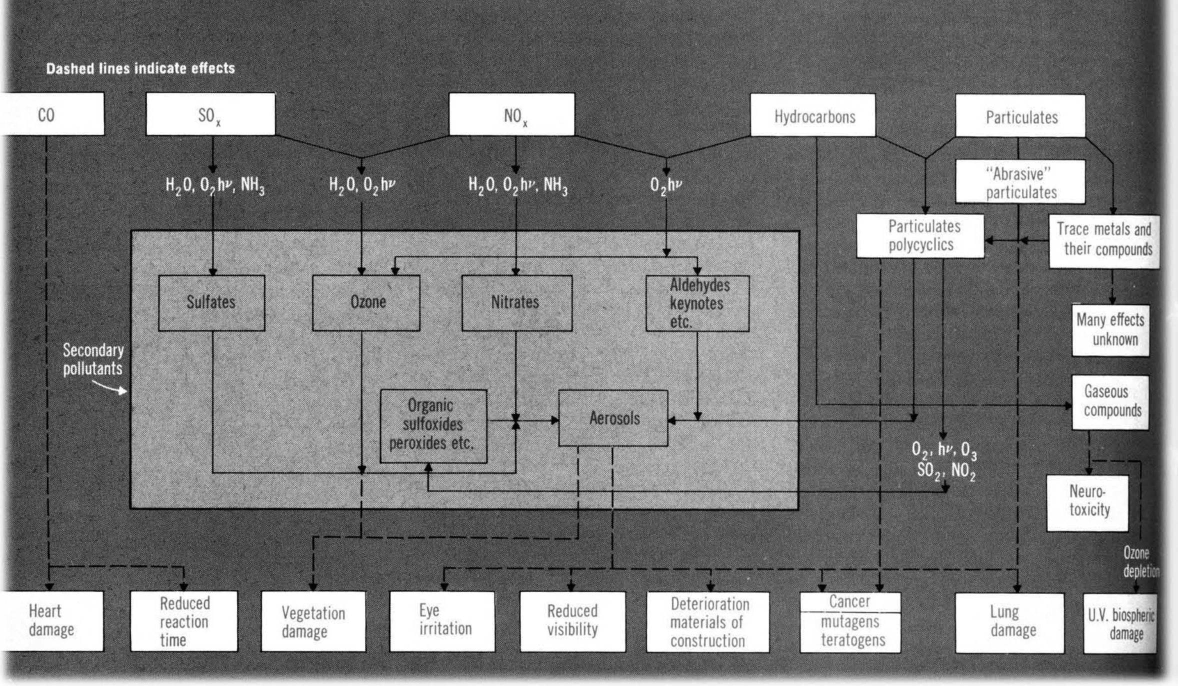
Inhaled asbestos has been implicated in the etiology of lung cancer, but no one knows its effects in man when it's ingested. Epidemiological studies are not conclusive. The fibers have only been in Duluth's drinking water for 20 years, too short a period for carcinogenic effects to show up.

About 3000 people in Silver Bay work for Reserve. These people are concerned about the long-term health effects of asbestos, but they also fear for their jobs.

EPA sued Reserve Mining in 1972 for polluting Lake Superior. In April 1974, after nine months of inconclusive hearings, a federal judge ordered the plant closed. Two days later, on appeal, the 8th Circuit Court of Appeals permitted the plant to reopen. In March 1975, the appeals court ruled that since Reserve's wastes are only "a potential threat to public health," the plant could remain open. However, Reserve, working with the State of Minnesota, was ordered to devise an alternative plan to dispose of its wastes on land (and also to clean up its air emissions). If the State and Reserve are unable to agree on a method of land disposal, the plant will have a year in which to phase out its operations.

In the meantime, Duluth, at its own expense, is spending $5.25 million to update its antiquated water system, which meets all present water quality standards but wasn't designed to re-

Primary and secondary air pollutants and their health & ecological effects



OSHA promulgations to date

Some 500 exposure limit standards[a] (adopted from ACGIH standards)

16 complete health standards: 14 for carcinogens; 1 for asbestos; 1 for vinyl chloride

23 proposed standards: 6 for ketones; 11 for toxic substances; 1 for lead; 1 for toluene; 1 for asbestos (revised); 1 for beryllium, 1 for trichloroethylene; 1 for coke oven emissions

[a] 400 are in the Standards Completion Project to be expanded into complete health standards

move cancer-causing substances. Filters are being built at the central water treatment plant that will remove the asbestos fibers before the water is pumped into the distribution system. The city hopes the courts will eventually award it damages in the Reserve Mining Case.

Water disinfection

Present disinfection processes may not be as effective in combating viral contamination of drinking water as they are in controlling bacterial contamination. The coliform test, the current proof of disinfection, may not be a reliable indicator of viral infection.

Viruses of major concern, the enteric viruses that infect the digestive tract of man and are excreted in the feces, are likely to be found in waters recently contaminated with sewage. Very little is known about enteric virus levels in U.S. drinking water. Documented evidence for waterborne virus disease exists only for hepatitis type A. But, even if enteric virus levels are found to be very low, these low levels may well be capable of causing infection in man.

Experimental evidence indicates that enteric viruses are much more resistant to conventional sewage and advanced wastewater treatment processes than are coliform bacteria. Little is known about the ability of ozone, an alternative disinfectant to chlorine, to inactivate enteric viruses.

A first step in evaluating the public health significance of enteric viruses in drinking water would be the determination of the presence and amount of these viruses in potable water supplies.

Beyond criteria pollutants

EPA's latest estimate (1970 data) of damage to health from air pollution is $4.6 billion. No mere pittance. So the EPA, under the Clean Air Act mandate, has established ambient air standards for a half dozen materials—sulfur oxides, nitrogen oxides, carbon monoxide, hydrocarbons, photochemical oxidants and particulate matter. As defined by EPA, particulate matter covers hundreds of substances that may have harmful biological effects. But secondary particulates, those formed in the atmosphere by the reaction of a primary pollutant (emitted directly from a source) under the influence of such factors as water vapor, ultraviolet radiation and ozone, are also of concern. These are generally very fine particles in the aerosol class (0.01 to 10–20 μ), and those less than 3 μ in size are termed respirable particulates.

When air containing aerosols is inhaled, 80% of the respirable particles will be deposited deep in the lungs, in the alveolar ducts and sacs. It is these very small particles that contain the higher concentration of hazardous materials that are adsorbed onto the primary pollutant.

Airborne pollutants besides the primary pollutants include polynuclear aromatic hydrocarbons, largely adsorbed onto particulate matter, many of which are carcinogenic, mutagenic and teratogenic; trace elements such as arsenic, mercury and chromium present as inorganic salts adsorbed onto particulate matter; gases such as carbon dioxide and fluorochloromethanes; pesticides; abrasive particulates such as silica and asbestos; and miscellaneous compounds such as sulfates, nitrates and nitrosamines—the reaction products of primary pollutants. Some of the health effects of these pollutants are shown in the box material.

Complicating the picture of pollution and human health is the fact that many natural and manmade pollutants interact synergistically. Here, a not-so-harmful pollutant alone becomes an extremely harmful one in the presence of a second or third material.

The sulfate problem

Respirable particulates of increasing concern for which no ambient air quality standard now exists are the sulfates and sulfuric acid. Sulfates, according to the air quality criteria document for SO_x, account for 5–20% of the total suspended particulates in urban air. With the advent of the catalytic converter, this percentage may rise.

Evidence for adverse health effects associated with sulfates, especially for lower respiratory infections has been increasing. The acid, irritating aerosol sulfates and sulfuric acid are believed to be more toxic than the parent SO_2, and are suspected of being the moieties responsible for the increase in diseases and deaths associated with air polluted by SO_x emissions from stationary sources.

EPA has estimated that when daily sulfate levels exceed 6–10 $\mu g/m^3$, the frequency of asthma attacks increases; at levels greater than 25 $\mu g/m^3$, the elderly experience exacerbation of heart and lung disease and mortality rates increase; at levels greater than 13 $\mu g/m^3$ for several years, an increase in acute lower respiratory disease in children occurs. These levels are often exceeded today, especially in the urban centers of northeastern U.S.

Because of many factors, including unknown synergistic effects, latency effects or chronic illness, and lack of interrelating clinical, epidemiological and occupational data, there is not enough information available today to establish a national air quality standard for sulfates, or a strategy for achieving reduction in ambient levels. The EPA feels that it cannot realistically set a national standard for sulfates before 1980 or 1981.

Until then, EPA has adopted the policy of limiting further increases in areas of the U.S.—especially a 24-state region mainly in the northeast—with higher than average sulfate levels. In these states, sulfur emissions from power plants and other stationary sources will be limited.

Concerning the emission of sulfuric acid from catalytic converters, the National Research Council recently stated that experience with these devices is too limited and sufficient information is lacking. At this time, there is no way to quantitate the potential health hazards arising from catalyst operation with health effects to be gained by controlling hydrocarbon and carbon monoxide emissions.

A form of tyranny

Recognition of health problems has increased at a rapid rate but only because modern analytical methods have become so sophisticated, so sensitive, that previously undetectable but potentially harmful materials are now "routinely" detectable in a variety of environmental samples.

Recently, minute amounts of chlorinated hydrocarbons have been found in the waters of the Mississippi River. But, what do these compounds in the amounts detected mean? Do they bode ill-tidings for man? At this point, no one knows.

Rational regulation of pollutants through legislated standards should not be based on the sensitivity of available analytical techniques. Acceptable levels for naturally occurring "pollutants" should be considered in relation to their background levels in the environment. For manmade "pollutants," safe (threshold) levels may not exist and acceptable levels must be "man-devised." These levels must be set so that the risk to man is greatly minimized. To accomplish this, all sources of information, including clinical, epidemiological and toxicological as well as analytical measurements, must be considered.

FEATURE

Viruses in water: the problem, some solutions

Planned water reuse
requires the establishment
of virus standards now

Charles P. Gerba
Craig Wallis
Joseph L. Melnick

Department of Virology and Epidemiology
Baylor College of Medicine
Houston, Texas 77025

Increased demands on our available water resources because of the concurrent increase in world population and industrial demand make recycling of domestic wastewater inevitable in the future. This plus the provisions of the Federal Water Pollution Control Amendments of 1972 (P.L. 92-500), which require zero discharge of pollutants into the nation's water by 1985, have placed an urgent need on the development of recycling methods. One of the major problems to be overcome is the development of adequate methods to ensure the elimination of human pathogenic viruses from reclaimed water. Compounding this problem is the concern that present water treatment procedures may not regularly be sufficient in preventing viruses from reaching community water supplies.

The first studies on the presence of human enteric viruses in water began in earnest more than 30 years ago, but the public health significance has yet to be ascertained. This has been due, in part, to the inapparent or latent nature of the viral infections and the lack of methodology for detection. Studies have shown that enteric viruses easily survive present sewage treatment methods, and that many can persist for several months in natural waters. Their behavior may be considered analogous to refractory chemicals found in some wastes.

Viruses are ultramicroscopic intracellular parasites, incapable of replication outside a host organism. They consist of a nucleic acid genome enclosed in a protective protein coat. Viruses that are shed in fecal matter are referred to as enteric viruses; they are characterized by their ability to infect tissues in the throat and gastrointestinal tract, but are capable of replicating in other organs of the body as well. More than 100 different enteric viruses are known to be excreted in human feces. Table 1 lists the major groups of enteric viruses that have been found in raw sewage or are known to be present in the feces of infected persons, including healthy carriers. Enteric viruses are excreted in concentrations as high as one million viruses per gram of feces, and concentrations as high as 463,500 infectious virus particles per liter have been detected in raw sewage.

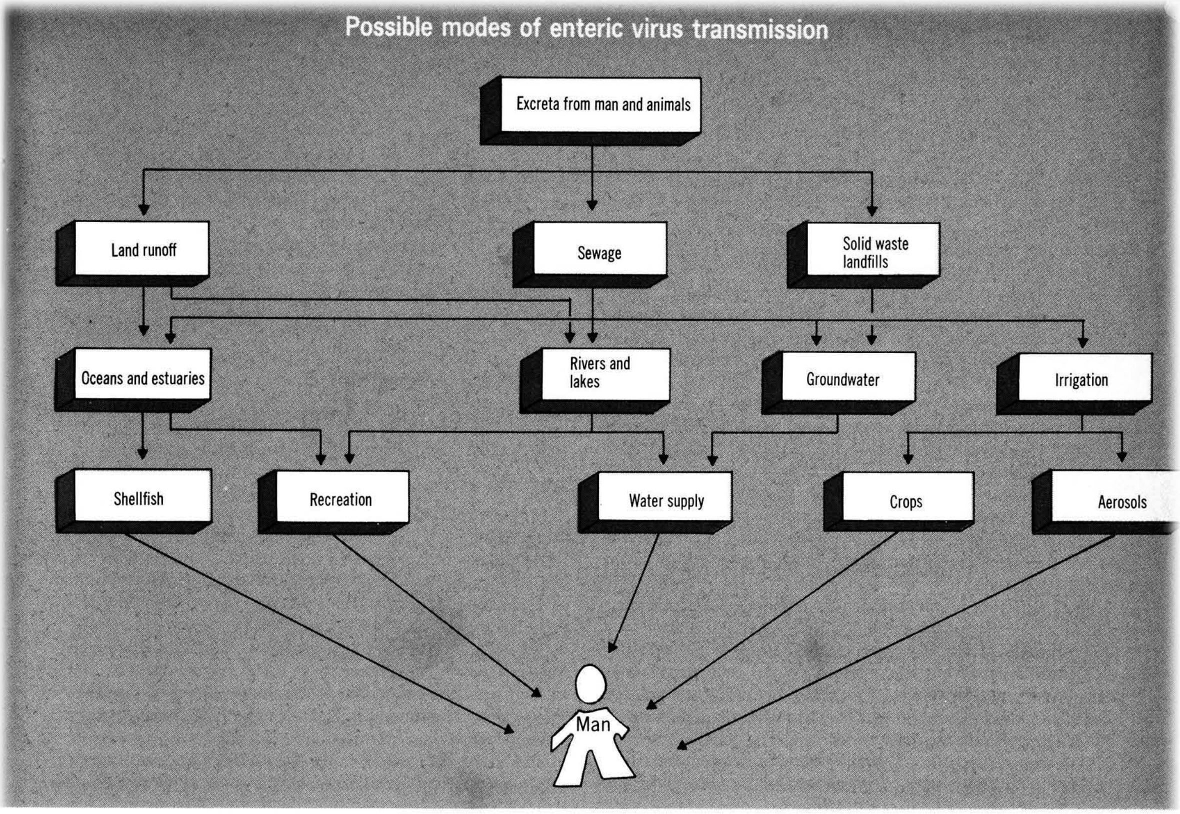
Waterborne viral diseases

Documented water outbreaks of viral disease have largely been limited to the agent of infectious hepatitis, mainly because of the explosive nature of these outbreaks and their characteristic symptomatology. Other waterborne virus disease outbreaks are not so easily recognized, and well-documented outbreaks attributable to specific enteric viruses are lacking. This is largely because:

- Many of these viruses cause inapparent or latent infections, which makes them difficult to recognize as being waterborne. A person may contact a viral infection by drinking contaminated water, and the virus may actively multiply in his upper respiratory tract and intestine without his developing overt symptoms of the disease. He may have only a mild cough or diarrhea for a few days or no symptoms at all; yet he can act as an effective carrier and transmit the disease by

Table 1. Human enteric viruses

Virus group	Number of types	Disease caused
Entero-viruses		
Poliovirus	3	paralysis, meningitis
Echovirus	34	meningitis, respiratory disease, rash, diarrhea, fever
Coxsackie-virus A	24	herpangina, respiratory disease, meningitis, fever
Coxsackie-virus B	6	myocarditis, congential heart anomalies, rash, fever, meningitis, respiratory disease, pleurodynia
Hepatitis type A	1	infectious hepatitis
Reovirus	3	gastroenteritis, respiratory disease
Adenovirus	31	respiratory disease, eye infections


Possible modes of enteric virus transmission

droplet infection (by coughing) or by contaminated fingers (cooks) to a large segment of the population, who may then develop acute symptoms of the disease.

- Epidemiological techniques are not sufficiently sensitive to detect low-level transmission of viral diseases through water.

These reasons probably account for the fact that almost 60% of all documented cases of disease attributable to drinking water were caused by agents of unknown etiology. In addition, at present no field-proven method exists for the detection of the agent of infectious hepatitis. These difficulties have led to an emphasis on the detection of enteric viruses in water as an indication of the presence of human pathogens and the possibility of contracting viral disease.

It has been shown in the laboratory that as little as one virus infectious unit for a host cell system is capable of producing infection in man. Thus, the presence of even one detectable virus unit in a water supply poses a potential disease hazard. It has been calculated that if a water supply contains as little as one plaque-forming unit of virus per 50 gal of drinking water in a community utilizing 50 mgd (0.2% of which is ingested as drinking water), at a 30% infection rate, 600 individuals would daily contact a variety of clinical and subclinical infections.

The expected average enteric virus density in domestic sewage has been estimated to be about 700 viruses per 100 ml, but as many as 46,350 viruses per 100 ml have been detected in some parts of the world. The amount of virus present in raw sewage is highly variable and depends on such factors as the hygienic level of the population, the incidence of disease in the community, the socio-economic level and the time of year. In the U.S. peak levels occur in the late summer and early fall. Enteric viruses survive secondary sewage treatment and chlorination in sufficient numbers to be isolated easily by present procedures at all times of the year. Thus, it is not surprising that these viruses have been detected in several of the major rivers of the U.S.

Little is known about the occurrence of viruses in drinking water because, until recently, methods for the concentration of viruses from large volumes of water have been lacking. A few reports do exist in the literature. For example, in a study during the 1960's in Paris, France, enteric viruses were detected in 18% of 200 samples, and the average virus concentration was estimated at one infectious unit per 300 liters. In another French study, viruses were found in 8% of samples collected from water destined for human consumption. More recently, the finding of enteric viruses in 10-liter samples of drinking water from communities in South Africa has been reported. Initial reports of virus isolations from drinking water in two New England communities in 1972 are now considered questionable because of the likelihood of laboratory contamination of the samples. In fact, subsequent studies failed to show the presence of virus.

Virological surveys of drinking water supplies are sorely needed to determine if currently practiced water treatment methods are adequate. Unfortunately, few laboratories at the present time are equipped or staffed to undertake such studies.

The concerns

The release of virus into the marine environment through sewage outfalls and polluted rivers has also been an area of concern from the recreational standpoint and as a threat to the commercially important shellfish harvesting areas of the U.S. The eating of raw or inadequately cooked shellfish from polluted waters serves as a vehicle for the transmission of hepatitis and gastroenteritis. Hundreds of cases of shellfish-transmitted hepatitis have been reported, and enteric viruses have been detected in oysters taken from both the East and Gulf coasts. In at least one case, poliovirus was detected in oysters taken from a shellfish-growing area that met accepted bacteriological criteria for shellfish harvesting. Shellfish take in viruses during feeding and accumulate them in digestive tract tissue, but there is no evidence that viruses multiply in these organisms. However, a recent outbreak did indicate that hepatitis virus can survive for over two months in oysters.

Another recent concern is the presence of viruses in untreated human fecal material in solid waste disposal sites. This material originates largely from the increased, widespread use of disposable diapers, which often send feces to landfill sites rather than to the sewage plant. Small children and babies often excrete large numbers of enteric viruses in their feces, and viruses from landfill sites might be leached out and contaminate underground water supplies. The density of enteric viruses based on recoveries from municipal solid wastes has been calculated to be about 32 virus units per 100 g. Viruses have been sporadically recovered for periods of up to 20 weeks (see Table 2) in leachates generated in lysimeters containing municipal solid waste. Limited work, however, suggests that soils with high clay content underlaying landfills have the capacity to protect groundwaters from these pathogens.

Various forms of land disposal of domestic wastes, including crop irrigation, have been proposed as major alternatives for wastes previously discharged directly into rivers and other bodies of water. While land disposal of domestic wastewater has been practiced on a large scale in Europe for several decades, little is known about the fate of viruses during and after application to the soil.

It has been feared that without dilution in receiving waters a greater threat will exist to groundwaters if sewage is discharged directly onto the soil in large quantities. It is also felt that the deep well injection of wastes may pose similar problems if not controlled. There are many instances of waterborne diseases spread by groundwater; between 1946 and 1960, 61% of all waterborne outbreaks in this country were caused by contaminated groundwater.

Field and laboratory studies indicate that large numbers of viruses may be removed from sewage or other waters after percolation through relatively short distances (1–2 ft) in soils of uniform composition. Removal is believed to be largely due to the adsorption of viruses onto soil particles. However, these adsorbed viruses are not inactivated and may remain viable for many months in the soil matrix, perhaps to be released again when the proper conditions for elution or desorption develop. Work done at a spray irrigation site in Florida has indicated that such factors as heavy rainfall may induce changes that affect virus adsorption and desorption, and result in the release of virus into the groundwater. In this particular instance, virus was observed to move as a band through the soil after a heavy rainfall and was detected in wells 10 and 20 feet below the surface. No virus had previously been detected in these wells even after several months of sewage application onto the land. The production of aerosols during spray irrigation of these wastes is another area that needs investigation.

There is increasing evidence that viruses are often associated with suspended solids in sewage effluents and natural bodies of water. For example, human enteric viruses have been detected in sludges from activated sludge plants and in marine sediments. It has been demonstrated conclusively that virus association with solids does not result in inactivation; in fact, virus survival appears to be prolonged. Human viruses adsorbed to clays and soil particles have been shown to be infectious for both animals and laboratory tissue cultures. Since this adsorbed state is affected by such factors as pH, salts and soluble organic matter, viruses could persist in river and marine sediments and not be detected in the overlaying water for long periods of time, or until they later become desorbed as a result of changes in the above factors.

Table 2. Reported survival times of enteric viruses in various environments

Sea or estuary water	2–130 days
River water	2 >188 days
Tapwater	5–168 days
Soil	25–175 days
Oysters	6–90 days
Landfill leachates	7 >90 days
Marine and freshwater sediments	?

Treatment methods

Processes available for virus removal from water and wastewater include those involving physical removal and those causing inactivation or destruction of the particle. Processes that involve actual removal include sedimentation, adsorption, coagulation and precipitation, and filtration. Conditions that cause inactivation are high pH, chemical oxidation by disinfectants such as halogens, and photo-oxidation by certain dyes in the presence of light. Processes that bring about virus inactivation are preferable to those of simple removal since the latter present a problem of the disposal of potentially infectious material.

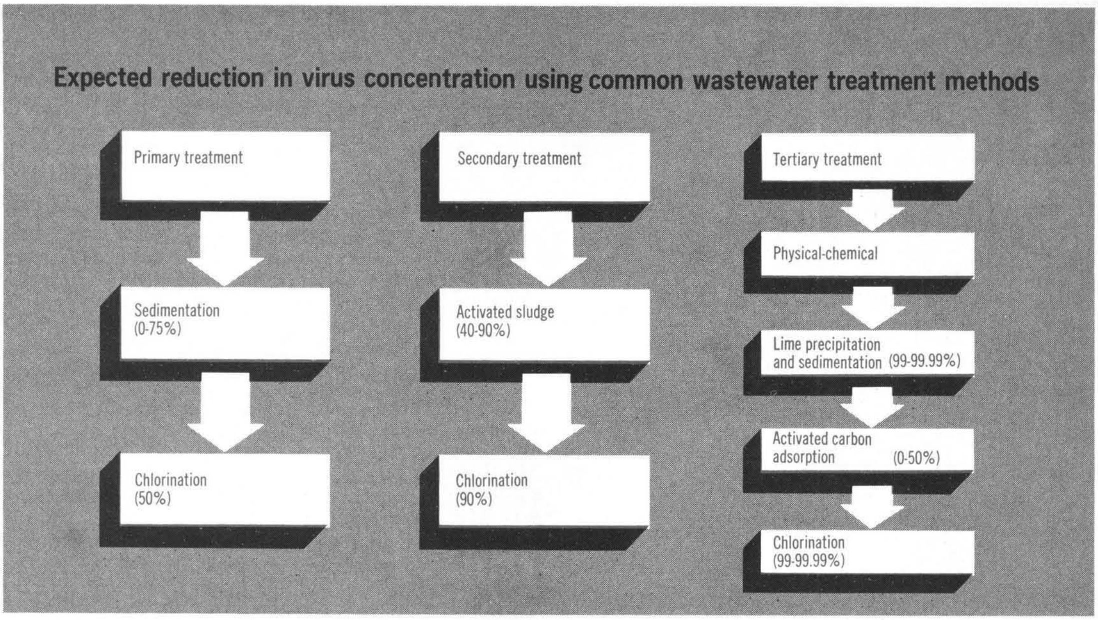
There are several shortcomings to the field evaluation of treatment methods. For example, the number of viruses entering a sewage treatment plant during a 24-hr period varies greatly, making temporal coordination of samples for treatment effectiveness difficult. Seeding experiments have been used to overcome this problem, but they too may yield misleading data because many of the viruses naturally present in sewage may be deeply embedded in or adsorbed to suspended solids.

Primary treatment of wastes, involving only settling and retention before discharge, removes little or no viruses. Any virus removal that occurs during this treatment probably results from the sedimentation of viruses associated with sewage solids.

Virus removal of up to 90% has been observed after activated sludge treatment, but large variations in removal have been reported, probably because of lack of temporal coordination of sampling. Antagonism by sewage microflora and virus adsorption to floc during this process are believed to be the main factors in virus removal. These same mechanisms are believed to be involved in virus removal observed by lagooning sewage in oxidation ponds.

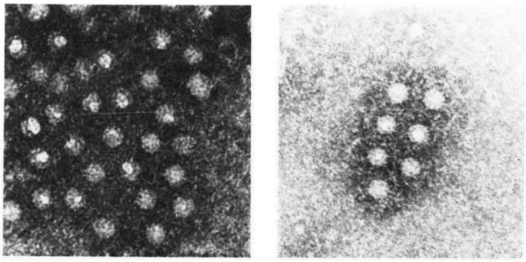
The physical-chemical treatment of sewage can result in large reductions of virus. Viruses are readily removed by coagulation and, aside from disinfection, this is probably the single most effective chemical procedure for removing viruses from water and wastewater. Alum (aluminum sulfate), lime (calcium hydroxide), and salts of iron compounds as well as polyelectrolytes, are capable of removing as much as 99.99% of virus suspended in water. It has been postulated that coagulation results in the formation of a coagulant-cation-virus complex that settles from solution. The virus is not inactivated by this process, and in fact such coagulation has been used as a method to concentrate viruses from water.

The high pH that can be attained during lime treatment can also result in very large reductions of virus. If pH levels above 11 are maintained for sufficiently long periods, 99.9% inactivation of the viruses present can result. Large variation in the reported times required for inactivation exist in the literature, and there is a need for a much closer look at such factors as concentration of organics, time, and temperature.


Expected reduction in virus concentration using common wastewater treatment methods

Under appropriate conditions, viruses are readily adsorbed to a wide variety of surfaces including activated carbon, diatomaceous earth, glass, membrane filters, colloidal organic matter, clays, and soil. Adsorption is reversible by alteration of ionic levels or pH or by the addition of competing organic matter. Activated carbon removes virus, but its capacity is soon reached and virus desorption often occurs as organic substances replace the adsorbed virus. Sand filters can remove virus by adsorption onto substances trapped by the sand, but little adsorption onto the sand itself occurs.

Although chlorine treatment has been the mainstay of water disinfection for over 50 years in this country, little is known about the mechanisms by which it renders the virus nonviable. Chlorine's effectiveness as a viral disinfectant is highly dependent on a number of factors including temperature, pH, the presence of organic matter, and the physical state of the virus (that is, whether it is adsorbed or aggregated). Because of the presence of large amounts of organic matter in the effluents from activated sludge plants, large reductions of virus are not possible because of the combination of the chlorine with the residual organics. It has been observed that application of 8 mg of chlorine per liter of sewage effluent resulted in no decrease in virus. With very high doses (40 mg/l for 10 minutes), 99.9% destruction of virus in sewage has been achieved, but then the problems of expense, chlorine toxicity to higher forms of life if such effluents are discharged, and the production of carcinogenic substances remain. Further complicating the problem is the wide variability in resistance of different enteric viruses to inactivation by chlorine. In a study of the resistance of 25 human enteric viruses, the time required for 99.99% inactivation of the viruses, under the same conditions, varied from 2.7 min to 2 hr.


Hepatitis A virus (216,000 x) recovered from stools of infected patients[a]

[a] From Gravelle et al. *J. Infect. Dis.* **131** 163–171 (1975).

Ozone has been widely used in many parts of the world as a disinfectant for water and wastewater, but little information is available to indicate its virucidal efficiency, especially under field conditions. Limited studies indicate that under certain conditions (low organic loads), ozone may be effective against viruses, but not against bacteria when similar concentrations are used. French workers reported that 0.3 mg/l ozone remaining at the end of a four-minute contact period was sufficient to inactivate 99.99% of poliovirus in batch studies. When some organic matter was present, residual ozone of 0.1–0.2 mg/l inactivated 99% of poliovirus type 2 and coxsackievirus B3 in 10 minutes. One of the main arguments against the widespread use of ozone is that it lacks a residual effect since it has a half-life of only 25 minutes. Perhaps, as has been proposed, a combination of ozonation and chlorination may be a more desirable disinfection procedure.

Monitoring techniques

Virus monitoring techniques, although not perfected for all types of water, have been developed to detect virus present in samples as large as 1000 gal of drinking water. New and improved techniques have also been developed for the quantitation of viruses in shellfish and landfill leachates. While few laboratories at present have the equipment and experienced personnel to perform these tests, we and others believe that it is now time to consider the establishment of virus standards for potable and nonpotable waters. Such guidelines will be absolutely necessary for the planned use of renovated wastewater for domestic consumption. It has been suggested that renovated water be treated in such a manner so as to be capable of destroying at least 12 log units of virus. Advanced wastewater treatment, involving physical treatment as well as breakpoint chlorination or ozonation, may well be capable of achieving this end. This has led to the suggestion that the maximum limit of viruses in drinking water supplies be the

minimum number that can be detected by using current technology. In June 1974, scientists from around the world met in Mexico City at the International Conference on Viruses in Water, which was sponsored by the American Public Health Association and the World Health Organization (WHO), to propose recommendations for detection and control of waterborne viruses. A prior recommendation that less than one infectious virus unit per 10 gal be present in recreational water, and less than one virus in 100–1000 gal of drinking water was reaffirmed. It was the consensus of this group that an international body, such as WHO, identify provisional methods for determining virus concentrations in water and establish virus standards. While at present there are no virus standards recommended by the Environmental Protection Agency, surveillance and methodology studies on enteric viruses in water supplies of several U.S. communities are now being conducted. Such studies may form the basis for further recommended virus standards in this country.

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Charles P. Gerba *is assistant professor of environmental virology at Baylor College of Medicine. He is conducting research on development of new methods for the concentration of viruses from large volumes of water, virus removal by soil during land application of sewage, the use of photodynamic oxidation for sewage disinfection, and viral aerosols.*

Craig Wallis *is professor of virology at Baylor College of Medicine. He has been active in the development of virus concentration technology. In 1971 he was co-recipient of the Industrial Research-100 Award, which cited his development of a virus-removal filtration apparatus, and in 1972 he was co-recipient of the Inventor of the Year Award awarded by the Houston Patent Law Association.*

Joseph L. Melnick *is distinguished service professor and chairman of the Department of Virology and Epidemiology, Baylor College of Medicine. He has actively studied viruses in water for over 30 years. He is a member of the World Health Organization Expert Advisory Panel on Virus Diseases. He received the Modern Medicine Distinguished Achievement Award for Contribution to Medical Sciences (1965), and served as Chairman of the International Conference on Viruses in Water, held in Mexico City in 1974.*

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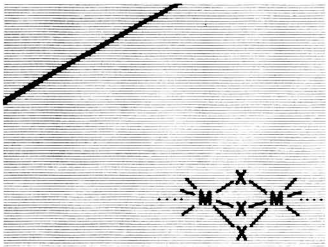

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The new lead belt in the forested Ozarks of Missouri

Lead industries, scientists and regulatory agencies work together to mine this resource while they solve environmental problems

Bobby G. Wixson
University of Missouri-Rolla
Rolla, Mo. 65401

J. Charles Jennett
Syracuse University
Syracuse, N.Y. 13210

FIGURE 1.
The New Lead Belt of southeast Missouri

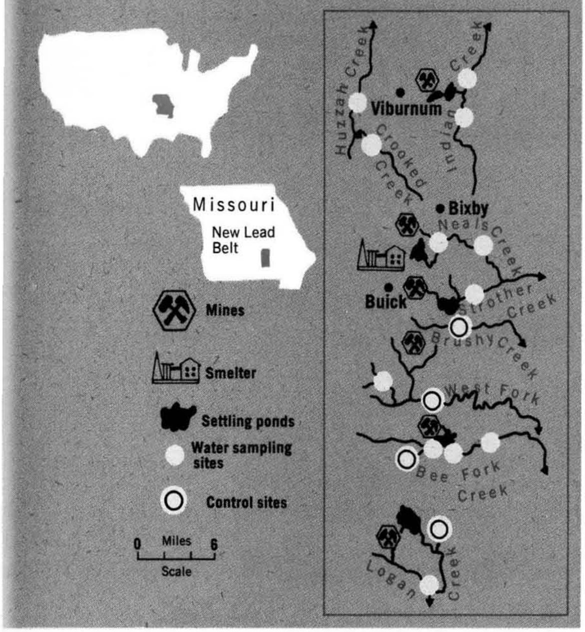
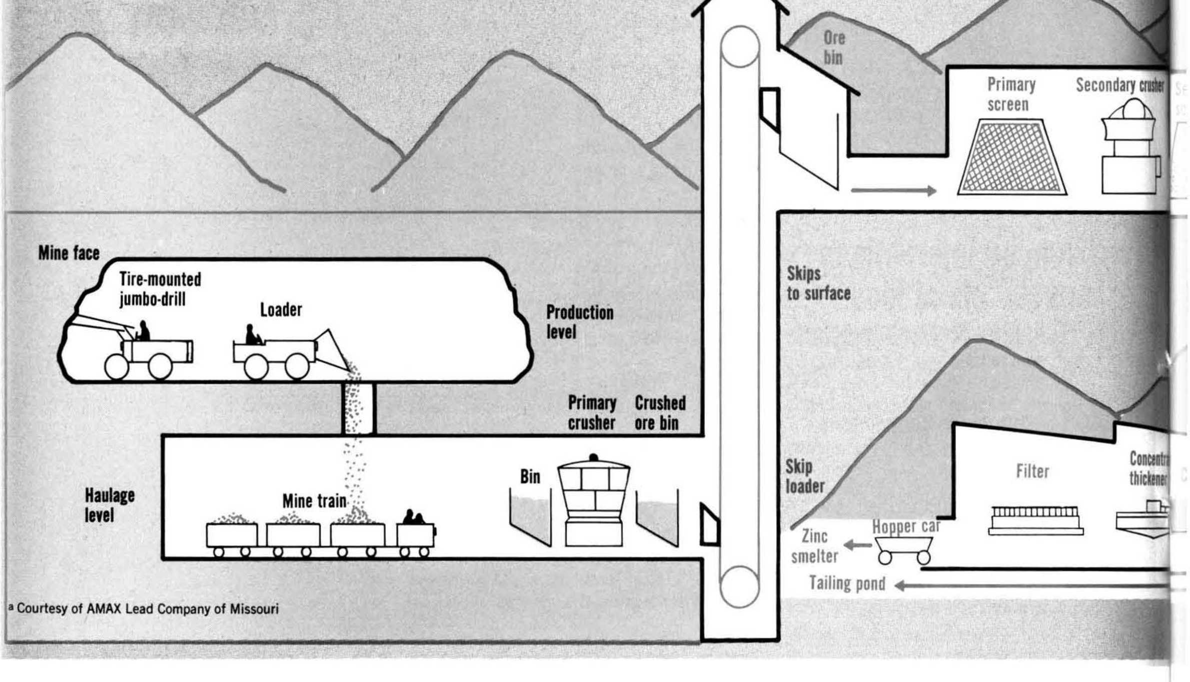


FIGURE 2.
Typical mine-mill production flow chart[a]



[a] Courtesy of AMAX Lead Company of Missouri

Lead, depending on its use or misuse, has been of increasing scientific and technological concern in the U.S. One approach to a better understanding of this necessary but controversial metal is to study the magnitude, distribution and impact of lead in the environment at the source of mining, milling and smelting. Presently, seven modern mines in close proximity to two lead smelters in the forested Ozarks of southeast Missouri are the largest source of lead in the world.

Since lead, zinc, copper, silver, cadmium and many other heavy metals are potentially hazardous when released into the environment in certain forms, they have been of considerable concern to governmental agencies, industry and the public at large. In response to this potential hazard, the National Science Foundation (NSF)-RANN's (Research Applied to National Needs) interdisciplinary research team at the University of Missouri has studied trace contaminants associated with the production of lead for the past six years. The research team has disseminated information to industries, regulatory agencies, the general public and the scientific and engineering communities as rapidly as it has become available, and in a form that could be practically applied to the user's need. From the inception of this research, it was a stated goal that the environment of this unique region not only be studied but improved, if possible, and that to accomplish this goal, all interested parties had to be actively involved. One of the most important benefits of this study was the demonstration that diverse interest groups could work together to develop common solutions to environmental problems. Even more importantly the experience in establishing such working relationships has been transferred to similar situations throughout the U.S. and the world.

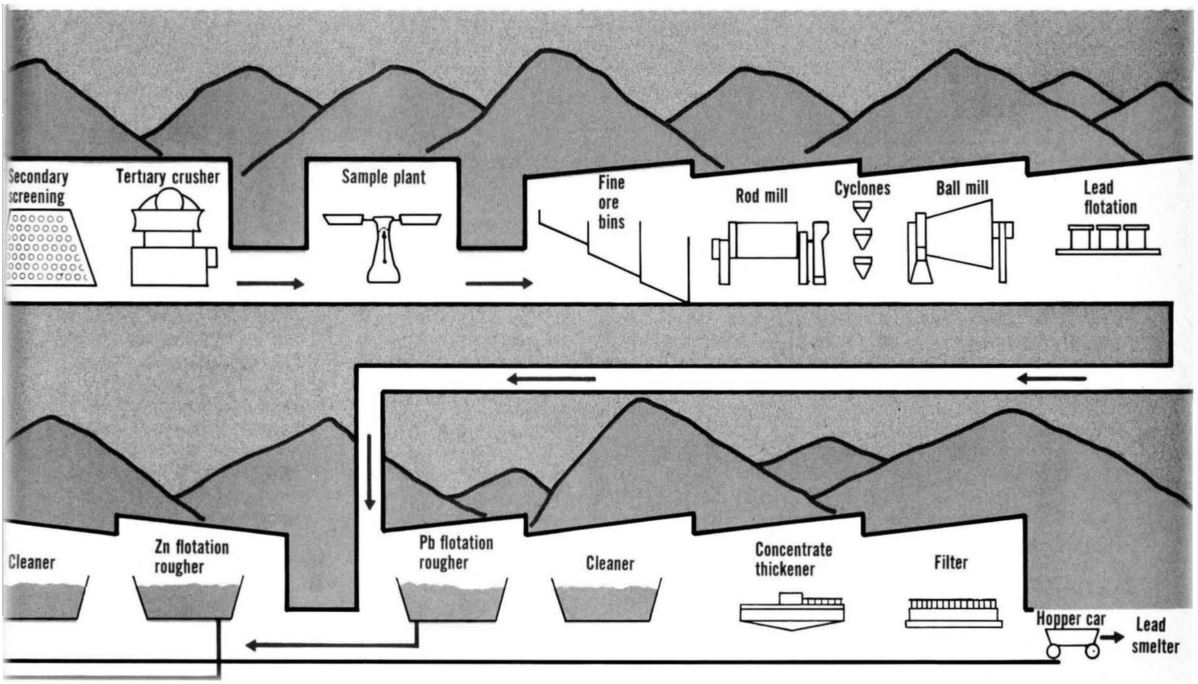
History

Since the early 1900's Missouri has been recognized for the production of lead. Lead in Missouri was first discovered by French developers as early as 1701 and mined from shallow surface deposits in 1720.

Between 1800 and 1900 some 25,330 short tons of lead were produced and in 1818 a lead smelter was established on the Mississippi River at Herculaneum. Additional lead deposits were discovered in 1840 near Joplin, Missouri, and from 1850 to 1860, three major lead and zinc mining districts were developed. By 1902 Missouri had become the leading mine producer of lead in the U.S. and has maintained that position until the present, with the exception of 1962 when strikes decreased production.

Increasing production of lead occurred during the period of 1906 to 1918 with the largest amounts being produced during World War I. Most of this production was from the "Old Lead Belt" in Madison and St. Francis counties, with the St. Joseph Lead Company (now St. Joe Minerals Corporation) being the main producer. However, in 1943 St. Joe realized the importance of finding new ore reserves to replace those that were being rapidly mined out and embarked on an extensive exploration program outside the older established areas.

In 1955, St. Joe discovered a rich lead-zinc deposit that extended approximately 40 mi due south from Viburnum, Missouri. Grades of ore varied from low to very high, but have



since proven to be of higher quality (8–12%) than initially forecast. Most of this discovery was on federal lands (the Clark National Forest), which meant that planning concerned with the development of a major mining industry within the multiple-use program of the National Forest had to be done. This lead-rich area was called the "Viburnum Trend" or "New Lead Belt" of Missouri. The geographic location of the New Lead Belt with its stream-drainage pattern in relation to the mines and one lead smelter is shown in Figure 1.

Economic significance

The economic significance of this unusual mineral district is just being realized, and promises to offset predictions that additional lead mineral reserves need to be discovered to meet resource demands during the balance of this century. The Third Annual Report of the Council on Environmental Quality emphasized that the modern low-cost lead producers in southeast Missouri would be able to maintain peak production and be able to absorb pollution control costs, while high-cost lead producers in other states might be unable to raise the required capital for necessary pollution control and would be forced to close.

In 1970, the New Lead Belt ranked first in the world; the area produced 432,576 tons of lead ore. The area has continued in its role as the major lead producer, and has established new records in 1974 with the estimated lead production of 576,300 short tons of metal, or approximately 85% of the total output mined in the U.S. Zinc, copper and silver production also increased as co-products and the combined value of these four metals was estimated to have a value of $352 million in 1974.

Technology

Efficient and modern engineering designs have been incorporated into the mines, mills, and smelters servicing the area.

FIGURE 4.

Sources of trace metals in the environment of the New Lead Belt area

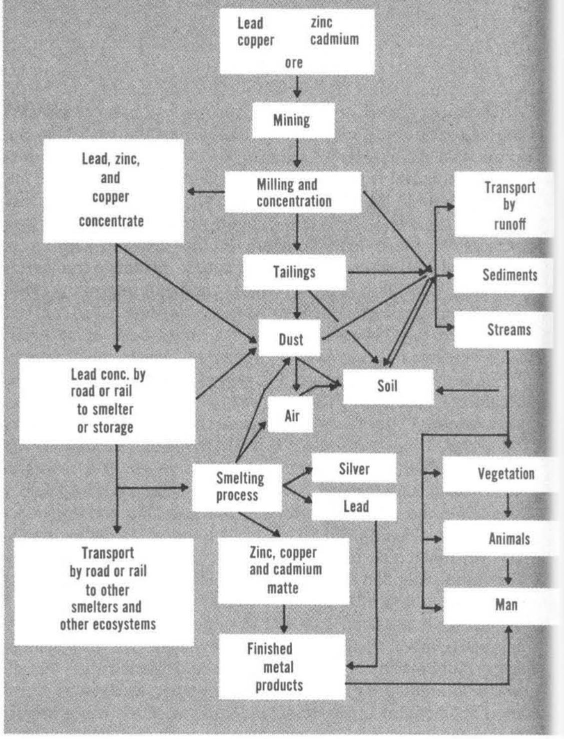
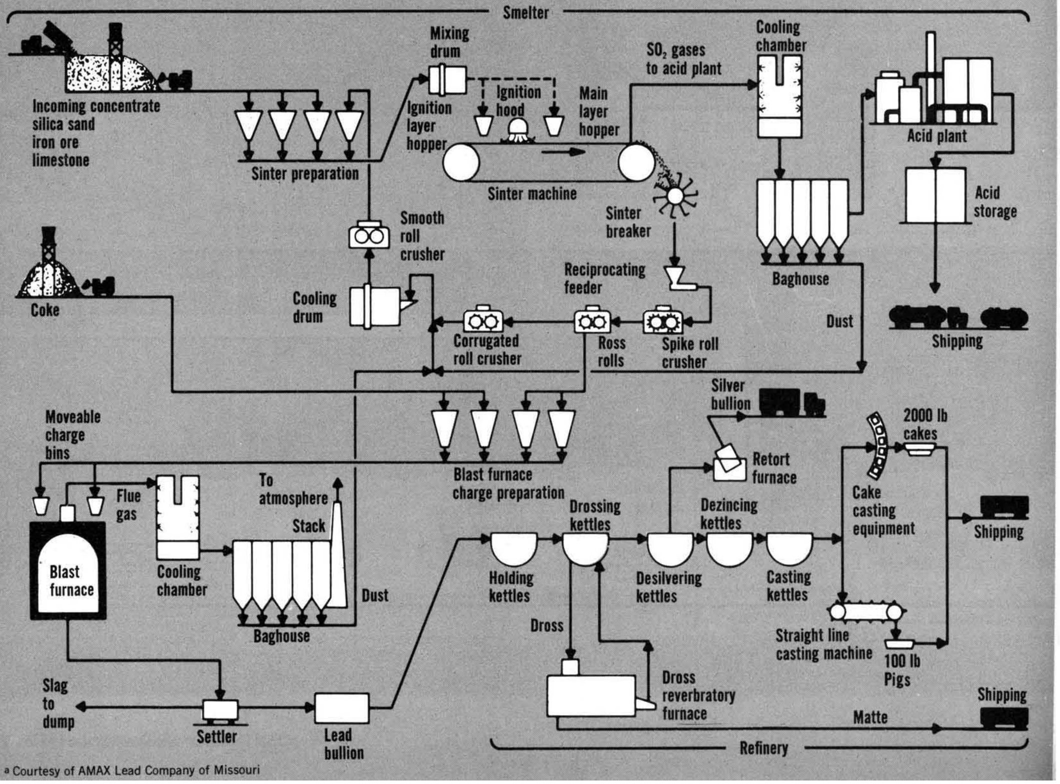


FIGURE 3.

Smelter-refinery production flow chart[a]



[a] Courtesy of AMAX Lead Company of Missouri

Galena (lead) is the principal ore mined with lesser quantities of sphalerite (zinc), chalcopyrite (copper) and silver recovered as economic co-products.

The lead ore is disseminated throughout the mostly dolomite Cambrian Age Bonneterre Formation, at depths ranging from 700–1200 ft (213–366 m). Since the producing formation is also a good aquifer, some mines must employ constant pumping to prevent flooding. This inflow of water has reduced mine dust as a potential problem, but mine water pumped to the surface contains an appreciable amount of fine galena and other trace metals as well as associated spillage from equipment and maintenance operations.

Generally, mines are worked by the standard "room and pillar" method. The back ore is drilled and shot in one or two passes followed by haulage to a gyratory crusher via large diesel loaders or locomotive-drawn railcars. After primary crushing underground, the ore is hoisted to the surface in a skip. Most of the mines also have two shafts—one for men and equipment and the other for ore hoisting and charging of the ore bin at the mill. Automation is a key factor and the most advanced mining equipment and technology are used at the mines.

Part of the water pumped from the mines is utilized as process water for the milling procedure in which chemical reagents are added during the flotation circuit to separate the lead, zinc, or copper from the finely ground rock or gangue. The flotation reagents usually consist of chemical collectors, frothers, depressants and activants.

The lead and zinc (and sometimes copper) minerals from the flotation process are pumped into thickeners where the concentrate settles leaving the water, excess flotation reagents, and the colloidal and supracolloidal minerals as milling effluent. The concentrate is vacuum dried by various methods and then transported to smelters for the final conversion to metal. A typical mine-mill production flow chart is shown in Figure 2.

The water and tailings wastes from the mine and mill operations are discharged into settlement and treatment ponds. The tailings pond dams are usually constructed to tails (generally less than 200 mesh in size) materials from the ore concentration process; the tailings are separated into fine and coarse fractions by cyclones (centrifugal separators). Once the dams have been initially constructed, the tailings and other liquid wastes are introduced upstream from the dam until the lagoon is effectively filled. The lagoons are designed to settle out residual tails and biologically degrade any spent organic reagents discharged from the milling process.

Figure 3 illustrates a typical smelter-refinery production flow chart for a modern lead smelter with several types of emission controls such as an acid plant, baghouse, atmospheric stack and other modifications. These operations must be carefully monitored so as to control the emissions of lead and other trace metals.

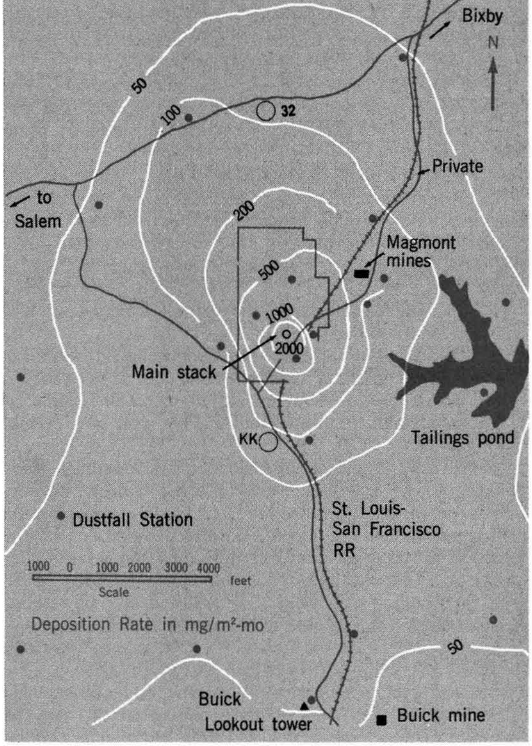
Environmental impacts

This rapid industrial development in a sparsely populated, rural forest region has caused various forms of lead, copper, zinc, cadmium and other trace metals to be released into a formerly "pristine" ecosystem. Because of this abrupt change, the mining district offers a unique area for studying the impact of trace metals and developing improved techniques to control detrimental effects. In addition to studies made in the New Lead Belt area, soil and vegetation investigations have been made near the ASARCO Lead Smelter at Glover, Missouri, as well as along the haulage roads used to transport lead concentrates from the mines to the smelter.

Research has been done to determine background values, to establish natural baselines and to evaluate the lead mining and smelting industry as a source of trace metals in the environment. Sources of trace metals in the environment were found to be associated with

- the mining-milling operations with problems of grinding, concentrating and transporting ores and disposal of tails along with mine and mill wastewater
- the smelter-refinery process with problems of concentrate haulage, storage, sintering, refining, atmospheric discharges and blowing dust. Figure 4 depicts the possible sources of trace metals in the environment of the New Lead Belt area.

FIGURE 5.
Settleable particulate lead around a lead smelter



Data utilization

The air quality data collected during this study has been used as the basis for negotiating differences in standards set by the Air Conservation Commission in the Missouri Department of Natural Resources and the U.S. EPA. The data were selected not only for their uniqueness but also for their rigid neutrality in arbitrating differences among agencies, industries, and the populace.

The information on heavy metal transport from fugitive sources has resulted in improved procedures for controlling problems at the smelters and at the mine-mill complexes of the region. Ore concentrates are stored under roof or sprinkled with water to prevent blowage. The area around the AMAX Smelter has been paved (at a cost exceeding $1 million) so that metal-rich dust can be washed into containment ponds and recycled through the smelting facilities thereby preventing resuspension by truck traffic through the area. Figure 5 illustrates the distribution of settleable particulate lead around one smelter that has been used by the industry as a model in developing improved control procedures and equipment.

Information on the efficiency of the various smelter emission control devices has been used to develop plans for improving emissions. The implementation of improved pollution control technology has resulted in the expenditure of millions of dollars for capital improvements. For example:

- A "high efficiency" mist eliminator and additional cooling equipment were installed to the acid plant for increased acid production, improved sulfur recoveries and reduced sulfur dioxide emissions.
- Four permanent sulfur dioxide ambient monitoring stations were installed at a cost of $50,000 and a fifth station is planned. Whenever the sulfur dioxide ambient level at any station exceeds the Missouri 1-hr ambient standard (0.25 ppm) for more than 10 minutes, the sinter-acid plant is shut down.
- A continuous sulfur dioxide stack analyzing system was installed at an estimated cost of $20,000.
- The acid plant baghouse has been replaced with a hot electrostatic precipitator at an estimated cost of $1 million.
- Two dams were constructed to catch and settle all stormwater runoff from the smelter plant area at a cost of $50,000.
- Improved baghouse maintenance and operation were developed and a well-qualified, full-time, inhouse, environmental group was established to monitor operations and work with agencies and researchers on effective pollution control procedures. Other air quality control applications have been developed from research recommendations by Ernst Bolter, Kris Purushothaman, Delbert Hemphill and Ivon Lowsley of the RANN-University of Missouri interdisciplinary team.

Pertinent studies

Soil and geochemical research studies led by Ernst Bolter have indicated the extent of the geochemical anomaly surrounding mines and lead smelters. This information, coupled with air quality and other data, has shown the need for controlling fugitive emissions. The U.S. Forest Service is considering the possibility of establishing a wilderness buffer area immediately adjacent to one smelter to eliminate some of the possible hazards to animals through the accumulation of metals in vegetation and soil.

Studies have also indicated that the tailings dams are sources of windblown lead and zinc; several mining and milling companies have responded to this problem by planting appropriate native vegetation to hold fine materials in place.

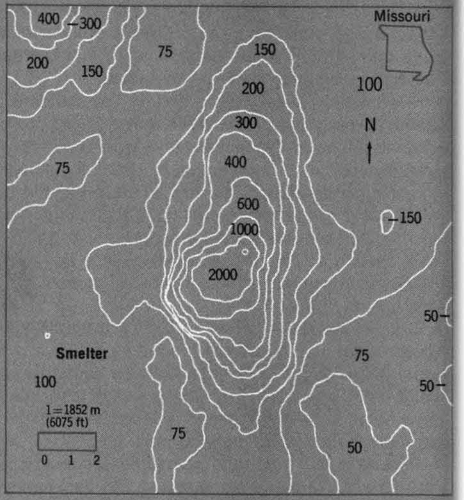
Evidence also exists that the accumulation of heavy metals in the soil and leaf litter may be a more sensitive and practical indicator of cumulative pollution than current air pollution technology methods. Methods of illustrating these zones through the use of computer plotted isopleths based on soil analysis are illustrated in Figure 6.

Studies of the interrelationship between humic acids and heavy metals have also opened a number of new possibilities for treating heavy metals-containing wastes from industries other than the mining industry. Interesting results have been reported by Ernst Bolter (of the interdisciplinary team) and research continues in this area.

Data collected from the long-term water quality studies were utilized to adjust the Missouri Clean Water Commission Effluent Guidelines for heavy metals; the ratio of actual to allowable effluent concentrations was adjusted from 1 to 2.

In another case, a biological meander treatment system was developed through cooperative efforts between one company and researchers that has been demonstrated to be a superior mine-mill waste treatment technique. The system has been found to be economical, effective, and has decreased the incidence of excessive algal growth and heavy metals buildup in receiving streams. Since once-affected streams have recovered through the utilization of this improved control technology this technology is now considered by some mining engineers to be a practical and economical solution to certain stream problems.

FIGURE 6.
Lead (ug/gm dry wt.) in upper layer of partly decomposed leaf litter on the ground surrounding a lead smelte



Research on the algae and stream macrofauna by Nord Gale and others of the interdisciplinary team has indicated that lead is not biologically concentrated by aquatic organisms. The possibility of bioaccumulation up the aquatic food chain has long been a concern of state agencies and the public who use this recreational area. Studies have also demonstrated that the inorganic nutrients in the mine water are contributing factors in producing undesirable algal blooms in receiving streams; improved treatment schemes are being further refined to eliminate these problems.

Interestingly enough, a stream pollution incident was produced by one lead smelter attempting to meet an OSHA standard that resulted in serious amounts of heavy metals entering the aquatic environment when the plant area was washed down to eliminate dust. This incident has stressed the need for continued vigilance on the part of industry in handling these metals.

It has also been found that heavy metals are washed from the soil into the streams and carried therein as suspended solids. These findings have resulted in the mine-mill complexes developing more efficient solids-retention devices. Research has also shown that stream velocities of this region are too rapid for heavy metals to settle at dangerous levels in the sediments. Most of the area's streams drain into Clearwater Lake and metal-containing sediments have not been found to have accumulated to a significant level over the past eight years.

Studies of the leachates from naturally and artifically contaminated soils have shown that, under present conditions, no hazard exists for the possible heavy-metal contamination of the water table resulting from the downward percolation of rainfall. Evidence has been found, however, that humic acids leached from the forest litter layer can mobilize lead and other heavy metals dramatically, and the long-term effects of this litter layer on heavy metal mobility requires further investigation.

Research on vegetation has been coupled with data from the geochemical and air quality studies to show that the ore haulage roads and railroads are another source of heavy metals emissions. As a result, planning is underway to retain all metal concentrates within some type of transport container, or at least under cover.

Dramatic research experiments have shown that lead can not only be removed from the soil and translocated to plant leaves, but that certain plant leaves can take up lead from aerial sources and translocate it to its roots. These findings have raised questions about allowing certain animals to graze close to the sources of heavy metals emissions. Research by Jim Pierce and Roy Koirtyohann of the interdisciplinary team has indicated that deer from the New Lead Belt region have a higher level of lead in their leg bones than deer from control areas; but as yet no clinical symptoms have been observed. This information has been used by the Missouri Department of Conservation and the U.S. Forest Service in the development of management plans for future recreational uses of this region.

Remote sensing and data handling research by William Tranter and Jerry Sandvos of the interdisciplinary team have developed new techniques for rapidly evaluating biological activities in the mine-mill treatment ponds. This has been of great value to the research team, and computer-aided techniques are being developed to improve currently existing aerial surveillance and optimal sampling programs.

Results from the remote sensing studies are additionally being utilized by the University of Kansas in a collaborative study for NASA. This project has also developed improved methods to permit ground truth correlation with NASA's ERTS remote sensing program, which allows large area maps to be made at minimum cost for use by industry and governmental agencies.

Dissemination of data

Selected samples from this multi-disciplinary study may be utilized for the National Environmental Specimen Bank System (NESBS) proposed by the National Academy of Sciences Subcommittee on the Geochemical Environment in Relation to Health and Disease at the May 1973 workshop at Capon Springs, W. Va. Pertinent environmental samples from the project should be stored as a base for determining long-term changes in environmental quality.

Information and knowledge gained through this study have been presented to appropriate user groups for the development of policies and implementation of improved pollution abatement technology to control trace contaminants in the environment. Throughout this program, research information and techniques have been exchanged with Colorado State University and the University of Illinois, which are participating in other aspects of lead and trace metal research under the NSF-RANN Trace Contaminants Program.

A collaborative effort between the University of Missouri and Oak Ridge National Laboratories is underway to determine if realistic models can be developed and tested under field conditions. Practical models would be of considerable value to both industry and regulatory agencies in predicting and controlling possible effluent or gaseous emissions from sources in the lead-zinc industries.

Data utilization of the lead studies performed under grants from the NSF-RANN Trace Contaminants Program have been beneficial to industries, regulatory agencies, the scientific community, and the interested general public. Research findings have been applied by industries to the development of improved pollution technology, both controls and monitoring. Federal and state regulatory agencies have utilized research data for the development of more effective standards and for long-range planning to protect the health of people and their environment. The practical, common sense working partnership developed in this NSF-RANN Project—with the University of Missouri serving as an unbiased intermediary between agencies and industry—has allowed environmentalists to work with industrial and agency representatives to define and resolve problems for social and economic benefits. This unique partnership has been called a model for environmental cooperation, and was cited by the Zuckerman Commission Report to the United Kingdom of Mining and the Environment as being beneficial to the local community and its surroundings.

In this time of energy conservation, increased resource needs, scientific and technologic advances and environmental awareness, a practical, cooperative approach among industry, regulatory agencies, decision-makers, the engineering and scientific communities and the general public must be maintained if needed mineral resources are to be produced without a detrimental effect on the environment.

Additional reading

Wixson, B. G., Bolter, E., Gale, N. L., Jennett, J. C., and Purushothaman, K., "The Lead Industry as a Source of Trace Metals in the Environment," in Cycling and Control of Metals, U.S. Environmental Protection Agency, National Science Foundation and Battelle Memorial Institute, National Environmental Research Center, Cincinnati, Ohio, 11 February, 1973.

"Lead, a Four Letter Worry." 5 minutes, sound and color motion picture available in 16 mm film. RANN Document Center, Office of Intergovernmental Science and Research Utilization, National Science Foundation, 1800 G Street, N.W., Washington, D.C. 20550.

This project was supported by the RANN Environmental Aspects of Trace Contaminants Program of the National Science Foundation. The AMAX Lead Company of Missouri, the St. Joe Mineral Corporation and the American Smelting and Refining Company are also acknowledged for their continued support of research and technical assistance. Sincere appreciation is also due the National Forests of Missouri, the Missouri Department of Natural Resources, the Missouri Department of Conservation, the U.S. Bureau of Mines, and EPA/Region VII for assistance and cooperation in this study.

Bobby G. Wixson *is professor of environmental health and director, Center for International Programs and Studies, University of Missouri-Rolla. For the past six years Dr. Wixson has served as project director of an interdisciplinary team studying the effects of environmental pollution of lead and other heavy metals in the "New Lead Belt" of southwest Missouri, funded by the National Science Foundation RANN Programs.*

J. Charles Jennett *is chairman and associate professor of civil engineering at Syracuse University. Dr. Jennett was formerly co-director of the NSF-RANN-supported trace contaminants project at the University of Missouri-Rolla.*

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Monitoring organic vapors

A portable mass spectrometer can be used in the field to detect
thousands of these materials at the parts per billion level
in the ambient and workplace air environments

Joseph E. Evans
Finnigan Corp.
Sunnyvale, Calif. 94086

James T. Arnold
Varian Associates
Palo Alto, Calif. 94303

The problems involved in measuring and identifying organic compounds in the environment have been of constant concern to the environmental scientist. Industrial hygiene, an allied area, which is concerned with occupational health in the workplace, is experiencing many of the same problems. The more stringent regulations, requiring specific compound identification, have forced both groups to use sophisticated instruments that were seldom used in the past.

Mass spectrometry and gas chromatography–mass spectrometry are becoming two of the most popular and useful techniques available to the environmental chemist and industrial hygienist. Basically two reasons, high sensitivity and definitive identification, account for this popularity. The modern mass spectrometer is capable of detecting organics in the nanogram (10^{-9} g) and even picogram (10^{-12} g) range.

This sensitivity combined with the capability to identify specific sample materials in the presence of the many interfering compounds in an otherwise normal background often makes mass spectrometry the only applicable technique for monitoring abnormal materials in the environment. A recent augmentation of the technique, adding substantially to its utility, is the minicomputer-based dedicated data system. This has allowed for an efficient means of collection, reduction, and analysis of large volumes of data thus making feasible, for many laboratories, an instrument that was once considered only a tool of research.

Although the conventional mass spectrometer has gained a strong foothold in the environmental laboratory, it does not easily lend itself to portability and field use. It would, however, make an excellent field monitor if the problems involving size and weight could be overcome. Its sensitivity, specificity, and flexibility would allow it to replace many of the specific monitoring systems now in use.

For the past year, the U.S. Army Environmental Hygiene Agency has been using just such an instrument in the areas of industrial hygiene and air pollution monitoring. The system has proven extremely useful and has often provided information unobtainable by any other instrumental technique.

Background

The portable vapor detection system, based on a portable mass spectrometer, was developed for the U.S. Army Land Warfare Laboratory by Varian Associates under the technical direction of H. Clay McDowell. The original purpose of the project was to develop an instrumental system capable of detecting the presence and movement of concealed personnel. A mass spectrometer was chosen as the heart of the system because of its fast response and specificity of detection. Masses, indicative of organic compounds emitted by the human body, were monitored via specific or multiple ion detection and the processed data were displayed on an integral CRT (cathode ray tube) monitor. The presence and intensity of these masses, above background, demonstrated the presence of target personnel and to some degree their distance from the instrument.

The development cycle of the portable vapor detection system started with breadboard feasibility in 1968. Although

Leaks. *Persons check the escape of materials from ducts*

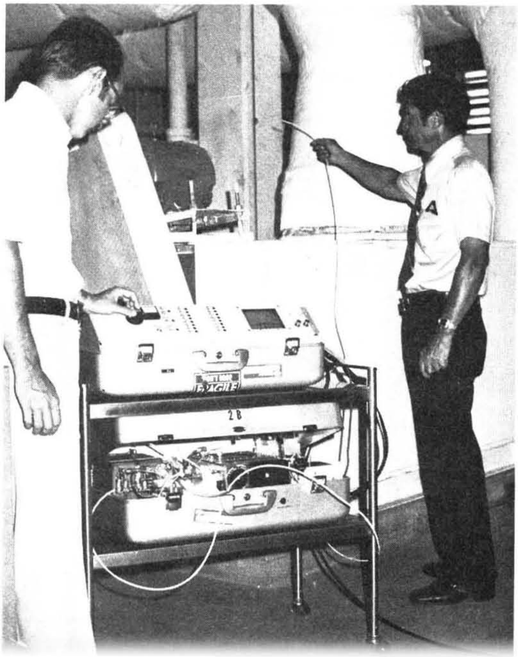

Figure 1. *Suitcase* (right) *shows the operator's control panel and CRT monitor; suitcase* (left) *with protective insulation and covers removed shows the quadrupole analyzer and its vacuum system (in the center and upper right-hand portions), and the membrane separator and its vacuum canisters (in the lower left-hand portion)*

development was essentially complete by 1970, small improvements were made through 1973 and consisted mainly of the replacement of some electronic components with "state of the art" ones as they became available. This ongoing development resulted in a lighter weight package with a high degree of electronic reliability. Weight and durability are especially important since the system usually travels as excess baggage on commercial airlines. Even though the initial development contract has been satisfied, continued improvement is imminent. An integrated gas chromatograph and an "idiot proof" color CRT display are to be added later this year. The addition of the GC will greatly increase our capability in water pollution monitoring and a color change of the data peaks on the video display at preset concentration levels will make the instrument a "technician level" system. Operation of the system in the field while unattended via an acoustic coupler from the agency is also envisioned.

Applications

Because of the inherent flexibility of the mass spectrometer, the system was ideally suited for a number of other projects. It underwent extensive field testing to determine its usefulness in detecting military explosives. The instrument was mounted in both fixed and rotary wing aircraft and flown over TNT (trinitrotoluene) melting operations in order to determine if the system could detect the plume given off by molten explosives. It was discovered that the more volatile MNT (mononitrotoluene) and DNT (dinitrotoluene) components present in TNT could easily be detected and thus provide information as to the locations of enemy explosive reclamation facilities.

Several other applications projects were also undertaken. In one, the system was installed in a Volkswagen Microbus. This resulted in a highly mobile system capable of detecting chemical effluents of military and environmental interest. Another project involved the analysis of drugs and drug metabolites in body fluids.

When the U.S. Army Land Warfare Laboratory was disestablished in 1974, the U.S. Army Environmental Hygiene Agency obtained, on loan, one of two mass spectrometer-based, portable vapor detection systems that had been delivered. For the past year, the agency has been involved in evaluating its utility in monitoring and detecting environmental and industrial hygiene pollutants.

The instrument package

The portable vapor detection system is housed in two heavy-duty aluminum suitcases. One contains the control panel and data display, the main power system, and a miniaturized general purpose computer. The quadrupole mass spectrometer, its vacuum system, and the specialized inlet system are housed in the other case. During operation, the two cases are interconnected and operated via switch commands from the control panel (See Figure 1). Although the system incorporates many unique features, the inlet system and the digital computer are probably the greatest contributions to its portability and success.

The inlet system consists of a dual section Llewellyn silicone membrane separator, a sample pump, and two interstage pumping canisters. Each separator section itself is a 3-stage device with each of the two sections operated at different temperatures (See Figure 2). In normal vapor sensing operations, the higher temperature section is normally set by thermostat at 60°C while the lower one is slightly above ambient. These temperatures are suitable for those materials that are sufficiently volatile to furnish partial pressures within the detection range of the system (nominally greater than 10^{-6} torr). For less volatile materials, the higher temperature section is used alone and is heated under external control (maximum operating temperatures 230°C). The interstage pumping requirements for the separator are met by two stainless steel canisters each of which contains 1 kg of specially processed zeolite. Upon evacuation, these canisters can meet the separator vacuum requirements for a normal day's operation thus precluding the inconvenience of transporting a mechanical pump to the investigation site. Normally the interstage canisters are pumped down on a daily basis by using a small fore pump; this procedure requires about one hour. The system can, however, sustain standby periods of up to three days without being replenished.

During operation, a small pump pulls ambient air across the face of the outer membranes of the separators at approximately 1 liter/min. Since the dimethyl silicone membrane material is more permeable to organic molecules than to the air gases, the relative concentration of transmitted sample is increased at each stage of the three-stage separator. Sample enrichment is compounded multiplicatively with each successive stage and, typically, is about 10^6. With ambient concentrations of 1 ppb the enrichment presents the spectrometer with a sample to air ratio of about 10^{-3}, which is easily managed by the dynamic range of the system. The small amounts of air gases that pass the first two membranes are quite effectively removed by the zeolite canisters. Depending on the volatility of the material to be analyzed, either a Teflon or heated probe may be used for sample collection. A high-temperature liquid inlet system is also available.

Spectrometer

The UTI Model 100B quadrupole analyzer used in the system is a very precise mechanical assembly. Therefore, the analyzer rods must maintain their alignment within 0.0001 inch. Since external forces on the rod assembly could alter alignment, the analyzer structure is floated within the vacuum housing. A radial clearance of 0.001 inch in its mounting prevents external forces from distorting the structure but still constrains its motion when the suitcase is subjected to shock loads.

High vacuum, within the source and analyzer, is maintained by an 11 liters/sec ion pump with resulting pressures of 10^{-7} to 10^{-6} torr. Power for the ion pump is supplied by the main power supply while the system is in operation and by a small external source during standby periods. During transit, three Leclanche lantern batteries, connected in series, will supply ion pump power for 24–48 hours.

The ion source is of the closed, electron impact type and is patterned after the Alpert ionization vacuum gauge. Dual filaments are provided for redundant electron supply. The ionizer will usually function for several hundred hours even after the failure of one of the two filaments. Normal electron energy is approximately 70 eV. The ionizer, the mass spectrometer, and the electron multiplier are protected from over pressure damage by an adjustable vacuum interlock.

One of the major problems in examining an unknown and uncontrolled mixture of samples lies in the dynamic range of detection required. This is compounded by the fact that in a normal background situation, and in the presence of samples, peak intensities may vary by a factor of 100 or more. To accommodate this problem, an autoranging electrometer was specially designed for the system. Coupled to the continuous dynode electron multiplier the system, when operating at a fixed gain setting, achieves a dynamic detection range of more than 1000.

Digital system

The operation and control of the vapor detection system is entirely under digital control. Analog data from the spectrometer is digitized and processed by the computer while digital operational commands are transmitted analogically to the spectrometer.

The computer was specially designed and developed in order to accommodate size, weight, and power constraints. It was designed around the Intel 8008 microprocessor and utilizes 1792 8 bit words of Read Only Memory (ROM) and 1024 8 bit words of Random Access Memory (RAM). The ROM contains the stored programs for instrument operation and data display while the RAM is used for data and program variables. A hardware multiply and divide capability substantially increases the computers overall speed for processing data.

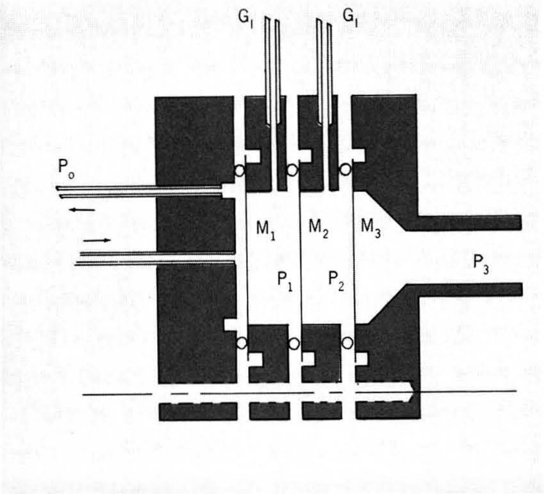

Figure 2. *Diagram of one of the three-stage silicone membrane separators. Pressure decreases from P_0 (sample inlet) to P_3 (spectrometer inlet). Membranes M_1, M_2, and M_3 are supported by gold-plated nickel and stainless steel screens on their low pressure sides. Air gases that penetrate M_1 and M_2 are removed by their respective zeolite canisters G_I*

Since all operational programs are stored in reprogrammable ROM, protection is complete. Neither manipulation of the panel switches nor power outages can disable the stored program, which adds a level of protection for the novice operator.

Operation

Three modes of operation are available with the system. One, a full scan from mass 10 to 346, is seldom used in the field as a separate oscillographic recorder would be required. A partial scan mode and a specific or multiple ion detection mode, however, output directly to an integral television monitor.

In the partial scan mode, 14 amu (atomic mass unit) segments of the spectrum from mass 10 to 346 may be assessed via switch commands from the control panel. Access to spectral segments is relatively fast (1–3 sec) and can be accomplished at any time. Once the operator has decided upon the segment of interest, background levels may be captured and retained directly on the monitor. These retained background readings may then be compared with the current values of the peaks of interest that are displayed adjacently.

This method of display allows precise measurement of very small changes in mass amplitude. Background levels have been shown to change slowly, but large excursions can occur over a period of time. Therefore background values can be automatically updated by the computer by using a moving average of background peaks to normalize the display amplitudes. In order to accommodate a wide dynamic range, mass intensities are displayed as the square root of the detected values.

For those compounds measured on a routine basis, the specific or multiple ion detection mode is used. In the present system, 256 words of ROM are reserved for signature peaks of specific compounds. Typically 2 to 5 masses that are indicative of a target compound are programmed into the ROM and displayed as a group. Both a static and moving average background display are available (See Figure 3). Depending on the number of peaks required for identification, 7 to 14 compounds may be programmed on a single chip. The compound library can easily be expanded by programming several chips and then exchanging them as needed.

Specificity and sensitivity

Mass spectrometry is, without question, the most definitive technique available for the identification of organic compounds. Although a complete spectrum is required to identify some compounds, many can be identified on the basis of a few well chosen signature masses. Multiple Ion Detection (MID) or mass fragmentography offers two major advantages. First, it reduces the amount of data that must be interpreted by the operator, and second it increases the sensitivity of the mass spectrometer.

Since target samples are to be detected in the presence of normal background, the signature masses must be selected with care if the identification is to be truly reliable. Peaks that are common to a number of different compounds must be assigned with caution and must be augmented with other masses of the target compound which, when combined, will serve to uniquely identify the sample. In general, combinations of peaks can be found that will permit discrimination against interferents with a high degree of confidence.

Generally speaking, the average mass spectrometer will detect organic concentrations of 10×10^{-9} g/sec in the full scan mode and as little as 10×10^{-12} g/sec in the multiple ion detection mode. The quadrupole analyzer used in the portable vapor detection system is quite sensitive and operates within these ranges. The determining factor in the sensitivity of the system is the efficiency with which sample materials can be transported to the ionizer of the mass spectrometer. The inlet system with its membrane separator is more efficient in transmitting reasonably volatile organic materials at ordinary temperatures.

Less volatile materials require higher membrane temperatures; for example, TNT is best transmitted with a separator temperature of about 200°C. Inorganic materials and highly polar compounds are not transmitted as well. The mechanism that determines the facility of the membrane to transmit a substance is its solubility in the dimethyl silicone polymer.

For the majority of organic compounds having vapor pressures of greater than 10^{-5} torr, solubility in the membrane is high and detection can be made in the parts per billion range. Less tractable materials can be introduced by using higher separator temperatures. An all glass evaporator for materials of low volatility is also available. Table 1 illustrates the sensitivity of the system for several compounds in ambient air.

Uses

The U.S. Army Environmental Hygiene Agency is charged with the occupational health and safety of Army personnel and civilian contractors and protection of the environment from adverse military and contractor activities. In order to support these activities, a wealth of laboratory and field instrumentation is required. Since obtaining the portable vapor detection system last year (1974) it has been integrated into more and more activities. Its extreme flexibility has allowed it to assume the duties of many other field instruments and in some cases to accommodate areas not covered by existing instrumentation.

Some of the past and present uses for the system include:

- detection of military explosives in water by direct injection and headspace analysis
- detection of solvents used in degreasing operations
- identification of pesticides
- detection of vinyl chloride
- monitoring of cholinesterase inhibiting chemicals. The system has also been used as a general purpose mass spec-

Organic compounds, for measurement purposes, can be placed in three distinct categories:

- those relatively non-polar compounds of moderate vapor pressure that give rise to distinct, identifiable mass peaks
- those similar to category 1 except that some mass peaks are shared by a number of naturally occurring compounds
- those compounds exhibiting low vapor pressures or high polarity.

Literally tens of thousands of organic compounds fall into categories 1 and 2 and are therefore detectable, by the system, at the ppb level. Although a significant number of category 3 organics exist, they are usually of less importance because their low vapor pressures, at normal temperatures, would limit their concentration in the workplace or the environment.

The portable vapor detection system has, so far, met many requirements in industrial hygiene and organic environmental monitoring. The following compounds, extracted from the Threshold Limit Value (TLV) list are detectable in the ppb range and are representative of the types of compounds monitored on a daily basis.

acetic acid
acetic anhydride
acetone
acrolein
2-amino pyridine
benzene
chloroform
carbon tetrachloride
bis-chloromethyl ether
cresol
dichloromethane
dichloroethane
dichloromonofluoromethane
diethylene triamine
diethylamine
ethanolamine
ethylamine
ethylenediamine
formaldehyde
hexachloroethane
methanol
methylamine
methyl ethyl ketone
methyl isobutyl ketone
β-naphthylamine
p-nitroaniline
nitrobenzene
parathion
pyridine
Stoddard solvent
1,1,2,2-tetrachloroethane
tetrachloromethane
methylchloroform
triethylamine
vinyl chloride
xylene

Sensitivity for some organics in ambient air with the portable vapor detection system

Compound	MW	Lower detection limit
Benzene	78	<1.0 ppb (<3.2 μg/m^3)
Mononitrotoluene (MNT)	139	<2.0 ppb (<12.0 μg/m^3)
Perchloroethylene	164	<0.1 ppb (<0.7 μg/m^3)
Phosdrin (an organophosphate)	224	<5.0 ppb (<45.7 μg/m^3)
Hexane	86	<5.0 ppb (<17.5 μg/m^3)
Acetic anhydride	102	<2.0 ppb (<8.3 μg/m^3)

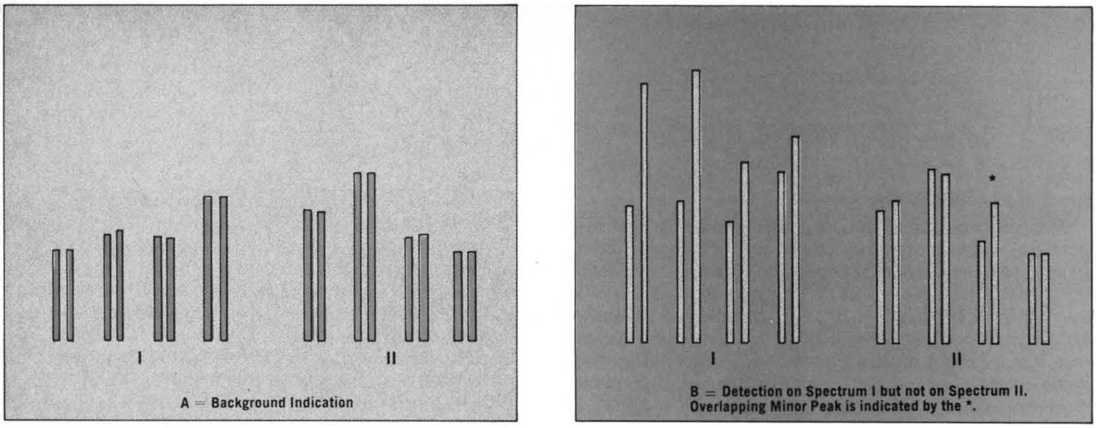

Figure 3. *Diagram of CRT display for both background* (A) *and detection* (B) *situations. Signature masses for bis chloromethyl ether (I) and chloromethyl methyl ether (II) are programmed such that both compounds may be monitored simultaneously. The left-hand peak in each doublet is the static background level for that particular mass while the right-hand peak represents the realtime level*

trometer during those times when a laboratory instrument was inoperable.

One of the most useful applications of the system is that of point source monitoring. Much of the Army work involves locating discrete sources of pollutants and toxic compounds. Because of the instrument's selectivity and fast response, it is able to measure local differences in concentration within a small area. This becomes extremely important in those cases where exposure levels differ drastically within a single work area.

A joint USAEHA-DEA (Drug Enforcement Administration) project also involves the portable vapor detection system. At this time, USAEHA is involved in a field evaluation of the system's capability in detecting the acetic anhydride plume given off by illicit morphine processing facilities. Based on earlier results, it is anticipated that the unit will be able to detect less than 1 ppb of acetic anhydride at a distance of one kilometer from the source. If the project is successful we will have an excellent weapon for combating drug traffic before it reaches the market place.

One of the most important future applications of the system may be field detection and identification of organic contaminants in drinking water and wastewaters. Some further development will, however, be required to implement this type of measurement. An integrated gas chromatograph and some additional data system capabilities will probably be required. Utility of the system will also be enhanced by developments designed to facilitate ease of operation by operators at the technician level.

Although the portable vapor detection system was designed primarily for qualitative measurement, reasonably accurate quantitative results can be obtained. Mass abundance vs. concentration curves can be constructed by measuring known concentrations of target compounds. The intensities of selected air gas background peaks can be used to adjust spectrometer gain.

Availability

At present, several companies show an interest in developing such a system. Litton Industries (Los Angeles, Calif.) is studying the feasibility of converting, for terrestrial use, the GC–MS system that will travel to Mars as part of the Viking Lander Project. Analog Technology Inc. (Pasadena, Calif.) has similar plans for their miniature quadrupole analyzer, which was developed for NASA. EPA has shown interest in this particular instrument as an environmental monitor; however, the absence of a separator or other enrichment device makes it too insensitive for their work. Varian Associates (Palo Alto, Calif.) is also considering further development of the system.

The system currently being developed for EPA by Analog Technology Inc. is expected to sell in the $20,000 range in production quantities. The more flexible system developed by Varian will probably be closer to $50,000. The original Army R&D contract provided for two complete systems at a cost of $60,000.

Although the portable vapor detection system exhibits some design limitations, it has illustrated the usefulness and flexibility of the mass spectrometer as a field monitor. Further development could make it the most powerful instrument in the field scientists' arsenal. Because of its sensitivity, specificity, and flexibility, the portable mass spectrometer may become the monitoring system of choice if exposure and pollution guidelines continue to increase the requirement to measure specific organic compounds.

The opinion or assertions contained herein are the private views of the authors and are not to be construed as official or as reflecting the views of the Department of the Army or the Department of Defense.

Joseph E. Evans *is currently the East coast GC-MS specialist for Finnigan Corp. At the time of this writing, Dr. Evans was Chief of the Air Chemistry and General Support Branch, U.S. Army Environmental Hygiene Agency, Aberdeen Proving Grounds, Md. A biophysicist by training, his primary interests include biomedical and environmental applications of gas chromatography–mass spectrometry.*

James T. Arnold, *a physicist and senior scientist for Varian Associates, was the primary force behind the design and development of the portable vapor detection system. Dr. Arnold's primary interest involves the application of physical principles to the design of novel and innovative instrumentation for chemical measurement.*

Color Removal by Clays

Kinetic Study of Adsorption of Cationic and Anionic Dyes

V. Venkatraman Sethuraman[1] and Bikash C. Raymahashay*

Department of Civil Engineering, Indian Institute of Technology, Kanpur, Kanpur 208016, U.P., India

■ Experiments were designed to study the kinetics of adsorption of two industrial dyes—methylene blue (cationic) and sulfur blue (anionic)—by kaolinite and montmorillonite clays. The cationic dye was removed from aqueous solution at a continuously decreasing rate from 10 mg/g min to 0.07 mg/g min by montmorillonite whereas kaolinite adsorbed the dye at a faster and uniform rate of 16 mg/g min. The anionic dye was removed at a uniform rate of 2.3 mg/g min by kaolinite and 2.6 mg/g min by montmorillonite. The apparent control of ion-exchange capacities and nature of exchange sites of the clays on the rates of color removal is pointed out.

In this paper we report on the kinetics of adsorption of two industrial dyes, methylene blue (cationic) and sulfur blue (anionic), from aqueous solutions by the clay minerals kaolinite and montmorillonite. This investigation is directly applicable to problems concerning discharge of textile dye wastes into the Ganges river near Kanpur as well as to disposal into groundwater seepage through soil zones.

The mechanism of adsorption of cationic dyes, particularly methylene blue, by clay minerals has been studied by several workers (*1–6*). Very little is reported, however, on the adsorption of anionic dyes and the rates of adsorption of dyes by clay minerals. Some related studies include adsorption of Orange I and Orange II on silica (*7*) and adsorption of pesticides on clay minerals (*8*).

Experimental Procedure

Commercial kaolinite and montmorillonite samples supplied by Industrial Minerals and Chemicals Co., Bombay, were used as adsorbents for dyes. Unlike many earlier investigations, the clays were used without any pretreatment like hydrogen saturation, so that natural conditions were simulated as far as possible. Distilled water suspensions were prepared in tall jars and the middle fraction, after oven drying, was used in the experiments. Some properties of the clay minerals are listed in Table I.

Two industrial dyes were used: BDH grade methylene blue, molecular weight, 319.87, and C-I sulfur blue 11, 53235, molecular weight, 305, manufactured by Imperical Chemical Industries (India) Private Limited. The second dye was obtained from the Elgin Mills, Kanpur, where it is widely used for dyeing cotton. According to a personal communication from the manufacturers, this dye is prepared by aqueous sulfurization of *p*-(2,4-dinitroaniline)phenol. It is used in the water soluble form by alkaline reduction with sodium sulfide.

Weighed amounts of clay were added to aqueous solutions of methylene blue and sulfur blue and the suspension was shaken for varying lengths of time. The temperature was maintained at 23 ± 1°C. At the end of a run, an aliquot was centrifuged at 5000 rpm for 10 min and the dye concentration in the clear supernatant was determined colorimetrically using Bausch and Lomb Spectronic 20 Spectrophotometer at 580 mμ for methylene blue and 620 mμ for sulfur blue.

Results and Discussion

Figure 1 is an adsorption vs. time plot for varying concentration of kaolinite in contact with 100 mg/l. methylene blue solution. Equilibrium is reached in a very short time

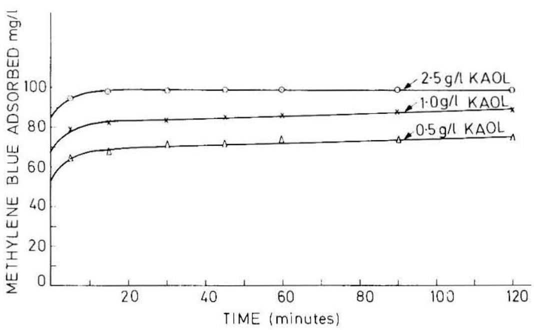

Figure 1. Kinetics of methylene blue adsorption on kaolinite

Table I. Some Physical and Chemical Properties of Clay Minerals Used in Adsorption Experiments

	Kaolinite	Montmorillonite
X-ray diffraction analysis	Presence of illite, montmorillonite and quartz (estimated 20% of total)	Trace of kaolinite
Average particle size by Fisher subsieve sizer	1.6 μ	2.4 μ
CEC by NaOH titration of H-saturated clay	5 meq/100 g	60 meq/100 g
Exchangeable cations by analysis of acid extract	—	Na:K:Ca:Mg = 2.3:0.1:1.0:0.3 meq/100 g

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[1] Present address, Graduate Engineer (Civil), Metallurgical and Engineering Consultants India Ltd., Bangalore-2.

(on the order of 5 min), and the amount of dye adsorbed at a given time increases with increasing clay concentration. Comparison with a similar graph for the methylene blue–montmorillonite system (Figure 2) shows that the rate of adsorption is much slower, steady values being attained only after 2 hr. The unit rate of adsorption by the two clays, as calculated from the curves for 1.0 g/l. clay, also shows striking differences. Kaolinite adsorbs methylene blue at a uniform rate of 16 mg/g min whereas adsorption by montmorillonite shows a steady decrease from 10 mg/g min in the first 5 min to 0.55 mg/g min in the next hour to 0.07 mg/g min for the final hour. The nonuniform adsorption by montmorillonite is further brought out in Figure 3 where the amount of dye adsorbed is plotted against the square root of time. The first or instantaneous adsorption, similar for both clays, may be related to ion exchange with surface cations on the clays whereas the intermediate (gradual) adsorption in montmorillonite may be due to cation exchange at the interlayer position of the clay.

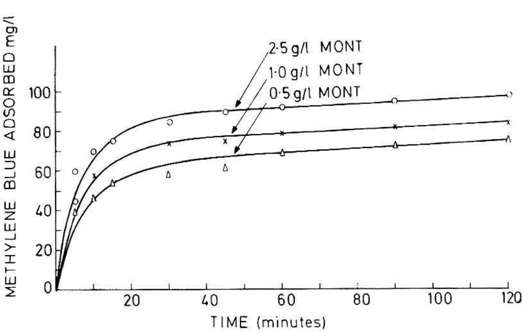

Figure 2. Kinetics of methylene blue adsorption on montmorillonite

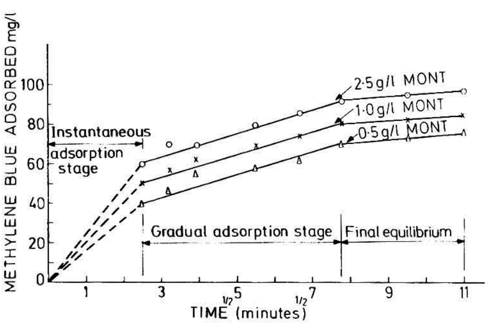

Figure 3. Three stages of methylene blue adsorption on montmorillonite, after Huang and Liao (*8*)

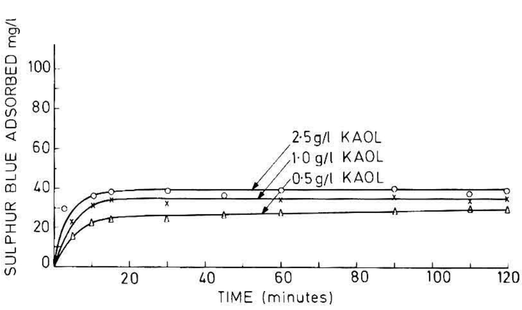

Figure 4. Kinetics of sulfur blue adsorption on kaolinite

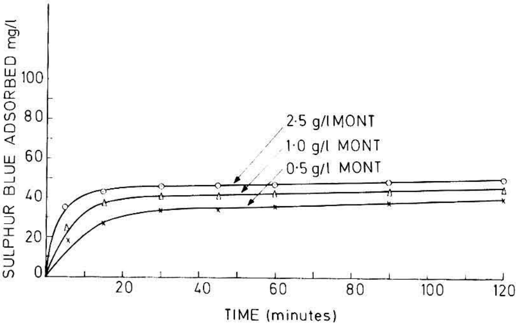

Figure 5. Kinetics of sulfur blue adsorption on montmorillonite

The unit rate for adsorption of the anionic dye, sulfur blue, is much lower (see Figures 4 and 5), the values being 2.3 mg/g min for kaolinite and 2.6 mg/g min by montmorillonite. This is explained by the comparatively lower anion-exchange capacities of clays. It is also interesting to note that anion exchange being restricted to the surface and edges of clay particles, the rates for the two clays are similar and there is no intermediate interlayer exchange stage for montmorillonite as was the case for cation exchange with methylene blue.

Conclusion

This series of experiments illustrates the strong control of the charge of the dye ion in solution and the corresponding ion-exchange capacity of clay minerals on the kinetics of color removal by clays.

The cationic dye, methylene blue, is adsorbed by kaolinite at a fast and uniform rate. Montmorillonite, on the other hand, adsorbs much larger amount of dye at a slower and nonuniform rate.

The rate of adsorption of the anionic dye, sulfur blue, is much lower and the rates for the two clays are similar. These differences in kinetics are apparently controlled by the nature of exchange sites of the two clay minerals.

Acknowledgments

The authors are indebted to the authorities of the Elgin Mills, Kanpur for facilities to conduct certain on-the-spot studies.

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Particle Size Distributions of Lead, Bromine, and Chlorine in Urban-Industrial Aerosols

John J. Paciga,[1] T. Michael Roberts,[2] and Robert E. Jervis*,[3]
Institute for Environmental Studies, University of Toronto, Toronto, Ont., Canada

■ A high-volume Andersen sampler has been used to measure particle size distributions for atmospheric Pb, Br, and Cl at urban control sites and near secondary lead refineries in Toronto, Canada. Bromine and Cl were measured by instrumental neutron activation analysis, while Pb was determined both by absorption spectrophotometry and by instrumental photon activation analysis. The Pb aerosol near roadsides was predominantly submicrometer in size, whereas elevated Pb concentrations in the vicinity of the refineries were attributed mainly to increases in Pb associated with larger particles which settle more rapidly. The strong correlation between Pb and Br from automobile emissions allowed an indirect estimate of nonautomotive Pb in the atmosphere near the refineries. Chlorine, although also associated with automobile emissions, appears to be derived from several additional sources. The localized contamination of residential areas, which has resulted from refinery emissions, emphasizes the importance of particle size considerations in establishing air quality standards.

An increasing amount of information on the multielement content of urban aerosols has led several investigators to deduce possible trace element sources and to estimate the relative importance of such sources to ambient air quality (*1–3*). The additional information provided by particle size sampling done in conjunction with multielement trace analysis greatly increases the possibility of source identification, occasionally allowing one to distinguish between different sources of the same element. This has been clearly demonstrated by Martens et al. (4), who have used aerosol size sampling and V/Al ratios to estimate soil dust and combustion source contributions to airborne V concentrations.

A strong correlation between Pb and Br from automobile emissions reported in this work and by others (*5, 6*) invites the possibility of using atmospheric Br to estimate the automobile contribution to airborne Pb concentrations in the vicinity of industrial point sources of Pb. Although abnormally low values of the Br/Pb ratio have been used to indicate the presence of nonautomotive Pb sources (7) a wide range of average Br/Pb ratios, viz. from 0.12–0.28 has been reported for automobile emissions (*5*). The fact that ambient Br/Pb ratios are lower than the ethyl fluid ratio of 0.39 has been attributed to a loss of Br from the automobile aerosol with time (*8*), and there is evidence that the ratio may be higher for fresh automobile exhaust (*6*).

This work is part of a comprehensive multidisciplinary study of the environmental effects of secondary lead refineries in Toronto, Canada (9) and reports on the presence of anomalous particle size distributions for the lead aerosol, as well as abnormally low Br/Pb ratios in the vicinity of two such refineries. Since automobiles are the major source of Br in the urban atmosphere, this element has been used to estimate the automotive contribution to atmospheric Pb, thereby allowing an indirect estimate of the contribution from refinery emissions.

Sampling and Analysis

In addition to urban control sites, the area studied included two battery recycling plants, hereafter designated as refineries A and B, with estimated annual Pb emissions of 15,000 and 30,000 kg, respectively, before the recent installation of control equipment (*10*). If we take the stacks as the emission center of each operation, both refineries lie within 100 m of residential areas. The most significant additional Pb emission source is an elevated expressway which passes within 250 m south of refinery A and 100 m south of refinery B. The 24-hr traffic volumes within the regions are 120,000 and 50,000 vehicles, respectively.

Two main air-sampling programs were carried out from June 1973 to August 1974:

1. Beginning in August 1973, a high-volume Andersen sampler (*11*) consisting of four polyethylene-covered stages followed by a Whatman 41 after-filter was used to collect 40 size-fractionated aerosol samples at various sites in Toronto. Two air-sampling sites were located approximately 100 m N of each refinery. Control sites were located in downtown Toronto and 100 m from the elevated expressway, a suspected contributor to the Pb levels in the areas studied.

The Andersen sampler was ideal for routine particle size monitoring because its air flow rate of 0.57 m^3/min (20 cfm) allowed the collection of sufficient material to split samples for analysis by atomic absorption spectrophotometry, neutron activation analysis, or photon activation analysis. The polyethylene collection surfaces of the Andersen sampler were not coated, so that they had low metal blank values and were quite suitable for multielement microanalysis. In common with other sizing devices, this sampler exhibits some particle "bounce-off" which contributes to wall losses, as well as cross-sensitivity between stages. Operating a standard high-volume sampler beside the Andersen sampler indicated that trace element losses reached 10–15% in some instances.

2. Since only one Andersen sampler was available for this study, standard high-volume (1.4 m^3/min) samplers were operated simultaneously at four different locations during June, July, and August 1974. These sites consisted of an urban control site, an expressway control site, a site 100 m N of refinery A, and a site 150 NE of refinery B.

All samples in this study were collected approximately 1 m above ground level for 24-hr periods unless stated otherwise. Hourly wind measurements were available from the Toronto Island Airport located from 1.5–5.5 km from the sampling sites.

Whatman 41 filter paper was used as a collection medium on the high-volume samplers and as an after-filter in the Andersen sampler because of its low blank values and ease of digestion in the atomic absorption procedure. Although the collection efficiency of the Whatman 41 filter

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[1] Present address, Health Physics, Nuclear Power Div., New Brunswick Power Comm., 527 King St., Fredericton, N.B., F3B 4X1.

[2] Present address, Department of Botany, University of Liverpool, Liverpool, U.K.

[3] Present address, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ont., M5S 1A4.

paper was expected to be greater than 80% (*12, 13*), a direct estimate was made by placing a filter on top of a high-efficiency Delbag polystyrene filter and sampling for 24 hr at approximately 1.4 m^3/min. The Whatman 41 filter trapped 85% of the total Pb and 83% of the total Br collected by the two filters. No measurement was made for Cl on the Delbag filters because of the high Cl blank in the polystyrene filter.

After sample collection, a section of each filter was irradiated in the University of Toronto's SLOWPOKE research reactor (*14*) to determine Br and Cl concentrations by rapid neutron activation analysis based on the short-lived nuclides ^{80}Br (17 min) and ^{38}Cl (37 min). Lead was determined by atomic absorption spectrophotometry (*15*), as well as by an instrumental nuclear technique based on the production of ^{203}Pb (52 h) by photon activation (*16*). This latter technique was used to analyze a limited number of samples primarily as an independent verification of the atomic absorption results. Agreement of approximately 10% between the two methods was within the combined precision of the two analytical techniques. Results on soil analyses from an analytical "round-robin" with 15 environmental laboratories in Canada and the U.S. also indicated agreement of better than 10%. Detection limits of 25 ng/m^3 and 2 ng/m^2 for Pb and Br, respectively, were sufficient to ensure an overall analytical accuracy of 15% or better on most samples; however, higher blank values for Cl resulted in some particle size fractions being at or below the Cl detection limit of 50 ng/m^3.

Results

High-Volume Samples. The average Pb, Br, and Cl concentrations measured at four sites during the summer of 1974 are presented in Table I along with values obtained for eight samples collected at the site 100 m north of refinery A but on a nearby rooftop at an elevation of 6.3 m. The ground-level sampler at this site was shielded by adjacent buildings, and consistently higher Pb concentrations were detected when it was moved to an unobstructed position on the nearby rooftop.

Excluding the rooftop samples, an analysis of variance on the 19 sets of complete data indicated that there were no significant differences in Br or Cl concentrations among the four sites. Lead concentrations, however, differed at the 1% significance level, with Scheffé's test (*17*) indicating that the highest Pb concentrations were near refinery A. At first sight, the Pb concentrations near refinery B did not appear to be greater than would be expected from an automobile source alone. A paired t-test on all the data, however, revealed that despite a lower traffic density at this site, the airborne Pb concentrations were significantly higher ($p < 0.01$) than for the expressway control site, suggesting smelter contributions.

The differences in findings among the air-sampling stations are more clearly illustrated by the correlation observed between Pb and Br. At the control sites where automobile emissions were expected to be the major source of atmospheric Pb, the Br/Pb ratio was 0.32 ± 0.05 with a correlation coefficient between Br and Pb of +0.93 (Figure 1a). Near industrial sources of Pb, however, the Br/Pb ratio decreased and the correlation between Br and Pb was weaker (Figures 1b and 1c). Whereas the control site ratio of 0.32 is comparable to the ethyl fluid ratio of 0.39, the ratio near refinery B (Figure 1b) was only 0.16 despite the similarity in traffic patterns. An appreciably lower ratio of 0.09 observed near refinery A (Figure 1c) is similar to short-term values judged by Wesolowski et al. (*7*) to indicate the presence of industrial Pb sources.

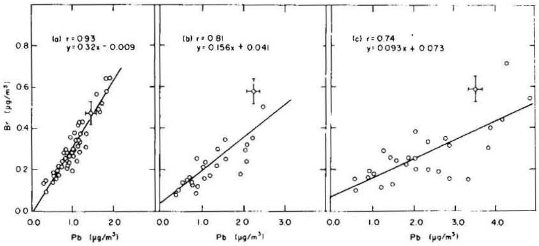

Figure 1. Correlation of Br and Pb concentrations for high-volume samples collected at (a) control sites, (b) 150 m NE of refinery B, and (c) 100 m N of refinery A. The correlation coefficient *r* and regression line are presented

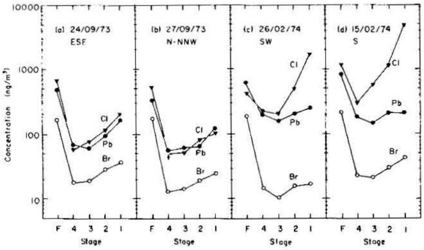

Figure 2. Particle size distributions for Pb, Br, and Cl measured with an Andersen sampler

(a) and (b) are from the urban control site. (c) and (d) are from a site 100 m N of an elevated expressway. The size fractions are <1.1, 1.1–2.0, 2.0–3.3, 3.3–7.0, and >7.0 µm diameter for the Whatman 41 after-filter F and stages 4 to 1, respectively. The sampling date and predominant wind directions are also presented

Particle Size Samples. At control sites, Pb and Br have very similar (small particle) size distributions as illustrated by the representative samples presented in Figure 2. The submicrometer size of the Pb and Br aerosols can be considered characteristic of automotive emissions (*5, 6*). The measured mass median diameters for Pb and Br were 0.7 µm and 0.3 µm, respectively, with the lower value for Br being a possible reflection of the absorption of gaseous Br by the Whatman 41 after-filter.

At the site near refinery A, the Br size distributions were indistinguishable from those at control sites; however, the

Table I. Atmospheric Pb, Br, and Cl Concentrations at Various Sites During June, July, and August 1974

Site	No. of observations	Average and range of concentrations, µg/m³		
		Pb	Br	Cl
Urban control	28	0.97 (0.28–1.8)	0.28 (0.094–0.59)	1.00 (0.40–1.9)
Expressway control	28	1.02 (0.36–1.8)	0.34 (0.10–0.65)	1.04 (0.59–1.9)
Refinery A	25	2.31 (0.56–4.9)	0.29 (0.10–0.72)	1.18 (1.02–3.3)
Refinery A—rooftop	8	11.5 (4.7–25)	0.35 (0.06–0.58)	1.75 (0.25–2.3)
Refinery B	26	1.28 (0.37–2.5)	0.24 (0.09–0.58)	0.90 (0.20–1.7)

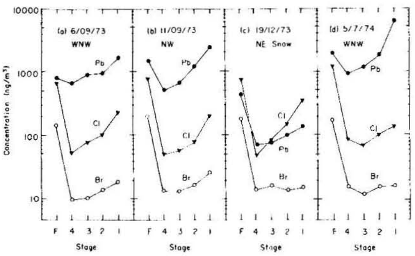

Figure 3. Particle size distributions for Pb, Br, and Cl measured with an Andersen sampler

(a), (b), and (c) were collected at a site 100 m N of refinery A. (d) is from the same site but was taken on a nearby rooftop 6.3 m in height. The size fractions are the same as in Figure 2. The sampling date and predominant wind directions are also shown

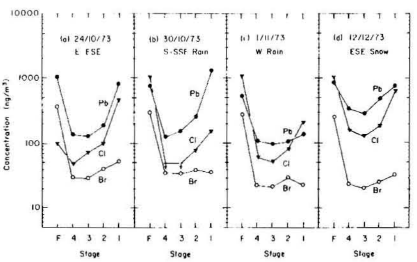

Figure 4. Particle size distributions for Pb, Br, and Cl measured with an Andersen sampler

All samples are from a site 100 m N of refinery B. The size fractions are given in Figure 2. The sampling date and predominant wind directions are also shown

Pb distribution was often shifted strongly toward larger particles (Figures 3a, b, and d). The detection of increased Pb concentrations on particles greater than 3.3 μm in diameter appeared to be related to plant operation as well as wind direction. It was only with persistent winds from a direction other than that of the refinery that the Pb size distribution resembled one typical of automobile emissions (Figure 3c). For samples collected near refinery B, there were similar increases in Pb associated with the larger particulates which settle rapidly (Figures 4a, b, and d). Although sampling periods 4b and 4c included periods of rainfall, extensive sampling indicated that wind direction and speed had a much more significant effect on the size patterns and concentrations of trace elements than did moderate precipitation.

Since Pb and Br from automobile emissions were strongly correlated with each other, and Br size distributions were independent of site, this element could be used to estimate airborne Pb concentrations using the relation

$$(\mathrm{Br})_{\mathrm{auto}} \times (\mathrm{Pb}/\mathrm{Br})_{\mathrm{control}} \approx (\mathrm{Pb})_{\mathrm{auto}} \qquad (1)$$

For the high-volume samples collected during the summer of 1974 (Table I), inserting the Br/Pb ratio of 0.32 for the control sites indicated that the average automotive contribution to total atmospheric Pb concentrations in the vicinity of refineries A and B was about 40% and 60%, respectively. For the samples collected at the rooftop site 100 m north of refinery A, the automobile contribution averaged less than 10%. These data indicated that the average automobile contribution to airborne Pb in urban Toronto was approximately 1 μg/m^3, and concentrations in excess of 2 μg/m^3 near either refinery could be expected to have a significant nonautomotive component.

It was evident from particle size considerations that the refinery emissions were characteristic of fugitive sources from low-level material handling operations rather than well-controlled stack emissions, and the effect on air quality was to increase the incidence of short-term, local, high Pb levels. It is notable, however, that the ambient Pb concentrations near these refineries were infrequently in violation of Ontario's 24-hr ambient Pb criterion of 5 μg/m^3. Since standard high-volume samplers are not designed to collect large particle fallout, the suspended Pb levels may be consistently within criteria although localized contamination from fallout may constitute a major source of Pb for ingestion by children (*9*). Consequently, a dustfall standard, in addition to a standard for Pb in suspended particles, is desirable, for although these two measures of atmospheric Pb burden are closely related for rural areas, dustfall may increase much more rapidly near point sources. In light of observations that emissions from industrial sources are often short-term, episodal, and large particle in nature, dustfall measurements also provide a convenient integrated estimate of contamination, and a guideline of 100 mg Pb/m^2/30 days has been recommended in Ontario (*10*).

Chlorine

Since the Cl/Pb ratio in ethyl fluid is 0.34, automobile emissions can be expected to contribute to Cl concentrations in the urban atmosphere. Chlorine was, in fact, well correlated with Pb at the expressway control site during the summer months ($r = +0.87$). Also, Cl particle size distributions in Toronto were typically submicrometer during the summer and often followed the Pb-Br distributions closely (Figures 2a and b). This pattern is different from that in a marine environment where Cl and Na are strongly correlated and both are concentrated on larger particles (*3*). In Toronto, summer Cl concentrations were usually more strongly correlated with Pb and Br than with Na, and it was only during the winter months when salt is applied to roadways that Cl and Na were strongly correlated and associated mostly with large particles (Figures 2c, 2d, 3c, and 4d).

Nevertheless, the Cl/Pb ratio was considerably higher than the ethyl fluid ratio of 0.34 and during the summer approached unity for control sites. Thus, there are apparently additional sources of atmospheric Cl other than automobiles or road salt. These sources appear to have a significant submicrometer component indicative of combustion sources such as municipal incinerators or fossil-fueled generating stations, or, are perhaps in a gaseous form which can be absorbed by the cellulose Whatman 41 filter paper. The labile nature of Cl, however, limits its usefulness as a tracer (*18*).

Conclusions

The usefulness of particle size measurements in examining the nature of emissions from a localized source in the presence of other disperse sources has been demonstrated. In particular, if emission sources exhibit correlations between independent co-contaminants it is possible to estimate the relative significance of different sources to air quality, even in complex urban systems.

The importance of particle size measurements must be stressed in the assessment of air quality. In situations similar to those described here, air quality standards may be violated only occasionally, if at all, despite the fact that high concentrations of a contaminant on large-particle fallout can be of considerable environmental significance. This is especially important where adequate buffer zones do not exist between industries and the neighboring community. Dustfall measurements in the Toronto study indicate that a buffer zone of about 200–300 m from an operational center would be necessary to prevent unacceptable contamination of soil in adjacent residential areas. This conclusion is supported by views extant that exposure to contaminated surface soils and street dusts can constitute an ingestion hazard, especially to children.

Acknowledgment

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Dynamics of 2,4-D Esters in Surface Waters

Hydrolysis, Photolysis, and Vaporization

Richard G. Zepp*, N. Lee Wolfe, John A. Gordon, and George L. Baughman

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

■ The chemical hydrolysis, photolysis, and volatilization of several commonly used 2,4-D esters were studied. The hydrolysis rates are strongly dependent upon ester structure; esters possessing ether linkages near the carboxyl group generally hydrolyze more rapidly than hydrocarbon chain esters. The rapid hydrolysis rates observed in basic water suggest that hydrolysis is often the major pathway for transformation of 2,4-D esters in natural waters. Photoproducts of 2,4-D esters are monochlorophenoxyacetic acid esters in hydrocarbon media and in ester–water emulsions; in aqueous solution, chlorohydroxyphenoxyacetic acid esters and 2,4-dichlorophenol are formed. Direct photolysis in water is a slow process; the minimum photolysis half-life of the butoxyethyl ester under September sunlight is about 14 days in the southern United States. The photolysis rate is pH-independent, but it depends strongly upon time of day, season, and latitude. Calculations based upon solubilities and vapor pressures of 2,4-D esters indicate that volatilization may be a significant mechanism in the loss of hydrocarbon chain esters from environmental waters.

Pesticides represent an increasingly important type of synthetic chemical introduced into the environment by man. Chlorinated phenoxyacetic acids and their derivatives are among the most widely used pesticides in the world. Although production of 2,4-D (2,4-dichlorophenoxyacetic acid) and other phenoxyacetic acids decreased sharply in the late 1960's because of reduced Vietnam usage, recent U.S. production figures suggest that this downtrend has been reversed (*1*).

The widespread application of phenoxy herbicides has prompted numerous studies of their biological, chemical, and photochemical degradation (*2, 3*). However, few publications concerned with the chemical behavior of the esters of 2,4-D have appeared, although 2,4-D frequently is introduced into the environment formulated as an ester. The esters are often sprayed onto surface waters to control aquatic weeds; they also enter lakes and rivers in the runoff from field application (*4*). Their fate is of interest to the Environmental Protection Agency because they are known to be toxic to fish and other types of wildlife (*5*).

Our studies have yielded quantitative data that can be used to predict rates of hydrolysis and photolysis of several commonly used 2,4-D esters. Volatilization rates were calculated by a recently published technique (*6*).

Experimental

Materials. Reagent-grade 2,4-D was purified by recrystallization from 50% water–ethanol. The 2,4-D esters were prepared by acid-catalyzed esterification of 2,4-D by corresponding alcohols. The methyl ester was recrystallized from a hexane–methanol mixture and the other esters were vacuum distilled. Monochlorophenoxyacetic acids (ortho and para derivatives) were obtained commercially and esterified as above. The chlorohydroxyphenoxyacetic acids were prepared as described elsewhere (*7*). Water used in most of the experiments was distilled, passed through ion-exchange columns, and redistilled. Natural waters were collected from the Suwannee River (pH 4.7) and Withlacoochee River (pH 8.1) in South Georgia. The river water used in the photolysis experiments was filter sterilized by passage through a 0.22-μ Millipore filter immediately prior to use.

Equipment. Hydrolysis kinetic studies were conducted in a thermostated oil bath that regulated temperature within ±0.05°C. Quantum yields were measured in an apparatus previously described (*8*). The light used in the laboratory studies was derived from a 450-W medium-pressure mercury vapor lamp. For the quantum yield studies at 313 nm, the light was filtered through 3-mm Pyrex glass and a 1-cm thick solution of 0.001*M* potassium chromate in 3% aqueous potassium carbonate. The light was filtered through 2-mm Pyrex glass for product studies; wavelengths of the filtered light (>290 nm) corresponded to those in sunlight. Analysis of the reaction mixtures was performed on a Tracor MT-220 gas chromatograph equipped with flame detector and a ^{63}Ni electron capture detector. Infrared and mass spectra were obtained on a Perkin-Elmer Model 621 infrared spectrophotometer and a Finnigan 1015 SL quadrupole mass spectrometer coupled with a Varian Model 1532-B gas chromatograph. Ultraviolet spectra were obtained on a Perkin-Elmer Model 602 digital spectrophotometer.

Procedures. Hydrolysis of the esters was followed by periodically analyzing benzene extracts of the reaction mixtures. The mixtures were analyzed by GLC on a 3% SE-30 column with the electron capture detector, using a chlorinated biphenyl as internal standard. Kinetic studies were run in phosphate, borate, or acetate buffers. The hydrolysis reactions were followed through one to two half-lives. Second-order rate constants and activation parameters for hydrolysis were calculated by computer using a least-squares analysis of data (*9*).

Quantum yields were calculated from the slopes of logarithmic plots of ester concentration vs. time. For weakly absorbing systems (absorbance <0.02), the slope is equal to 2.303 $\epsilon_\lambda I_\lambda l \phi$, where ϵ_λ is the molar extinction coefficient of the ester at 313 nm, I_λ is a constant proportional to incident light intensity at 313 nm, l is the cell path length, and ϕ is the quantum yield. The value of I_λ at 313 nm was measured using valerophenone actinometers (*10*).

A series of cells containing solutions of 2,4-D butoxyethyl ester ($1.00 \times 10^{-5}M$) in the Suwannee River water (pH 4.7) and in distilled water phosphate buffered at pH 5.3 were simultaneously exposed to equal amounts of polychromatic light (>290 nm) in the photochemical apparatus. Benzene extracts of the photolyzed solutions were analyzed by GLC to follow ester disappearance and product formation. No change in ester concentration occurred in dark controls during the experiment.

Photolysis product studies were conducted in hexane, in distilled water buffered at pH 5.3, and in Suwannee River water. Solutions were analyzed by GLC on 10% SE-30 and 10% Silar 5CP columns after about 30% conversion to products. Photolyzed solutions of the methyl and butoxyethyl esters ($1.00 \times 10^{-3}M$) in hexane were concentrated and the products were collected by preparative GLC; alternatively, the solutions were directly analyzed by combined GLC-mass spectrometry (GLC-MS). The isomeric products, esters of 2- and 4-chlorophenoxyacetic acid, that formed in hexane were partially separable on the 10% SE-30 column. Product studies in both distilled and river water were conducted by irradiating 1 l. of ester solution ($1.0 \times 10^{-5}M$), acidifying the solution to pH 2 by hydrochloric acid, then analyzing concentrated chloroform extracts by combined GLC-MS. One of the photoproducts, an ester of 4-chloro-2-hydroxyphenoxyacetic acid, readily cyclized to a lactone during GLC (Figure 3). The infrared spectrum of the photoproduct mixture had no absorption at 1790 cm^{-1}; a characteristic absorption band of the lactone. Products derived from photolysis of emulsions of the butoxyethyl and octyl esters were identified by combined GLC-MS. All photoproducts were identified by comparison of their infrared and mass spectra to those of authentic samples.

The hydrolysis product, 2,4-D, was extracted with ether, reacted with diazomethane, and determined by GLC analysis as the resulting methyl ester.

Sunlight irradiations were carried out during September. Solutions of the butoxyethyl ester ($1.00 \times 10^{-5}M$) in tightly stoppered quartz tubes were exposed for five sunny days. To minimize reflection, the tubes were positioned over a black background. Dark controls showed no change in concentration during these experiments.

Calculations. Specific sunlight absorption rates were calculated according to Equation 1:

$$k_a = \frac{\Sigma\,[\mathrm{I}_{d\lambda}\,(1 - 10^{-\alpha_\lambda l_d}) + \mathrm{I}_{s\lambda}\,(1 - 10^{-\alpha_\lambda l_s})]\,\epsilon_\lambda {\alpha_\lambda}^{-1}}{D} \tag{1}$$

where $\mathrm{I}_{d\lambda}$ and $\mathrm{I}_{s\lambda}$ are direct and sky irradiance, respectively; α_λ is the decadic absorption coefficient of the water; l_d and l_s are pathlengths for direct and sky irradiance beneath the water surface; ϵ_λ is the molar extinction coefficient of the 2,4-D ester; and D is the depth of the water body. Values of $\mathrm{I}_{d\lambda}$ and $\mathrm{I}_{s\lambda}$ were taken from a report published by Bener (*11*). Average values for l_d and l_s were calculated according to Equations 2 and 3:

$$l_d = \frac{D\mu_r}{\sqrt{{\mu_r}^2 - \sin^2 z}} \tag{2}$$

$$l_s = 1.2\,D \tag{3}$$

where μ_r is the refractive index of water and z is the solar zenith angle. Detailed derivations of Equations 1–3 will appear elsewhere. Surface reflection from water bodies was ignored because it is <10% for most solar zenith angles (*12*). Data concerning the time-of-day dependence of z in the southern United States were obtained from Figure 2, Chapter 2 in Leighton's book (*13*).

Empirical photolysis half-lives were calculated assuming first-order kinetics for disappearance of the esters under natural sunlight.

Solubility Studies. A large excess (0.1 g) of each ester was magnetically stirred in 100 ml of distilled water for up to three days; saturation by the butyl, octyl, and butoxyethyl esters was achieved within 3 hr. The solutions were centrifuged at 15,000 rpm for 1 hr in a Sorvall RC-2 centrifuge set at 25° C. Aliquots taken from the upper half of the centrifuge tubes were extracted with benzene. The benzene extracts were analyzed by GLC using an electron capture detector. Temperatures of the solutions in the centrifuge tubes were measured with a calibrated thermometer immediately after the aliquots were taken.

Results and Discussion

Hydrolysis Rates. In accord with previous extensive studies of ester hydrolysis (*14*), three reactions considered in kinetic studies of the 2,4-D esters were acidic, neutral, and alkaline hydrolysis. As expected, product studies showed that 2,4-D was formed quantitatively in these reactions.

Detailed studies of the reactions of the 2-butoxyethyl and methyl esters indicated that the hydrolysis rate ($-d[E]/dt$) could be expressed by Equation 4:

$$-\frac{d[E]}{dt} = k_{ac}[H^+][E] + k_n[E] + k_b[OH^-][E] \qquad (4)$$

where k_{ac}, k_n, and k_b are the rate constants for acid-catalyzed, neutral, and alkaline hydrolysis, respectively, and $[E]$ represents ester concentration. The observed rate constant, k_{obs}, is expressed by Equation 5:

$$k_{obs} = k_{ac}\,[H^+] + k_n + k_b\,[OH^-] \qquad (5)$$

A plot of log k_{obs} vs. pH for the butoxyethyl ester was nearly V-shaped (Figure 1), indicating that neutral hydrolysis is unimportant relative to acidic and basic hydrolysis (*14*). Table I presents rate constants for acidic and alkaline hydrolysis in water, measured by hydrolyzing the esters at low and high pH. Activation parameters were determined by measuring hydrolysis rates at different temperatures (Table I).

The kinetic data in Table I can be used to calculate hydrolysis rates as a function of pH and temperature. Reaction kinetics become pseudo-first-order when the water is buffered, as often occurs in natural water. For such a case, the reaction half-life ($t_{1/2}$) may be expressed by Equation 6:

$$t_{1/2} = \frac{0.693}{k_{ac}[H^+] + k_b[OH^-]} \qquad (6)$$

Since k_b is much larger than k_{ac}, the half-life for the pH 5–9 range can be adequately expressed by Equation 7:

$$t_{1/2} = \frac{0.693}{k_b[OH^-]} \qquad (7)$$

Using Equation 7 and structure-reactivity relationships (*14*) for the alkaline hydrolysis of various acetic acid esters (*15*), we have estimated hydrolysis half-lives for commonly used 2,4-D esters (Table II). These data demonstrate that the chemical hydrolysis rate for a given ester varies greatly within the pH range normally found in natural waters (pH 6–9) and that hydrolysis rates are much higher in basic than in acidic waters. Ester structure also strongly influences hydrolysis rates. The esters possessing ether linkages near the ester carboxyl group generally hydrolyzed more rapidly than the hydrocarbon chain esters. For example, the hydrolysis rate of the 2-butoxyethyl ester was about an order of magnitude greater than that of the 1-octyl ester.

The rapid hydrolysis of 2,4-D esters in basic distilled water suggests that chemical hydrolysis is often the major pathway for alteration of the esters in basic natural waters. To check this point, the disappearance of the butoxyethyl ester was studied in water collected from the Withlacoochee River in South Georgia. As shown in Figure 2, the observed disappearance rate matched the hydrolysis rate calculated from data in Table I, using the pH of the river water (pH 8.1). Since 2,4-D esters hydrolyze much more slowly in acidic waters, other processes such as those discussed below are probably more important in such waters.

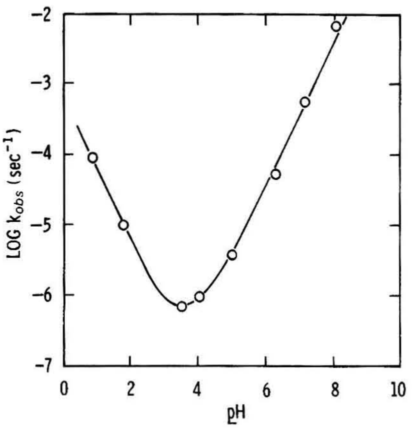

Figure 1. pH-Rate profile for 2,4-D butoxyethyl ester at 67°C in water

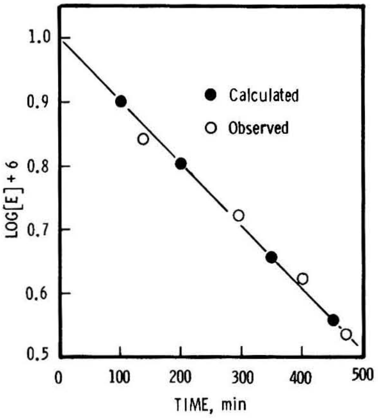

Figure 2. Hydrolysis of butoxyethyl ester in water from the Withlacoochee River

Photolysis of 2,4-D Esters. Conflicting reports concerning the photoproducts of 2,4-D esters in water have appeared in the literature. Aly and Faust (*16*) reported that several 2,4-D esters yielded 2,4-dichlorophenol as the photoproduct. Identification of this photoproduct, however, was based upon a colorimetric technique that would not have distinguished 2,4-dichlorophenol from other phenolic products. Binkley and Oates (*17*) have recently reported that only monochlorophenoxyacetic acid (2- and 4-CPA) esters result from photolysis of 2,4-D esters in water. Other workers have shown that photolysis of halogenated aromatics in water usually results in replacement of chlorine by a hydroxyl group (*18*).

Table I. Kinetic Data for Acid and Base Hydrolysis of Methyl and *n*-Butoxyethyl Esters of 2,4-D

2,4-D esters	Temp., °C	k_{ac},[a] M^{-1} sec^{-1}	k_b,[a] M^{-1} sec^{-1}	ΔH‡, Kcal/mol	ΔS‡, eu
BEE[b]	28		$(3.02 \pm 0.23) \times 10^{1}$	20.1 ± 1.4	14.8 ± 4.2
	47		$(2.35 \pm 0.13) \times 10^{2}$		
	67	$(6.59 \pm 0.13) \times 10^{-4}$		17.6 ± 0.9	−21.29 ± 2.9
	87	$(2.96 \pm 0.18) \times 10^{-3}$			
	28	$(2.0 \pm 0.5) \times 10^{-5}$[c]			
ME[d]	28		$(1.73 \pm 0.23) \times 10^{1}$		

[a] Determined from pseudo-first-order rate constants. [b] Butoxyethyl. [c] Extrapolated value. [d] Methyl.

Table II. Kinetic Data for Hydrolysis of 2,4-D Esters in Water at 28°C

Ester	k_b, 1 mol^{-1} sec^{-1}	$t_{1/2}$	
		pH 9, hr	pH 6, days
Methyl[a]	17.3	1.1	44
2-Propyl[b]	1.1	17	710
1-Butyl[b]	3.7	5.2	220
1-Octyl[b]	3.7	5.2	220
2-Octyl[b]	0.52	37	1500
2-Butoxyethyl[a]	30.2	0.6	26
2-Butoxy-methylethyl[b]	4.3	4.4	180

[a] Calculated from data in Table I. [b] Calculated assuming structure-reactivity relationship for 2,4-D esters is same for acetic acid esters (*15*).

Table III. Disappearance Quantum Yields for Photolysis of 2,4-D Esters at 313 Nm (28°C)

Ester	Solvent	Quantum yield, ϕ
BEE[a]	Water, pH 5.3	0.056
	Water, pH 6.6	0.052
	Water, pH 7.8	0.056
	n-Hexane	0.17
	n-Hexadecane	0.17
ME[b]	Water, pH 6.6	0.031
ME	*n*-Hexadecane	0.13
BEE	*n*-Hexane, acetone sensitized	0.0080

[a] Butoxyethyl. [b] Methyl.

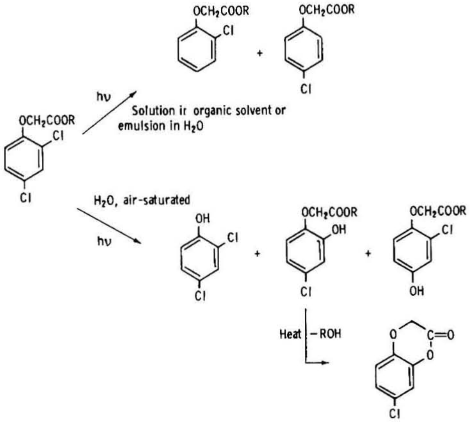

Figure 3. Photoreactions of 2,4-D esters

Our product studies were carried out in both water and organic solvents. The latter studies were prompted by the suggestion that organic films are a likely site for photolysis of pesticides (*19*).

In the hydrocarbon media, photoreaction involved quantitative replacement of one of the chlorines by hydrogen, likely via free radical intermediates (*20*). In both hexane and hexadecane, replacement of the ortho chlorine accounted for >90% of the photoreaction.

Studies in water were conducted at several concentrations. At concentrations well exceeding their solubility limits (>300 ppm), the esters formed emulsions and the major photoproducts, 2- and 4-CPA esters, were the same as those formed in the hydrocarbon solvents. However, irradiation of very dilute (<1 ppm), air-saturated solutions yielded products very similar to those resulting from photolysis of the 2,4-D acid (*21*). Major photoproducts were 2,4-dichlorophenol and compounds resulting from replacement of one chlorine by hydroxyl. The lactone formed by elimination of alcohol from the ester of 4-chloro-2-hydroxyphenoxyacetic acid was eluted from the gas chromatograph. The alcohol elimination, however, was the result of thermal degradation in the injection port (180°C). Results of these product studies are summarized in Figure 3.

Kinetics of phenoxy herbicide photolysis have received very little study. Photolysis of 2,4-D and its esters was reported to be rapid when short-wavelength, high-intensity light is employed (*16*); however, Crosby and Wong (*3*) have reported that photolysis of 2,4-D is relatively slow when less intense, longer wavelength light is used.

In our study, the rates of photolysis under solar radiation ($-d[E]/dt$) were calculated by Equation 8:

$$-\frac{d[E]}{dt} = k_a\Phi[E] \tag{8}$$

where k_a and Φ are, respectively, the specific rates of sunlight absorption and quantum yields for photolysis of 2,4-D esters. Often it is convenient to express the kinetic data in terms of half-lives ($t_{1/2}$). The half-life for photolysis is

$$t_{1/2} = \frac{0.693}{k_a\Phi} \tag{9}$$

Specific absorption rates (k_a) can be calculated from extinction coefficients and tables of actinic irradiance. This approach has been used to calculate photolysis rates of atmospheric pollutants (*13, 22, 23*) and phenylmercury compounds in water (*24*).

Quantum yields for photolysis of 2,4-D esters (Table III) were far lower than unity and were considerably lower in water than in hydrocarbon solvents. Variations of pH (between 5 and 8) caused no change in quantum yield although the phenolic photoproducts were further photodegraded at higher rates in basic water. The quantum yields in hexane and hexadecane, solvents with very different viscosities, were identical, although photoreactions involving formation of free radicals are often viscosity dependent (*25*). The lack of efficient photosensitization by acetone, a triplet sensitizer, indicated that the direct photolysis proceeds from the excited singlet state of 2,4-D esters. The extremely short lifetimes of the excited states that lead to 2,4-D ester photolysis preclude any significant quenching by species dissolved in natural waters. Ester structure also affected the photolysis rate. The methyl ester had a lower quantum yield and therefore a lower photolysis rate than did the butoxyethyl ester.

Since, as indicated by their electronic absorption spectrum (Figure 4), the 2,4-D esters are affected most strongly by light of wavelengths <320 nm, their photolysis rates would be expected to reflect fluctuations in intensity of the short-wavelength (280–320 nm) component of sunlight. This component, which also causes sunburn, is often called UV-B radiation. Measurements of UV-B radiation have shown that there are dramatic differences in intensity between summer (maximum) and winter (minimum) in the middle latitudes (*26, 27*). UV-B intensities also depend upon time of day, reaching their maximum values when the sun is at its highest point in the sky (*28*). Using solar intensities published by Bener (*11*) and our quantum yield and spectral data, we computed photolysis half-lives and rates of the 2,4-D butoxyethyl ester as a function of season and

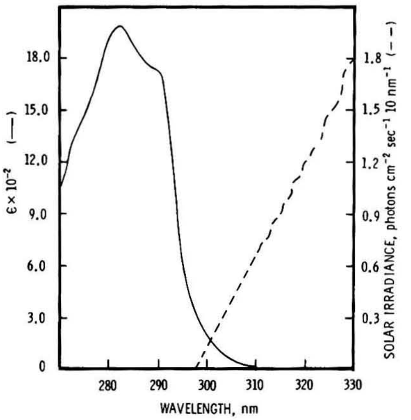

Figure 4. Comparison of 2,4-D ester ultraviolet spectrum with solar irradiance

Table IV. Comparison of Calculated and Empirical Photolysis Half-Lives for 2,4-D Butoxyethyl Ester

	Medium	
	Water	Hydrocarbon
$(k_a)_{\mathrm{intg}}$, day^{-1} [a]	1.04	1.07
ϕ	0.056	0.17
$(k_a)_{\mathrm{intg}}\phi$, day^{-1}	0.058	0.18
Calculated half-life, days[b]	12	3.8
Empirical half-life, days[b]	14	4.0

[a] Integrated over 12-hr period of daylight during September, lat. 34° N. [b] Expressed as 12-hr days.

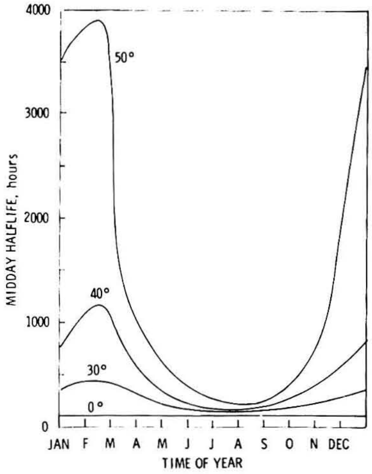

Figure 5. Dependence of 2,4-D butoxyethyl ester photolysis half-life upon season and northern latitude

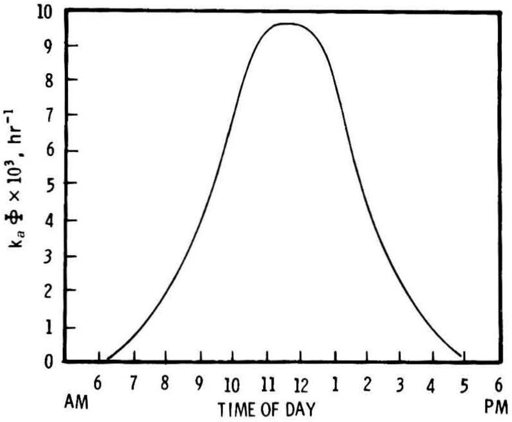

Figure 6. Dependence of 2,4-D butoxyethyl ester photolysis rate upon time of day in the southern United States

latitude (Figure 5) and time of day (Figure 6). The calculations indicate that half-lives increase sharply with increasing latitude during most of the year, but during the summer there is only a twofold increase from the equator to latitude 50°N. At middle latitudes, photolysis is most rapid during the summer. Photolysis rates are much lower in the morning or afternoon than at midday.

The above calculations are based upon average intensities derived from the sun and the whole sky on cloudless days at sea level. Clouds decrease the intensity of UV-B radiation up to about 50% for overcast conditions (*29*). On the other hand, the intensity values increase 15–20% per kilometer increase in elevation (*11*). Deviations from the average intensities for cloudless days are caused mainly by fluctuations in atmospheric ozone amount (*29, 30*). Our experiments have indicated that the calculated photolysis rates for a wide variety of pesticides are generally within 30% of the rates measured under sunlight in Athens, Ga. Photolysis rates and half-lives for the 2,4-D butoxyethyl ester measured under natural sunlight in late summer agreed closely with the calculated values (Table IV).

The above is valid only near the water surface. Competitive light absorption by water and other absorbing species (*31, 32*) decreases the rates of direct photolysis of 2,4-D esters with increasing depth. Using the above data and absorption coefficients for pure water (*31*), we calculated for several latitudes the dependence of 2,4-D butoxyethyl ester photolysis half-life on depth (Figure 7). Photolysis half-lives increase more rapidly with increasing depth in most natural waters due to competitive light absorption by other dissolved organics, light scattering, and lack of complete mixing. Concentration of the 2,4-D esters into surface slicks would obviously accelerate their overall photolysis rates. Unfortunately, only limited data on the concentration of pesticides into surface slicks are available (*33*), and no data on 2,4-D esters have been obtained.

We also investigated the photolysis of an ester in a natural water sample. The butoxyethyl ester (1.0 ppm) was irradiated (>290 nm) in filter-sterilized water from the Suwannee River (pH 4.7). This particular river contains a large amount of dissolved humic material that absorbs strongly in the ultraviolet and visible. The major photoproducts found in distilled water (Figure 3) were also found in the river water although the yield of 2,4-dichlorophenol was much higher, and the yields of the hydroxylated phenoxy esters were lower. As with distilled water, no monochlorinated phenoxy esters were formed in the river water. The overall photolysis rate was twice as rapid in the river water as in distilled water. This acceleration is attributed to photosensitization by the substances dissolved in the river water.

Since photolysis of 2,4-D esters by direct absorption of sunlight is slow, sensitized photolysis may be more important in many natural waters.

Evaporative Loss. Field studies by Bamesburger and Adams (*34*) have shown that various 2,4-D esters exist in the air near sites of application, but the importance of vola-

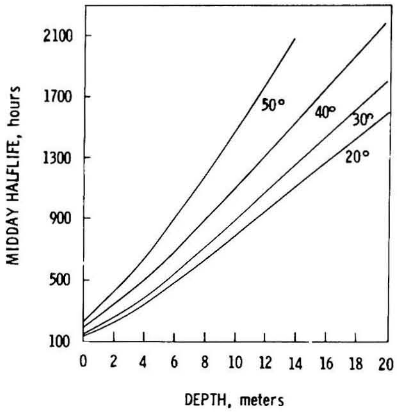

Figure 7. Depth dependence of 2,4-D butoxyethyl ester photolysis half-life at several northern latitudes in completely mixed pure water

tilization from surface waters has not been assessed. Recently Mackay and Wolkoff (*6*) have shown that volatilization rates of pesticides from completely mixed water bodies are not only proportional to their vapor pressures but are also inversely proportional to their solubilities. We measured solubilities of several commonly used 2,4-D esters and then calculated their volatilization half-lives using published vapor pressures (*35, 36*). The calculated half-lives for a surface-water depth of 1 m ranged from about one day for the butyl ester to over two years for the low-volatile butoxyethyl ester (Table V). Observed half-lives in natural waters are likely to be longer because of sorption or diffusion limitations and the presence of organic surface films (*37*). Moreover, in deeper water bodies the calculated half-lives are much longer. For example, the calculated half-life for the butyl ester is 11 days in a water body that is 10 m deep.

Conclusions

In the preceding sections, we have assessed the rates for three competing processes that remove 2,4-D esters from a body of water. Some illustrative data for a water body 1 m deep are presented in Table VI. Conclusions derived from this table are summarized below.

- In basic waters, hydrolysis is the most important of the three processes for all the esters.
- In acidic water, the relative importance of the three processes depends on the ester structure. Photolysis is the most important process for the butoxyethyl ester, vaporization is most important for the butyl and octyl esters, and both vaporization and photolysis are important processes for the methyl ester.
- The overall loss rate due to the three processes is much more rapid in basic than in acidic water.
- Transformation of the butoxyethyl ester by chemical and photochemical processes is more rapid than transformation of the hydrocarbon chain esters.

Hydrolysis rates measured in solutions containing no microorganisms, however, are not necessarily representative of those found in natural waters. Studies in our laboratory (*38*) have shown that bacteria and fungi can enzymatically catalyze the hydrolysis of the butoxyethyl ester.

The hydrolysis product, 2,4-D, is resistant to chemical degradation (*39*) and is nonvolatile; photolysis is probably an important pathway for its disappearance from natural waters. Using a recently published quantum yield for 2,4-D in water ($\Phi = 0.044$) (*40*), we calculated the half-life under conditions noted in Table VI as 20 days.

Table V. Calculated Vaporization Half-Lives for Several 2,4-D Esters at 25°C

Ester	Solubility, mg/l	Vapor pressure,[a] mm Hg	Half-life for 1-m depth
Methyl	113	2.3×10^{-3}	21.7 days
1-Butyl	1.0	3.9×10^{-4}	1.1 days
1-Octyl	7.0×10^{-2}	2.0×10^{-6}	11.5 days
2-Butoxyethyl	12	4.5×10^{-6}	895 days

[a] Previously published data (*35, 36*).

Table VI. Comparison of Hydrolysis, Photolysis, and Vaporization Half-Lives for Several 2,4-D Esters at 25°C[a]

	Hydrolysis, days		Direct photolysis,[b–d]	Vaporization,[d]
Ester	pH 9	pH 6	days	days
Methyl	0.04	44	29	21.7
1-Butyl	0.2	220	—	1.1
1-Octyl	0.2	220	—	11.5
2-Butoxyethyl	0.02	26	16	895

[a] For water body 1-m deep. [b] For September in southern United States (lat. 34°N); average value for 1-m deep pure water. [c] Expressed in terms of 12-hr days. [d] Calculated for a completely mixed water body.

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Elemental Ratios Along Human Hair as Indicators of Exposure to Environmental Pollutants

Vlado Valković* and Dubravko Rendić,

T. W. Bonner Nuclear Laboratories, Rice University, P.O. Box 1892, Houston, Tex. 77001, and
Institute "Ruder Bosković," Zagreb, Yugoslavia

G. C. Phillips

T. W. Bonner Nuclear Laboratories, Rice University, P.O. Box 1892, Houston, Houston, Tex. 77001

■ Trace element ratios along human hair on a population group have been measured using the technique of proton induced X-ray spectroscopy. It has been shown that the elements whose concentrations increase along the hair can be identified as pollutants in the area. For widespread pollutants (such as lead) even the medium value of a group of subjects can be used as a measure of the exposure.

Some 27 elements have been identified in human hair (*1*). Concentrations of elements vary from individual to individual and could be caused by sex, age, color. The growth of hair is approximately constant and continuous during the lifetime of an individual (children: 10.1–13.5 mm/month; adults: 7.1–12.0 mm/month). Since hair accumulates elements for longer periods, and it is metabolically inert, it is assumed that hair might serve as an indicator of elemental concentrations in the body (*2, 3*). The efforts to correlate hair trace element concentrations in other parts of the body have given different results (*4–7*). However, heavy metal poisoning has been successfully correlated with hair trace element content (*8–10*).

Several investigators have shown that trace element contents vary with geographical location, indicating the importance of environmental effects. Some authors (*11*) suggest the use of measurements of trace element concentration for geochemical prospecting, assuming that hair reflects the soil composition. We refer to the results of Hammer et al. (*12*), who studied the concentrations of As, Cd, Cu, Pb, and Zn in the hair of schoolchildren in five cities. Their results show that the concentrations of As, Cd, and Pb accurately reflect the exposure to these metals. It seems that Cu and Zn concentrations in hair do not depend on their concentrations in the air, perhaps because of their large concentrations in human nutrition.

Because of its growth, hair reflects previous elemental concentrations in serum and body (history of previous biochemical and medical events in man), as well as previous environmental effects. Several measurements of trace element distributions have been reported (*13–16*). The investigators agree that the variations are characteristic of the subject and that Zn variations along hair are negligible. This latter fact may be also due to the relation of Zn with the production of melanin pigment in hair. Assuming constant distribution of Zn along the hair, only the ratios of elemental concentrations to Zn concentration need be measured to obtain elemental concentrations along hair. Such relative measurements can be easily performed on single hairs using proton-induced X-ray emission spectroscopy (*17*).

If the exposure of hair to the elements in the air and water is constant, the elemental concentrations will increase with distance from the scalp. Results of the measurements of Pb concentrations along a single human hair reported by Renshaw et al. (*14*) show almost linear increase in Pb concentration with the distance from the scalp. This indicates that Pb has entered into hair by deposition on its surface and by later diffusion into hair structure.

As it is for lead, this should be a case with other environmental pollutants. Therefore, the measurements of trace element concentrations along the hairs of a population group might give an indication of the presence of environmental pollutants.

Experimental

In the measurements reported here trace elements in hair samples from schoolchildren from three schools in the city of Rijeka, Yugoslavia, were investigated. Relative concentrations of different trace elements have been determined by proton-induced X-ray emission spectroscopy. Hair targets were prepared by cutting a single hair or bunch of hairs into pieces of approximately 3.5 cm in length. Each sample was then fixed to an aluminum frame. Each target was exposed to the beam of 3 MeV protons from the Rice University tandem Van de Graaff accelerator. Detector efficiency for elements lighter than Ca and for low-energy bremsstrahlung background were artificially reduced by introducing a polystyrene absorber in front of the detector. The resulting X rays were detected by a Si(Li) detector, amplified, then processed, and stripped for peak intensity by an IBM-1800 computer. Peaks associated with Fe, Ni, Cu, Br, Sr, Pb, Mn, As, and Se characteristic X rays were present in most measured X-ray spectra.

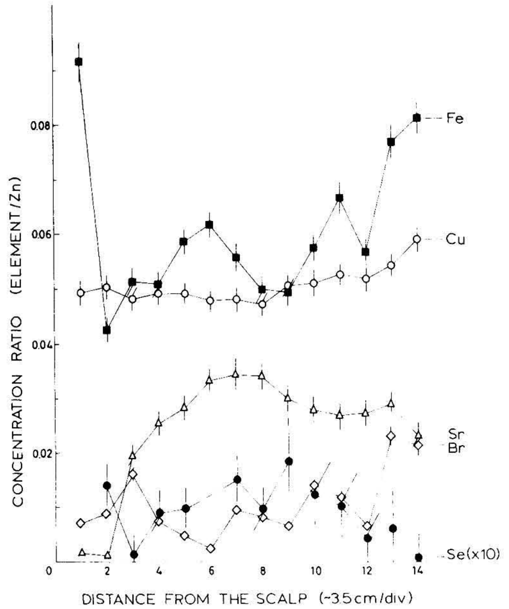

Figure 1. Concentration ratios: Fe:Zn, Cu:Zn, Sr:Zn, Br:Zn, and Se:Zn as functions of distance from the scalp. Se:Zn ratio has been multiplied with a factor 10. The errors shown are the statistical ones

Absolute elemental concentration could not be measured in the absence of either doping with some element or proton elastic scattering information. Therefore, the concentration ratios to Zn have been determined.

Results and Discussion

The measured population group consisted of 100 schoolchildren, boys and girls, living in different parts of the city of Rijeka. Trace element concentrations along the hair for each child reflects the personal medical and environmental history of the subject. Only some aspects of the effect of environmental pollution on hair trace element concentration will be discussed in this paper.

As an example, Figures 1 and 2 show the ratios Fe:Zn, Cu:Zn, Sr:Zn, Br:Zn, Se:Zn, Ni:Zn, Pb:Zn, and As:Zn as a function of distance along the hair of one girl from the group. The elements can be divided into two groups: Figure 1 shows the group of elements in which concentrations do not show marked increase along a hair; on the contrary, the group of elements in Figure 2 shows a marked increase in concentrations along a hair. Fe:Zn, Sr:Zn, Br:Zn, and Se:Zn ratios show different behavior for different subjects; for some subjects their concentrations increased along the hair. Concentration ratio Cu:Zn seems to be extremely constant indicating that Cu and Zn are highly correlated in hair structure.

The concentration ratios As:Zn, Pb:Zn, and Ni:Zn for the same subject are shown in Figure 2. It is important to note

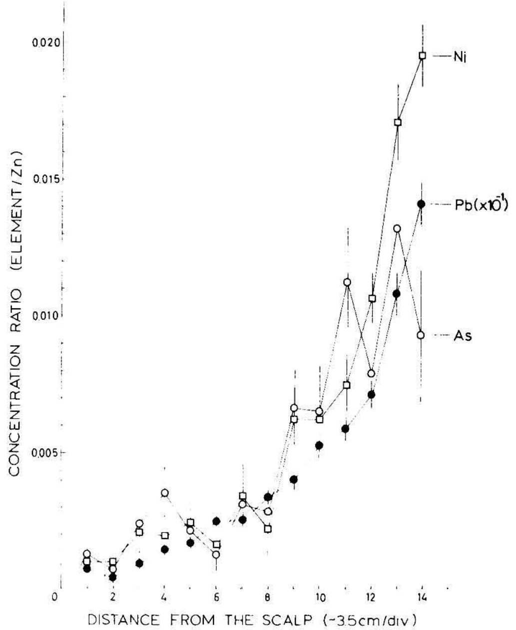

Figure 2. Concentration ratios: Ni:Zn, Pb:Zn, and As:Zn as functions of distance from the scalp. Pb:Zn ratio has been divided by a factor 10. The errors shown are the statistical ones

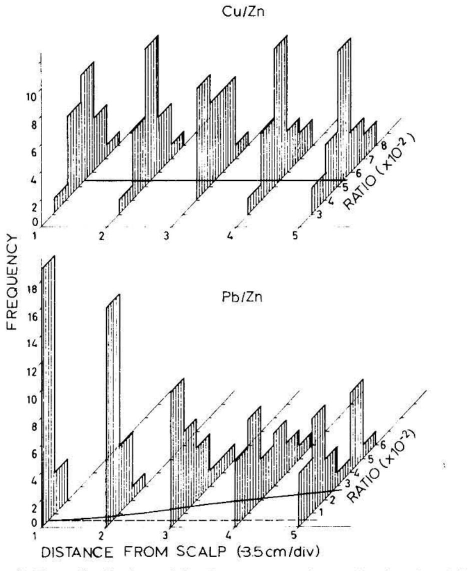

Figure 3. Top: distribution of Cu:Zn concentration ratios for the children with long hair (first five segments are presented)

The solid curve is a medium value

Bottom: distribution of Pb:Zn concentration ratios

The solid curve represents medium values of different segments, while the dashed curve is a medium value for the first segment. The difference between these two values increases along the hair that the shape of the dependence on the distance from the scalp is similar for all three ratios.

This would indicate that elements As, Pb, and Ni are contaminants in the environment of our subject. Note that the Pb concentrations are an order of magnitude higher than those of Ni and As.

Thus the measurement of trace element concentrations along a hair may indicate which elements are contaminants in the subject's environment. To obtain additional confirmation of this conclusion Cu:Zn and Pb:Zn concentration ratios for all schoolchildren with longer hair (5 or more pieces of 3.5 cm for 22 subjects) are presented in Figure 3 as the isometric plots. At the top of the figure are shown Cu:Zn ratios, the solid line indicating the medium value that is remarkably constant along the hair. At the bottom of the figure is shown Pb:Zn concentration ratios. Lead is a known environmental pollutant present in the air because of automobile traffic.

The dashed line shows the median for the first segment (near the scalp), the solid curve shows the medians for different segments of hairs. The increase in medium value for the Pb:Zn concentration ratio as the distance from the scalp increases is obvious. Segments 4 and 5 show a group of subjects with a significant increase of lead concentrations; these are the schoolchildren from the school near the exceptionally heavy traffic.

In conclusion, the study of the shape of elemental concentrations along human hair (actually in ratios to Zn) can be used as a method to identify the pollutants in the area. Such measurements give the information on the exposure of subjects to different pollutants, and the history of the exposure manifest in the variations of concentrations along the hair.

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Synthesis Gas from Feedlot Manure

Conceptual Design Study and Economic Analysis

Cady R. Engler, Walter P. Walawender*, and Liang-tseng Fan
Department of Chemical Engineering, Kansas State University, Manhattan, Kan. 66506

■ A conceptual process design for the pyrolysis of feedlot residues was employed as a basis for economic evaluation of the concept of pyrolysis as a disposal alternative. Sensitivity analysis with respect to plant size, residue moisture content, transportation costs, and other factors were conducted. The results indicate that only large-scale processing under the most favorable conditions will approach the point of economic competitiveness. The processing scales required are compatible with high-density cattle feeding regions and end uses of the product gas.

The cattle-feeding industry is important to the economy of a number of states in the mid-West. In the past decade this industry has grown rapidly, with increasing numbers of cattle on feed along with significant increases in the capacities of individual feedlots. In addition, the larger feedlots tend to be grouped within relatively small areas. The large animal-to-land ratios thus created have lead to serious manure disposal problems and environmental hazards in some locales.

On a weight basis, the manure generated by beef cattle is the major product of the industry. Approximately two tons per head per year of semicomposted manure containing 50% moisture are produced. Since the practice of using manure as a fertilizer is not feasible in most locales on a large scale, the manure must be disposed of at considerable expense to the operator or allowed to accumulate in the vicinity of the feedlot. Such disposal creates a high potential for causing environmental problems. Converting the manure liability into an asset could help to reduce beef production costs while preventing damage to the environment.

One approach to manure utilization is through chemical processing to provide material and energy resources. Our preliminary studies of three processes (*1*, *2*) indicate that a pyrolysis process to generate synthesis gas is most nearly compatible with present economics and waste availability. The resultant synthesis gas product could be used to provide a clean low-Btu gas for power generation, a starting material for ammonia synthesis, or a starting material for methanol production. In addition to the synthesis gas, the ash by-product of feedlot manure pyrolysis appears to be a potential nitrogen-free fertilizer (*3*).

This work presents a conceptual design for a manure gasification plant and an economic analysis of the process.

The conceptual design was based on a capacity of 1000 t/d (tons per day) of raw manure with a moisture content of 50 wt %. The selected capacity is representative of the manure generated by 200,000 head of cattle, and the moisture content is typical of semicomposted manure in a nonarid climate. It is not uncommon in major cattle feeding regions to find cattle densities of 200,000 or more head within a 50-mile radius. In a few regions, densities may approach 800,000 or more within an area of this size. In the economic analysis, it was assumed that raw material costs for manure would be only the charge for transportation to the plant and that the average haul would be 25 miles.

An empirical stoichiometry for the overall gasification reaction was developed on the basis of the manure composition data from studies conducted at the U.S. Bureau of Mines (*4*) and experimental gasification data obtained from municipal refuse of similar composition to manure (*5*). Gas yields and compositions predicted by the resulting material balance agreed favorably with experimental data reported for a variety of organic wastes including cow manure (*6*). The empirical stoichiometry was also used to evaluate the heat of reaction. The energy balance was formulated with the aid of estimated thermochemical data.

Table I presents the raw manure composition, dry ash-free (DAF) manure composition, and the heating value of DAF manure estimated from the DuLong formula. Table II presents the daily production of the synthesis gas constituents from a 1000 t/d plant. Clean synthesis gas production (CO, H_2, and CH_4) amounts to 10.7 MSCF per day, and the gas has a heating value of 380 Btu/SCF.

Table I. Composition of Manure[a]

Constituent	As used, wt %	Dry, ash-free,[b] wt %
Carbon	18.9	52.2
Hydrogen	2.3	6.4
Oxygen	13.3	36.9
Nitrogen	1.2	3.3
Sulfur	0.4	1.2
Ash	13.9	—
Water	50.0	—

[a] Appell et al. (*4*). [b] Heating value = 8750 Btu/lb (estimated from Dulong's formula).

Table II. Pyrolysis Gas Production from a 1000-Ton/Day Plant

Constituent	MM SCF/day	Constituent	MM SCF/day
CO	4.55	H_2S	0.10
H_2	5.20	NH_3	0.62
CH_4	0.98	H_2O	0.80
CO_2	1.43		

The conceptual process consists of three principal steps; waste preparation, gasification, and gas cleanup. The principal objective of the process is to maximize gas production. With this goal, it was decided to employ a fluidized bed gasification system. Gasification is carried out in an inert bed of fluidized sand to ensure controllable fluidization conditions. Feed preparation consists of flash drying to 10% moisture and size reduction to 60 mesh. These figures were somewhat arbitrarily selected and optimum conditions are subject to experimental determination. A simple water scrubbing system was selected for gas cleanup. The system has a large volume and high pumping and compression requirements and is perhaps overly conservative. The actual cleanup system should be selected with consideration of further processing or the end use of the gas.

The remainder of this project presents a description of the conceptual process, capital costs for a 1000 t/d plant, a sensitivity analysis, and a discussion of the factors that will influence the economic potential.

Conceptual Design

A process flow diagram for the conceptual plant is shown in Figure 1. Major sections of the plant include feed preparation, gasification, and gas cleanup. The plant produces

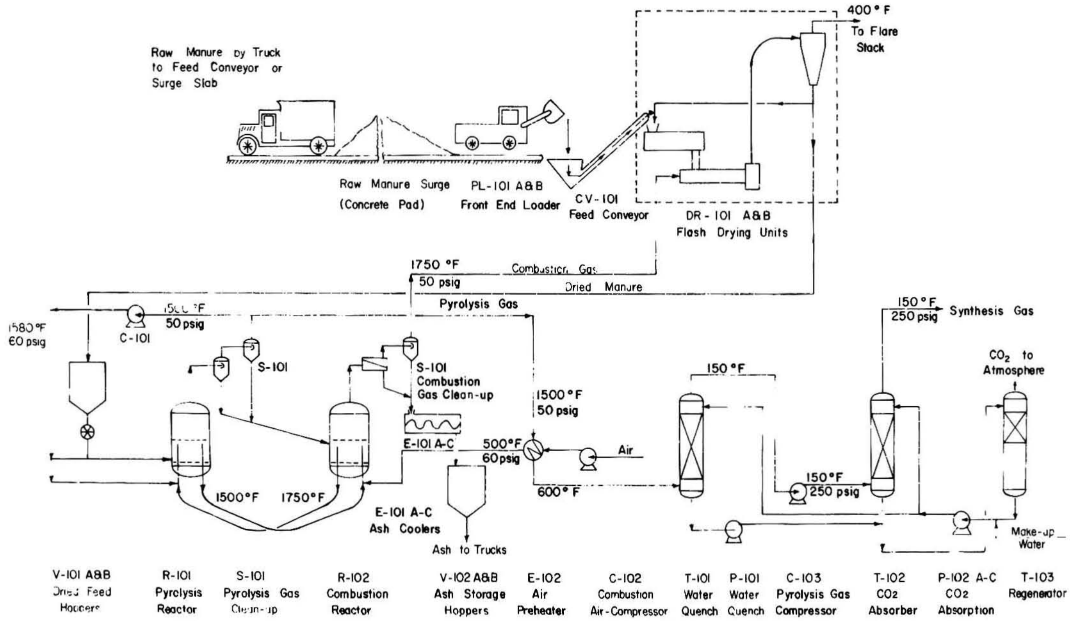

Figure 1. Process flow diagram

10.7 million SCF/day of clean synthesis gas having a heating value of 380 Btu/SCF (about 40% of the heating value of natural gas) and 139 t/d of ash residue. A detailed description is given in an earlier report (7); only an outline will be presented here.

Manure is transported from feedlots to the plant by truck. The receiving facility is a storage building large enough to store three days' supply of raw manure and provide room for unloading and transfer to the dryer feed conveyor.

The storage area is suitably enclosed to meet esthetic and environmental requirements.

A front end loader (PL-101) transfers the raw manure to the feed conveyor (CV-101), which in turn, takes it to the dryers (DR-101 A & B). Since particle size reduction is required as well as drying, a cage mill–flash drying system was selected to perform both operations in one step. In the dryer the moisture content of the solids is reduced to about 10 wt %, and the particle size reduced to 60 mesh. Wet gas leaves the dryer at about 400°F and is flared to control odor.

Dry solids are stored in hoppers (V-101 A & B) which contain approximately a half day's feed supply. The dry manure is metered continuously through rotary feeder valves into a high-velocity stream of recycle pyrolysis gas which conveys the feed into the bottom of the pyrolysis reactor (R-101).

The pyrolysis reactor consists of a bed of fluidized sand maintained at 1500°F and 50 psig. Previous studies (*5, 8*) have shown that the yield of synthesis gas increases as the heating rate of the solid increases. An efficient method to achieve this rapid heating rate is to use a fluidized bed of inert material such as sand maintained at a constant temperature.

Since the pyrolysis reaction is endothermic, heat must be supplied to the reactor. While heat can be supplied by partial combustion within the reaction vessel, there are advantages to circulating the sand to a separate combustion vessel. The primary advantage is that combustion gases do not dilute the pyrolysis product gas. The combustion reactor (R-102) is maintained at 1750°F and 50 psig for this design. Flow of solids between the two reactors is maintained and controlled by injecting gas into the vertical sections of the transfer lines to create specific gravity differentials.

Introduction of the manure into the pyrolysis reactor causes very rapid formation of gas and solid particles. The superficial gas velocity in R-101 is about 3.25 ft/sec. This velocity is below the terminal velocity of the sand (mean particle diameter 0.04 cm). It is, however, sufficiently high to entrain a portion of the ash and char produced. The gas, together with the entrained ash and char, passes through a two-stage multicyclone installation (S-101) for recovery of the solids, which are sent to the combustion reactor. Part of the gas is compressed to 60 psig to be recycled to the pyrolysis reactor for maintaining fluidization; the remainder is used to preheat combustion air in E-102 and then sent at 600°F to the quench column (T-101). The remainder of the ash and char in R-101 is transferred to the combustion reactor via the circulating sand.

In the combustion reactor (R-102), char formed in the pyrolysis reaction is burned to provide heat for the pyrolysis. Because more heat is available from the char than is needed for pyrolysis, excess air is used to maintain the combustion temperature at 1750°F. The hot combustion gases and air are then used to dry the raw manure, and the hot sand is circulated to drive the pyrolysis reaction. The superficial gas velocity in the combustion reactor (R-102) is also about 3.25 ft/sec. This velocity is sufficient to entrain the ash residue.

Table III. Installed Costs of Major Process Equipment Items

DR-101 A & B	$1,098,000
Compressors	747,000
R-101 & R-102	445,000
Pumps	353,000
Towers	308,000
S-101 & S-102	106,000
Miscellaneous	68,000
Total	$3,125,000

The entrained ash is then separated from the gas in a louvered collector followed by a multicyclone (S-102). The ash is cooled in hollow-flight cooling conveyors (E-101 A-C) and sent to collection hoppers (V-102 A & B). The hoppers hold approximately two days' production of ash.

The pyrolysis product gas flows to the quench column (T-101) where it is cooled to 150°F by countercurrent contact with recirculating water. The cool gas is compressed to 250 psig in the compressor (C-103) and fed to the CO_2 absorption column (T-102).

Acid gases are removed from the synthesis gas by high-pressure countercurrent contact with water. The synthesis gas product is available from the CO_2 absorption column (T-102) at about 150°F and 240 psig.

The water is regenerated in the regenerator (T-103). The upper part of the column is packed with Raschig rings, and the tower is constructed so that air can circulate upward through the packing. Water from the quench tower is also circulated through the regeneration column for cooling and removal of absorbed materials.

With the exception of the electric power for the pumps and compressors, no additional energy is required after start-up. The energy input to the process is less than 10% of the energy in the product gas. The thermal efficiency of the process (defined as the ratio of the energy in the product gas less the energy input to the process to the energy content of the feed) is 65%.

Economics and Sensitivity Analysis

To evaluate the economic feasibility of manure pyrolysis, investment and operating costs were estimated using the preceding conceptual design. With these estimated costs as a base, a sensitivity analysis of the plant was made. Variations in the size of the plant, raw manure moisture content, manure composition, and transportation costs were made to determine their effects on the profitability of the operation.

The fixed capital investment for a 1000 t/d plant was estimated to be $5.65 million based on mid-1974 costs. With working capital taken as 15% of the fixed capital investment, the total capital investment amounts to $6.5 million. The installed costs for the major items of equipment are summarized in Table III. Due to the high moisture removal requirements, the dryers account for about one third of the installed equipment costs. The gas cleanup system (water scrubber) accounts for another third of the costs due to the large volume and high pumping and compression requirements.

Annual operating expenses for the project were estimated to be $2.2 million. Costs for manure transportation amount to about 25% of the annual expense. It appears realistic to claim some credit for the ash residue. The material is a potential nitrogen-free fertilizer containing about 15% phosphate and 10% potash. A modest credit of $17.50/ton was assumed for the ash residue based on com-

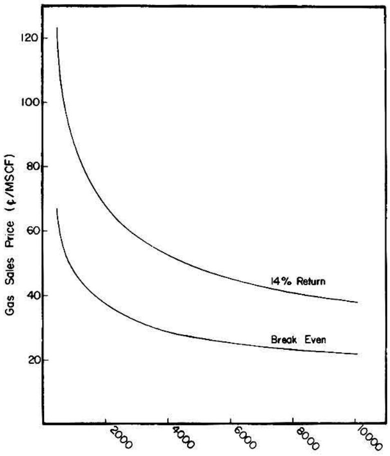

Figure 2. Plant capacity effect on sales price

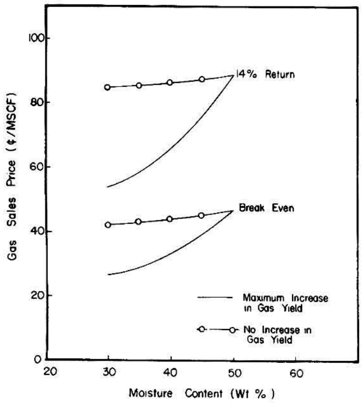

Figure 3. Moisture content effect on sales price

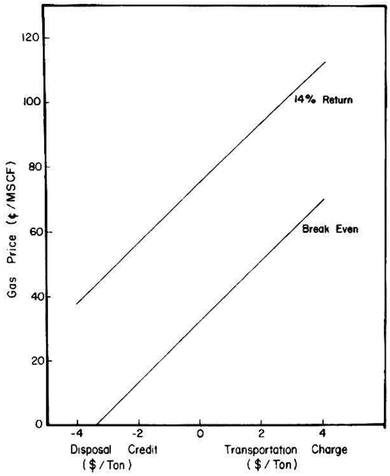

Figure 4. Transportation cost and disposal credit effects on sales price

parable costs for this kind of fertilizing material in 1972. This credit more than offsets the transportation charge for the raw manure. A credit of $10.79/ton would just balance the transportation cost.

The gas sales price was determined for a 14% after tax return using the discounted cash flow method with constant annual income. A project life of 15 years and no salvage value were assumed. The necessary gas sales price for these conditions was $0.89/MSCF or $2.34/MMBtu. Calculations for other values of rate of return and project life also resulted in relatively high costs. Only the case of a venture expecting no net profit and hence no tax to pay would begin to be competitive with new intrastate gas prices. For the conceptual plant with a 15-year life, the break-even gas sales price is $0.47/MSCF or $1.23/MMBtu. This price permits full recovery of the invested capital.

The influence of plant size on gas price was examined for plant capacities ranging from 500–10,000 t/d of 50% moisture manure. Fixed capital investments were calculated from the 1000 t/d base case using the six-tenths power rule. Working capital was taken as 15% of the fixed capital investment. Annual expenses ranged from $1.4 million for the 500-t/d plant to $15.1 million for the 10,000-t/d plant and vary approximately linearly with capacity. The variation in gas sales price for a 14% after tax return and a 15-year project life, is shown by the upper curve in Figure 2. As indicated, the gas price drops rapidly as capacity initially increases from 500 t/d and then begins to level off for capacities greater than 5000 t/d. Gas sales prices vary from $1.23 to $0.38/MSCF or $3.23 to $1.01/MMBtu for the range of gas prices. Break-even prices (shown by the lower curve in Figure 2) vary from $0.67–0.22/MSCF or $1.76–0.57/MMBtu.

The influence of reduced moisture content was also considered using a plant capacity of 500 t/d of dry manure. Moisture contents between 50% and 30% were examined. Capital investment was held constant at the value for the base case. Two cases were considered; one in which gas generation remained constant and one in which all of the excess char (not needed for process heat) was recycled and completely gasified. The results are shown in Figure 3 for both the 14% return and zero return. For constant gas generation a slight reduction in price is observed as a result of the reduction in transportation costs. The reductions in transportation costs are significant (up to 29% for the 30% moisture residue) but the overall result is minor as indicated in the figure. Gasification of all excess char on the other hand substantially increases gas production (up to 58% for the 30% moisture residue) and as a consequence has a significant effect on gas price. The two cases thus provide approximate upper and lower bounds on the influence of reduced moisture content. Inclusion of the variation in capital investment with moisture content should not alter the general trends indicated, since the decrease in drying capacity should be off set by an increase in clean-up requirements.

Data from five additional sources (*9–13*) were used to examine the influence of variability of manure composition. Pyrolysis gas compositions and yields were calculated in the same manner as for the base case using the different manure analyses. While the gas yields were somewhat scattered, there appeared to be only a slight increase in yield as carbon content increased. Thus, it appears that composition variation has a negligible effect.

The influence of transportation charges and disposal credits on the gas price for the base case are shown in Figure 4. These are shown together since the disposal credit can be considered as a negative raw material charge. From the upper curve (representing a 14% return), it can be seen that if the raw manure were delivered to the plant free of charge, the gas price would be reduced by about 16% to \$1.97/MMBtu. A disposal credit of \$4.00 per ton would permit the price to drop to \$1.00 per MMBtu. The variation with transportation charges is indicated in the upper part of the figure; a 50% variation about the base charge results in a 10.5% variation in gas price. The lower curve in Figure 4 presents the break-even case. For delivery of the residue free of charge, the gas price would drop to \$0.86/MMBtu.

Discussion

The economic estimates presented in this report are based on a conceptual process design, based on limited experimental data, that is by no means optimal. However we do believe that the results of the analysis can serve to provide bounds on the cost of gas production from feedlot residues, identify the principal factors influencing the process viability, and provide a basis for the consideration of potential applications of the process.

As would be expected, increase in plant capacity has a significant influence on the gas price. However, this feature cannot be utilized to full advantage due to the limitations of cattle population density. Each 1000 t/d of plant capacity requires about 200,000 head of cattle. For the geographic limitation of a 50-mile radius around the plant employed in the analysis, it is rare to find cattle concentrations in excess of 800,000 head. Thus a 4000-t/d facility represents a practical upper limit on plant size for the geographic limitation imposed. Of course, capacity can be increased by increasing the size of the geographic region. Our limited analysis of this possibility seems to indicate that the gains of increased capacity are just about offset by the increase in transportation charges (*14*). This observation would tend to indicate that the 4000-t/d facility can provide an indication of the lower limit on gas price with respect to capacity. For the base moisture content, the resulting gas price for a 14% return is \$0.53/MSCF or \$1.39/MMBtu. A lesser return will, of course, reduce the price and in the limit of zero return the break-even price amounts to \$0.29/MSCF or \$0.76/MMBtu. Moisture content is another factor that will influence the gas price. This influence will be slight if only transportation costs are involved, however it can be substantial if additional gas production results from the gasification of excess char. For the purpose of illustration, let us consider 40% moisture and 50% gasification of the excess char.

Moisture contents of 30–40% are not uncommon in many of the semiarid cattle-feeding regions. The figure of 50% gasification of the excess char appears reasonable on the basis of experimental data on the quantity of char remaining after the pyrolysis of municipal refuse (*15*). For the 2000-dry-t/d facility these conditions would result in a reduction in the gas price to \$0.44/MSCF or \$1.10/MMBtu for a 14% return. The break-even prices for this case are \$0.21/MSCF or \$0.55/MMBtu.

Other factors such as the variation of the dry ash-free composition of the residue and the local variation in transportation charges should have minor effects. The influence of the ash content of the residue was not examined in the sensitivity analysis, but it would appear that the principal influence would be through the alteration of transportation charges that would have only a limited influence on gas price.

The adoption of a disposal charge can have a significant effect on gas price. Unless all the cost for hauling the residue to the plant is charged to it, the remaining portion constitutes a disposal cost to the feedlot operator. If the plant receives the residue free of charge, this amounts to an average disposal cost of \$1.50/ton to the feedlot operators. For comparison with other disposal alternatives, this figure is approximately the disposal cost per market steer. For this disposal charge, the gas sales price (4000 T/D, 50% moisture) would be \$0.37/MSCF or \$0.97/MMBtu for a 14% return.

We have presented costs for both a profit and nonprofit venture. The indications of the discussion show that only under the most favorable circumstances will the price of the gas approach the point of being competitive with new intrastate natural gas prices (\$1.00 plus/MMBtu) for a commercial venture. The situation, of course, improves if a lower profit is sought such as might be the case with a cooperative association.

The conceptual process presented in this report provides an attractive disposal alternative with a minimum of process residues. The gas emissions are substantially less than from incineration as indicated by studies on municipal residues (*15*) and pollutants such as SO_2 and NO_x are within environmentally acceptable levels. The solid residue of the process appears to be a potential nitrogen-free fertilizer and thus represents a useful by-product. The principal product, on the other hand, is an intermediate which must be further processed before distribution to the consumer. Two possible uses of the gas are direct firing to generate electricity and as an alternate feedstock for the synthesis of ammonia. Each of these products can be used to considerable benefit in the centers of residue generation. However, the compatibility of the gas production potential with the gas requirements for the end use needs to be considered.

In this respect also large-scale processing needs to be considered. The 4000-t/d plant mentioned earlier could provide sufficient gas to operate a medium size ammonia plant (500 t/d). The gas would allow an alternative to the natural gas presently employed to provide both the hydrogen source and a portion of the energy requirements. Recent indications are that ammonia producers will begin to consider alternative feedstocks when the price of natural gas reaches \$1.00/MMBtu (*16*).

For electric power generation, the gas could fuel a power plant rated at 160 MW. Although small compared to most modern facilities, the size is comparable to proposed solar generating facilities. Additionally the low-sulfur content of the fuel and low-Btu content will result in low SO_2 and NO_x emissions.

In conclusion, the indications of this study are that only large-scale pyrolysis processes can approach the point of competitiveness for a commercial operation. The scales required are compatible with residue supply in high-density cattle-feeding regions and are also reasonably compatible with the scale of operation for potential end uses of the gas.

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Homogeneous Gas Phase Chemiluminescence Measurement of Reactive Hydrocarbon Air Pollutants by Reaction with Oxygen Atoms

Arthur Fontijn* and Roy Ellison

AeroChem Research Laboratories, Inc., P.O. Box 12, Princeton, N.J. 08540

■ A continuous flow method for measuring total (photochemical smog) reactivity of dilute hydrocarbon mixtures is described. The difference between the OH($A^2\Sigma$-$X^2\Pi$) emission intensities at 308.9 and 312.2 nm from O-atom/hydrocarbon reactions near 1 torr is measured. For C_2H_4, $I_{308.9} \gg I_{312.2}$ while for C_2H_2, $I_{308.9} \approx I_{312.2}$. All other hydrocarbons, HC (olefinic, dienic, paraffinic, and aromatic), tested yield the same spectral distribution as C_2H_4; CH_4 yields no observable emission. Two photomultiplier tubes are used for measurement at 308.9 and 312.2 nm, respectively. The apparatus is zeroed by adjusting the gain of the PMTs so that the device does not respond to C_2H_2. By adjusting operating conditions, the relative response to the individual *reactive* HC species can be set to give good agreement with reactivity ratings. The response to HC mixtures is additive. A limit of sensitivity of ≈ 0.2 ppm of C_2H_4-equivalent HC and a linear response to individual HCs to >1000 ppm are obtained. This sensitivity range is sufficient for mobile engine exhaust bag sample monitoring; greater sensitivity for ambient air-monitoring applications would appear feasible. CO, CO_2, SO_2, CH_4, C_2H_2, and NO_x do not interfere with apparatus response. A 1% change in $[O_2]$ causes <1% change in signal; the presence of 3% H_2O causes a $\approx$12% decrease relative to dry samples.

The formation of photochemical smogs requires the presence of both NO_x and organic pollutants, particularly hydrocarbons. However the ability of hydrocarbons to produce smogs varies greatly depending upon the rate coefficients of the many reactions involved (particularly attack by OH, O_3, and O) (*1, 2*). For example, methane and acetylene are considered to be "unreactive," while ethylene and *n*-butane are "reactive" hydrocarbons in terms of photochemical smog. However, severalfold higher *n*-butane than ethylene concentrations are required to produce similar atmospheric effects. Current U.S. hydrocarbon standards are based on total nonmethane hydrocarbons, the measurement of which requires several steps—e.g., a flame ionization total hydrocarbon analyzer in combination with an infrared methane monitor or a gas chromatographic methane separator (*3*). Alternatively a complete gas chromatographic analysis gives detailed information but is very time consuming. There is, accordingly, a need for a measurement method that gives an indication of total hydrocarbon reactivity—i.e., gives the sum of the concentrations of each hydrocarbon species multiplied by an individual or group reactivity factor. Since the reactivity of hydrocarbons differs with respect to several parameters—e.g., butane contributes more heavily in late or downwind than in early smog situations, any hydrocarbon reactivity scale is of necessity somewhat arbitrary (*4*); as a result a number of reactivity scales have been proposed. Recently Dimitriades (*5*) proposed a scale which combines several of the features of earlier scales. On this scale, organic pollutants are subdivided into five reactivity classes each with its own reactivity factor; the combined reactivity of a gaseous mixture is the sum of the molar concentrations of the individual hydrocarbons each multiplied by the reactivity factor of the group to which it belongs.

The present work was undertaken to develop a real-time continuous readout monitoring method for total hydrocarbon reactivity in the 0.1–1000-ppm concentration range of interest in mobile engine exhaust CVS bag sample monitoring (*6*). Initial studies were made in a survey apparatus suitable for detailed spectrometric and kinetic observations but not suited to measurements at realistic hydrocarbon concentrations. These studies, discussed first, suggested a practical method, the $\Delta I_{308.9}$ method, for hydrocarbon monitoring. This method was then tested with realistic hydrocarbon concentrations in a test apparatus, the design of which was based on information obtained in the survey studies. The $\Delta I_{308.9}$ method developed is designed to adhere reasonably close to the Dimitriades scale but can also be adapted to different scales.

Survey Study; $\Delta I_{308.9}$ Method

The goal of the initial survey work was to establish a method for C_2H_4 measurement free of interference by CH_4

and C_2H_2, the most prominent nonreactive hydrocarbons. Our earlier studies of chemiluminescence in reactions between hydrocarbons and O or N atoms (e.g., Refs. *7–9*) indicated that it might be possible to find such a method. Since chemiluminescence measurements have been found to provide sensitive and essentially interference-free monitoring methods for a number of air pollutants (for a review of these methods, see Ref. *10*), it was decided to examine these reactions further. Accordingly, an experimental survey of the chemiluminescence emission features from reactions of hydrocarbons with O and N atoms was undertaken.

A Pyrex cylindrical flow reactor described previously (*7, 8*), into which the reactant gases could be individually flow metered was used in this study. A Czerny-Turner-type 0.5-m Minuteman Model 305-MHA monochromator with a $f/6.9$ aperture ratio and equipped with appropriate photomultiplier tubes (PMTs), was used for spectral measurements. The spectral region, 150–600 nm, was investigated. Details of this investigation are given (*11*). The only emission found to meet the objective was that of the $OH(A^2\Sigma - X^2\Pi)$ system near 310 nm. Krieger et al. had previously suggested that this band system might offer promise for hydrocarbon monitoring (*12*).

Figure 1 shows a comparison of the pertinent portion of the $OH(A^2\Sigma - X^2\Pi)$ system from the $O-C_2H_4$ and $O-C_2H_2$ reactions. For both reactants the $(0,0)Q_2$ head at 308.9 nm is a dominant feature; however in the C_2H_4 case it is *the* dominant feature while for C_2H_2 it is just *a* dominant feature. Specifically, for C_2H_2, the 312.2 nm $(1,1)R_1$ head has almost the same intensity as the 308.9-nm head, while for C_2H_4, the $(1,1)R_1$ head is very weak. These observations suggest that a measurement of $\Delta I_{308.9} = I_{308.9} - I_{312.2}$ could provide a direct measurement of C_2H_4 in the presence of C_2H_2. (An alternate choice which might be suitable, but was not quantitatively investigated, is to subtract $I_{306.4}$ rather than $I_{312.2}$ from $I_{308.9}$.) To further investigate the usefulness of the $\Delta I_{308.9}$ method, we measured the spectral distribution of a number of other hydrocarbon species given in Table I. These species were selected as being representative of the hydrocarbons present in engine exhausts; for this reason no Dimitriades Class II compounds were included. All of these hydrocarbons (except CH_4, from which no emission could be detected) yielded the same spectral distribution as C_2H_4, further reinforcing the apparent suitability of $\Delta I_{308.9}$ measurements as a monitoring method for reactive hydrocarbons free from interference by C_2H_2 and CH_4. Changes in hydrocarbon concentrations and reaction time produced no noticeable changes in spectral distributions, nor did the spectral distribution from $O-C_2H_4$ change when the pressure was increased from 0.8–2.0 torr. The $O-C_2H_2$ spectral distribution showed some change with this increase in pressure: The intensity of the "subtract" wavelengths (306.4 and 312.2 nm) decreased somewhat with respect to that at 308.9 nm—i.e., the spectrum more closely resembled that of the other hydrocarbons.

The difference in spectral distribution resulting from the C_2H_2 and C_2H_4 reactions with O atoms had been observed previously and is indicative of two different $OH(A^2\Sigma)$ formation reactions leading to formation of rotationally and vibrationally "hot" and "cold" $OH(A^2\Sigma)$, respectively (*14*). The fact that the other hydrocarbons produce the same spectral distribution as C_2H_4 suggests that the mechanism of $OH(A^2\Sigma)$ formation is the same in all those cases; however, this reaction mechanism has not yet been established. The $O-C_2H_2$ mechanism has been shown to involve O_2 and can probably be attributed to Ref. *15*:

$$CH + O_2 \rightarrow OH(A^2\Sigma) + CO$$

While in accord with this reaction, the $OH(A^2\Sigma - X^2\Pi)$ emission from $O-C_2H_2$ increases initially with O_2 addition—that from $O-C_2H_4$, etc., only decreases in intensity upon such addition (*9, 11*), indicative of $OH(A^2\Sigma)$ quenching by O_2 and of free radical scavenging of an emission precursor by O_2. The observation that with increasing pressure the $O-C_2H_2$ spectral distribution becomes more like the $O-C_2H_4$ and so forth distribution is evidence for rotational/vibrational relaxation of the relatively long-lived ($\tau_{rad} = 8 \times 10^{-7}$ sec) (*16, 17*) emitter $OH(A^2\Sigma)$ with increasing pressure.

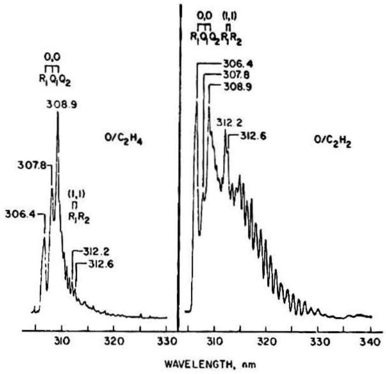

Figure 1. $OH(A^2\Sigma - X^2\Pi)$ emission from the O/C_2H_4 and O/C_2H_2 reaction in an O_2 bath at 0.8 torr

Comparison of the $\Delta I_{308.9}$ measurements given in Table I with the Dimitriades reactivity ratings (5) shows satisfactory agreement. The rate coefficients for O-atom attack on the hydrocarbons are shown in the last column of Table I.

Table I. Relative Chemiluminescence Signal Intensities and Rate Coefficients for O-Atom Attack of Classes V, IV, III, and I Hydrocarbons,[a] at High Hydrocarbon Concentrations[b] in Survey Apparatus

Class V, reactivity[a] = 14.3	$\Delta I_{308.9}$[c,d]	k[e]
Ethylene	100	4.9×10^8
Propylene	104	2.2×10^9
Butene-1	91	2.3×10^9
Butene-2	94	1.2×10^{10}
Isobutene	78	1.2×10^{10}
Propadiene	48	Unavailable
Butadiene	113	1.2×10^{10}
Class IV, Reactivity = 9.7		
Toluene	29	1.4×10^8
Class III, Reactivity = 6.5		
n-Butane	6	1.6×10^7
n-Heptane	10	7.7×10^7
Iso-octane	10	5.5×10^7
Class I, Reactivity = 1.0		
Ethane	3	5.5×10^5
Propane	7	9×10^6
Benzene	3	2.4×10^7
Methane[f]	$<10^{-2}$	$\approx 1 \times 10^4$

[a] Reactivity classes and numbers as suggested by Dimitriades (*5*). [b] In the experiments with the test apparatus (below) the hydrocarbons were introduced with a flow of air (the counterpart of hydrocarbon diluted in the N_2-O_2 mixture present in automotive exhaust bag samples) and the number of ppm (v/v) of hydrocarbon in the sample flow is a meaningful figure, the same as in most air pollutant analyzers. In the survey apparatus, the hydrocarbons flowed directly in the main gas flow and no such definition is possible. The total flow under the conditions of this table contained (before reaction) 1600 ppm of hydrocarbon, corresponding to 4800 ppm in the sample flow of the test section experiments where the reagent flow was twice as large as the sample flow. [c] Ethylene is taken as 100. [d] The observation conditions were the following: Reaction time = 2×10^{-3} sec; P = 0.8 torr; O_2 flow = 3 ml atm sec^{-1}; O-atom flow = 4.7×10^{-2} ml atm sec^{-1}; Hydrocarbon flow = 5×10^{-3} ml atm sec^{-1}. [e] Rate coefficients, in l $mole^{-1}$ sec^{-1}, at ≈25°C for the attack of O atoms on the specific hydrocarbons as recommended by Herron and Huie (*13*) from the available measurements. [f] No detectable signals from methane were obtained; the highest methane flow tested was 5×10^{-1} ml atm sec^{-1}.

In general the rate coefficients decrease in the same direction as the reactivity ratings. This appears to be a principal reason that the $\Delta I_{308.9}$ measurements give a reasonably good indication of photochemical smog reactivity (the reactions following the initial O-atom attack are of course also important in determining the light intensity). Because the less reactive hydrocarbons are consumed less rapidly than the more reactive hydrocarbons, their intensity will decrease less rapidly with reaction time (distance), which is the reason that temporal/spatial adjustment of the relative $\Delta I_{308.9}$ from the various hydrocarbons is possible (Table II). The fact that under the observation conditions of Table I the butenes give a lower reading than C_2H_4, notwithstanding their larger rate coefficients, is probably indicative of their faster consumption.

The basis for the $\Delta I_{308.9}$ method thus has been established. To test the method under realistic bag sample conditions, hydrocarbon concentrations of $\approx$0.1 to $\approx$1000 ppm should be used. This could not be done with the survey apparatus because a spectrometer is not a sufficiently sensitive tool and regular continuous flow-metering devices are not adequate for providing such low concentrations. Another flow tube apparatus (the test apparatus) was therefore built, in which interference filters replaced the monochromator, an exponential dilution flask was used to supply low concentrations of the hydrocarbons, and a differential electrometer was used to automatically subtract $I_{312.2}$ from $I_{308.9}$.

Test Apparatus and Experimental Procedure

The test apparatus is shown in Figure 2. The O atoms are produced by a 2450-MHz microwave discharge (not shown) in a 13-mm o.d. Vycor tube. The remainder of the apparatus is made of Pyrex. A 22-mm i.d. Pyrex reaction tube is used. The gas flowing into the discharge was, for most of the work, He–9% O_2 (1 ml atm sec^{-1} He per 1×10^{-1} ml atm sec^{-1} O_2). In some experiments 100% O_2 was used to provide a comparison. The He–9% O_2 was chosen since it yields a reasonably high [O], comparable to that available from 100% O_2, yet keeps O_2-quenching at a low level. We will refer to the O–O_2–(He) mixture flowing from the discharge into the reaction tube as the "reagent" ($\equiv$ second reactant) gas. The hydrocarbons were introduced through a 2-l exponential dilution flask (*18*) by a 0.5-ml atm sec^{-1} flow of Scientific Grade Air (obtained from MG Scientific and has the following stated impurities: $NO_x < 5 \times 10^3$ ppm; $CO_2 < 2$ ppm; $CO \approx 5$ ppm; total hydrocarbons, mainly methane, <0.1 ppm) as the carrier gas. The air–hydrocarbon mixture ("the sample gas") thus simulates the bag sample gas in automotive exhaust monitoring. The average gas velocity down the flow tube under these conditions was 270 cm sec^{-1}. In a few experiments at higher concentrations ($\approx$500—8000 ppm), the hydrocarbons were also flow metered in directly, bypassing the exponential dilution flask. These experiments served primarily to calibrate the dilution flask output. Gas-tight syringes were used to introduce the hydrocarbons into the dilution flask. Liquid hydrocarbons were injected first into a 5-l predilution flask and after evaporation and mixing were withdrawn from this flask with a gas syringe for injection into the apparatus dilution flask. Potential interference gases (see below) were co-injected with the hydrocarbons into the dilution flask. In the case of H_2O, it was noticed that the presence of H_2O interfered with the delivery of *n*-butane. Therefore, in all H_2O interference tests, H_2O was introduced with 0.5 ml atm sec^{-1} Scientific Grade Air, as shown in Figure 2, while a constant flow of hydrocarbon, corresponding to 850 ppm in the sample, was used. The pressure in the reaction tube was maintained at 1.2 torr using a throttling valve in the pump line and a 5-cfm mechanical vacuum pump. The exponential dilution flask was kept at 38 torr, which pressure gave a convenient decay time ($\approx$7 min for a factor 10 decrease in concentration).

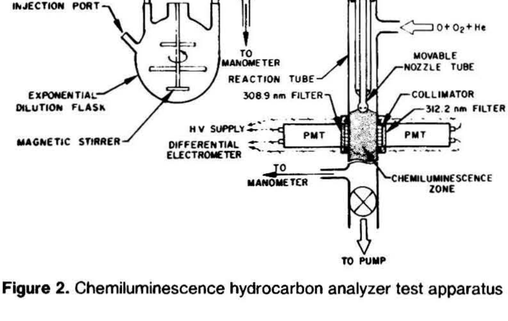

Figure 2. Chemiluminescence hydrocarbon analyzer test apparatus

The hydrocarbons were dried by passage through silica gel, the remaining reagent and sample gases by passage through activated alumina. Upstream from the microwave discharge and the exponential dilution flasks, the gases passed through liquid N_2 to remove most carbonaceous impurities (except CO, CH_4) that might have been present. To prevent interference from hydrocarbons which might have been present in the flow system, the apparatus was washed with dilute HF before it was put to use. Nonetheless, after several weeks running noticeable increases in the background emission were observed; these were traced to the hydrocarbon inlet nozzle, which was therefore frequently removed and washed with dilute HF. No such repeat cleaning of the rest of the apparatus was necessary. At the end of the day, the liquid N_2 traps were allowed to warm up and were backpumped; in this way, any accumulated impurities were prevented from entering the reaction tube.

Since absolute [O] measurements could not readily be made with this test apparatus and an exact value of [O] was not needed in this work, such measurements were not made. However, our past experience has shown that [O] is on the order of 1% of the total gas concentration—i.e., at the concentrations tested in quantitative hydrocarbon response measurements, O was present in large excess over the hydrocarbons. In most of this work [O] was kept constant by using constant flow conditions and microwave power. In some experiments [O] was deliberately varied by varying the microwave power. The relative O, $[O]_{rel}$, was then obtained in separate experiments in which NO rather than hydrocarbon was passed through the nozzle, and the intensity of the emission from the reaction

$$O + NO \rightarrow NO_2 + h\nu(\lambda > 387.5 \text{ nm})$$

was measured with a 1P28 PMT. Since (*19*) $I \propto [O][NO]$ and [NO] was kept constant, a factor x change in light intensity corresponded to a factor x change in [O].

The chemiluminescence was measured with two matched (approximately equal anode sensitivity, *A*/lm) Centronic 4242 bialkali PMTs, viewing the reaction zone through 308.9 and 312.2 nm interference filters, respectively (Figure 2). The filters were 2.5 cm in diam and had a 1-nm half-width with $\geq$20% peak transmission. These PMTs had been matched to obtain approximately equal intensities at both wavelengths for C_2H_2; electronic gain adjustment al-

Table II. Effect of Hydrocarbon Inlet Nozzle Distance on $\Delta I_{308.9}$ for He/9% O_2 Discharge Gas and 1250 ppm of Hydrocarbon

Distance from the nozzle to the center of the observation port, cm	$\Delta I_{308.9}$ C_2H_4 nA	$\Delta I_{308.9}$ n-C_4H_{10} nA	Ratio
2	1850	180	10
3	1100	160	7
4	1030	270	4
5	700	320	2

lowed the intensities to be made exactly equal. Since the stated wavelength for interference filters is that for perpendicular incidence, collimation is required when, as in the present case, a spatially extended glow is observed; the collimators between the reaction tube and the PMTs were 2.5-cm diam, 2.5 cm long (radiatior honeycomb) tubes with a 0.25-cm cell diameter.

Test Apparatus Results

Acetylene Zero. To confirm the absence of response to C_2H_2, a constant flow of C_2H_2 at 8000 ppm was introduced. The relative gain of the two PMT signals was adjusted to give a zero reading of $\Delta I_{308.9}$ under these conditions. If the spectral distribution of O–C_2H_2 does not change when smaller concentrations of C_2H_2 are used, no reading at those concentrations should be obtained either. C_2H_2 from the exponential dilution flask was therefore passed through the zeroed system at concentrations varying from 100–1 ppm. No $\Delta I_{308.9}$ signal was observed indicating that the spectral distribution is independent of concentration—i.e., once the $\Delta I_{308.9}$ instrument is zeroed with C_2H_2 at one concentration it is zeroed at all concentration ranges, which also implies that the spectral distribution from O–C_2H_2 is invariant with $[C_2H_2]$ in this range.

Response to Other Hydrocarbon Species. For comparison of the response to the individual hydrocarbon species, a nozzle distance favoring good agreement with the reactivity ratings (*5*) had to be determined. We chose to try to obtain an average Class III reading in roughly the proportion to ethylene indicated by these ratings. A number of experiments were therefore made in which the reaction time—i.e., the distance from the nozzle to the center of the observation port—was varied for ethylene and n-butane; the results are shown in Table II. Since Table I suggests that the response to n-butane is somewhat lower than that to the other Class III compounds investigated, a distance of 4 cm was selected, corresponding to a reaction time of 1.5 × 10^{-2} sec, for the measurements on the individual hydrocarbons.

The relationship between signal response and hydrocarbon concentrations had to be established for each hydrocarbon species. This was done by making a number of injections over a wide (typically factor of 100) range of concentrations (Figure 3). The points from the exponential dilution plots giving the same response were then assumed to correspond to the same concentrations. Plots of response vs. concentration—e.g., Figure 4—were prepared from these plots. The response to the individual hydrocarbon species was linear (first power) in their concentration (Figures 3 and 4) to within a factor of 2 over the full concentration range.

Table III compares the $\Delta I_{308.9}$ measurements thus obtained for the individual hydrocarbons. Since the plots are parallel (first order in concentration), any concentration point along the line can be used for this comparison (we used 125 ppm). Because of this linear response, the limit of sensitivity, which is ≈0.2 ppm for ethylene, is inversely proportional to the signal response given in Table III—i.e., ≈1 ppm for n-butane (Figure 4).

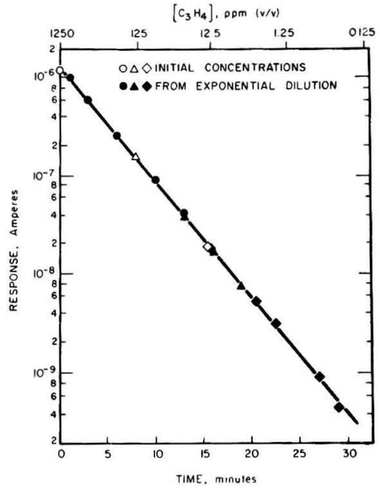

Figure 3. Exponential dilution plot for propadiene

Reaction time 1.5 × 10^{-2} sec; reaction tube P = 1.2 torr; reagent gas flow, He flow 1 ml atm sec^{-1}/O_2 flow 0.1 ml atm sec^{-1}; sample (cylinder air) flow from exponential dilution flask 0.5 ml atm sec^{-1} with variable hydrocarbon concentration; exponential dilution flask pressure, 38 torr

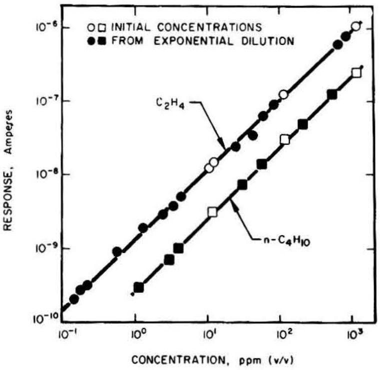

Figure 4. Response vs. concentration of ethylene and n-butane with He/9% O_2 reagent gas. Conditions as in Figure 3

In general, the $\Delta I_{308.9}$ measurements scale quite satisfactorily with the reactivity factors. Benzene appears to give too high a response and some compounds from Class V too low a response. This might be improved by decreasing the observation time (Tables I and II), but this presumably would lead to a decreased reading for Class III compounds as well. Further control over the relative $\Delta I_{308.9}$ response is possible by varying the [O]. See below.

Over a period of several months the response to 125 ppm of C_2H_4 was frequently checked. No systematic trends with time were observed, and the signal was constant to within σ = ±5%, about equal to the reproducibility of the data in a consecutive series of tests. This variation is, in part, due to uncontrollable variation in the amount injected. Test runs on the stability of the light output at a constant hydrocarbon flow showed a maximum ±3% variation, both in short-

Table III. Relative Chemiluminescence Signal Intensities of Classes V, IV, III, and I Hydrocarbons[a] Obtained at 1.5 × 10^{-2} sec Reaction Time for He–9% O_2 Discharge Gas

	$\Delta I_{308.9}$[b]
Class V, reactivity[a] = 14.3	
Ethylene	100
Propylene	42
Butene-1	79
Butene-2	53
Isobutene	38
Propadiene	133
Butadiene	56
Class IV, reactivity = 9.7	
Toluene	55
Class III, reactivity = 6.5	
n-Butane	23
n-Heptane	57
Iso-octane	43
Class I, reactivity = 1.0	
Ethane	1.3
Propane	7.9
Benzene	20
Acetylene[c]	0
Methane[d]	$<10^{-2}$

[a] Reactivity classes and numbers as suggested by B. Dimitriades (*5*). [b] Ethylene is taken as 100. [c] The acetylene signals are zero since the instrument is zeroed using acetylene. [d] No detectable signals from methane were obtained at concentrations up to 1250 ppm, the highest concentration investigated.

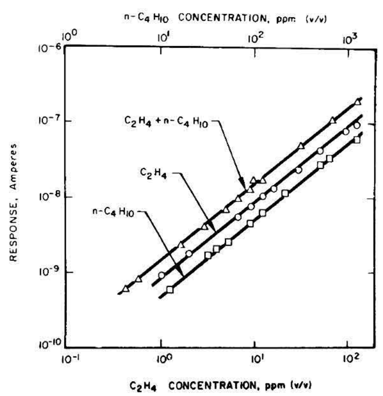

Figure 5 Comparison of response of ethylene and *n*-butane to that of their mixture at the same individual concentrations

The individual points on the C_2H_4 + *n*-C_4H_{10} line are from the exponential dilution trace of the mixture, the line itself represents the sum of the responses to the individual hydrocarbons as shown in the lower two lines. Conditions as in Figure 3, except for O-atom flow

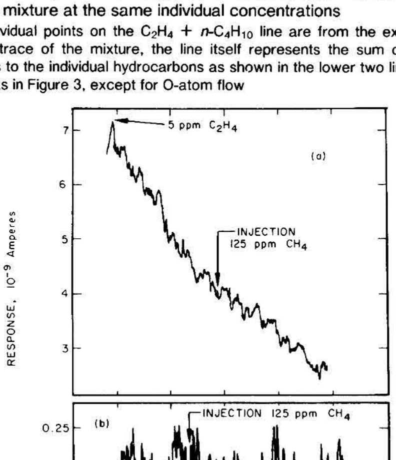

Figure 6. Absence of interference by methane

Recorder trace (a) co-injection with C_2H_4, and (b) CH_4 alone. Conditions as in Figure 3

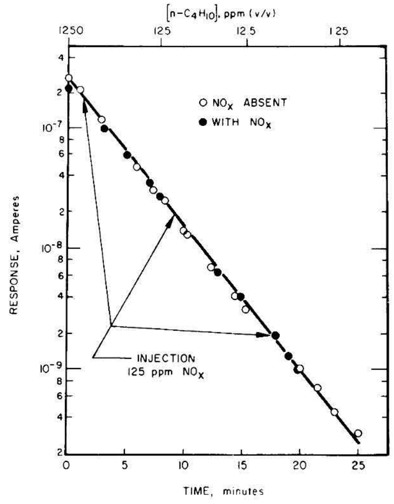

Figure 7. Absence of interference of NO_x with *n*-butane measurement

Exponential dilution plots with and without added NO_x. Conditions as in Figure 3

term stability (noise) and long-term drift (over a period of 3 days of unattended operation).

We have thus far discussed samples containing one reactive hydrocarbon, while bag samples contain a mixture of hydrocarbons. It is shown below that unreactive hydrocarbons—C_2H_2 and CH_4—do not interfere with the response of reactive hydrocarbons. To determine whether synergistic or interference effects between reactive hydrocarbons occur, we investigated mixtures of ethylene–*n*-butane (in a 1:10 concentration ratio) and ethylene–propadiene (in a 1:1 concentration ratio). The results obtained for the ethylene–*n*-butane mixture are shown in Figure 5 (those for the ethylene–propadiene mixture spanned a concentration range of 0.5–500 ppm). The signals obtained from these mixtures are, within experimental error, equal to the sum of those obtained from the same quantities of the individual compounds. Hence $\Delta I_{308.9}$ measurements are apparently additive for hydrocarbon mixtures.

Interference by Other Species Present in Mobile Engine Exhausts; Influence of Variable % O_2. Other compounds present in exhausts or bag samples could conceivably cause positive or negative interference with the $\Delta I_{308.9}$ hydrocarbon response (positive interference would be emission at the same wavelength, negative interference quenching of the hydrocarbon emission). These effects were investigated by making runs in which first only the interference gas was added to the sample air and then the interference gas was added in the presence of the hydrocarbon. Except for H_2O, for which a constant 3% in the sample was used (i.e., the sample was saturated), this was done by injecting the potential interference gas at intervals during an exponential dilution run; typically when the concentration of the interference gas had decreased by a factor of 10, it was reinjected. This is illustrated by Figures 6 and 7 giving typical recorder traces and an exponential dilution plot derived from such a trace, respectively. It may be seen from Figure 6 that methane does not interfere with ethylene measurement and does not produce any measurable emission itself, and from Figure 7 that NO_x does not interfere with *n*-butane measurement. NO_x was injected into the exponential dilution flask as NO, but in this flask the O_2 of the sample air partially oxidized it to NO_2, thus producing

Table IV. Concentration Ranges of Hydrocarbons (in ppm) for Which Interference Was Investigated at Indicated Interference Gas Concentrations (in ppm)

	CO 1250	CO_2 20,000	H_2O 30,000	SO_2 12.5	CH_4 1250	C_2H_2 1250–10	NO_x 125
Ethylene		825	850		6–1	1250–10	125–5
n-Butane	125–2	125–2		125–1			1000–5
Propadiene	1000–0.5	1000–0.5		125–0.5			12.5–0.5
Propane		1000–10					

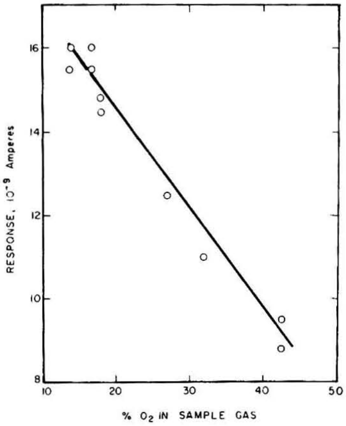

Figure 8. Effect of O_2 in sample gas on $\Delta I_{308.9}$ response for 12.5 ppm of C_2H_4

Reaction time 1.5×10^{-2} sec; $P = 1.2$ torr; reagent gas (He + O_2) flow 1.1 ml. atm sec^{-1}; sample gas from exponential dilution flask = 0.5 ml atm sec^{-1}

Table V. Changes in $\Delta I_{308.9}$ from 125 ppm C_2H_4 and *n*-C_4H_{10} as a Function of O-Atom Concentration for He–9% O_2 Reagent

Nozzle distance, cm	$[O]_{rel}$, arbitrary units	$\Delta I_{308.9}$ (C_2H_4), nA	$\Delta I_{308.9}$ (C_4H_{10}), nA	$\frac{\Delta I_{308.9} (C_2H_4)}{\Delta I_{308.9} (C_4H_{10})}$
6	2	23	100	0.23
6	1	34	11	3.1
2	2	200	10	20.0
2	1	135	5	27.0

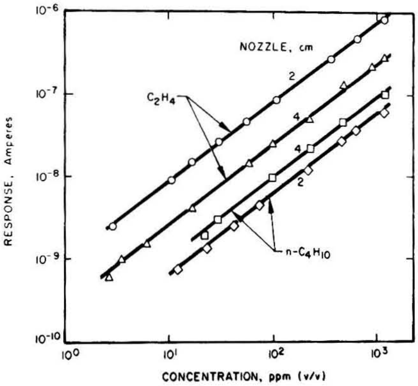

Figure 9. Response vs. concentration of ethylene and *n*-butane with undiluted O_2 reagent gas

$P = 1.2$ torr; O_2 flow 1.0 ml atm sec^{-1}; sample (cylinder air) flow 0.5 ml atm sec^{-1}

an NO–NO_2 mixture. (The same process occurs when NO from car exhaust is mixed with dilution air in CVS bag sample preparation—i.e., the samples tested are similar in this respect to bag samples.) Table IV summarizes the conditions for the interference runs made.

No evidence for positive interference by CO, CO_2, H_2O, SO_2, CH_4, C_2H_2, and NO_x was found. Of these compounds the only negative interference occurred from H_2O which caused a 12% decrease in intensity for 850 ppm of C_2H_4. (Because the interference is only a factor of two larger than the variation of consecutive exponential dilution runs, these H_2O measurements were made at a steady C_2H_4 flow after exponential dilution runs suggested that a quenching effect might occur.) The negative interference of the other gases thus was ≤5% at the concentrations tested, while the positive interference from any compound tested was ≤0.2 ppm equivalent C_2H_4.

Bag samples also will contain a somewhat variable amount of O_2 within the range 15–20%. To investigate the influence of variable O_2, the O_2 content of the sample gas was varied from 14–40% (remainder N_2) for 12.5-ppm C_2H_4 injections. This $[O_2]$ range is of course much larger than that of practical interest. The results are shown in Figure 8. They suggest that a 1% increase or decrease in O_2 content of the sample gases causes somewhat less than a 1% decrease or increase in the response to ethylene. Thus the effect of normal variations of the O_2 in bag samples is essentially negligible.

Measurements with Other Reagent Gas Compositions. Experiments have been made using undiluted O_2 as the reagent gas with ethylene and *n*-butane sample gas; two different nozzle distances were used under flow conditions otherwise very similar to those used for the He–9% O_2 experiments. The results are shown in Figure 9. At both distances the response is again first power in [HC]. The C_2H_4–*n*-C_4H_{10} response ratios at 4 and 2 cm are 14 and 2.5, respectively—similar to those obtained in the He–9% O_2 experiments; however, the absolute intensities are a factor of 2–3 lower for the undiluted O_2 reagent flow. (Compare Figure 9 to Figure 4 and Table II.) The experiments are not strictly comparable to each other since no attempt was made to keep [O] the same as in the He–O_2 experiments. Experiments in which $[O]_{rel}$ was measured at a number of discharge power levels for the two reagent gas compositions suggest however that [O] was similar for the discussed conditions. Thus, this comparison again suggests a quenching effect by O_2, similar to the experiments of Figure 8.

Experiments were next made in He–9% O_2 in which [O] was deliberately varied by a factor of 2 by varying discharge power input. The results are shown in Table V. It may be seen that decreasing [O] increases the ratio $\Delta I_{308.9}(C_2H_4)/\Delta I_{308.9}$ (*n*-C_4H_{10}). At a 6-cm nozzle distance, the absolute response to ethylene also increased with the decrease in [O]. The explanation of these observations is that at lower [O], the ethylene [which has a much higher reaction rate coefficient than n-butane for O-atom attack (Table I)] consumption is decreased and more of it remains to lead to a light-producing reaction after longer reaction times. Not enough n-butane consumption occurs on this time scale to observe a similar effect on the absolute $\Delta I_{308.9}$ signal from n-butane. The response under all these conditions is again proportional to [HC]. The conclusion from these experiments is that both nozzle distance and discharge power—i.e. [O], can be used to vary the relative $\Delta I_{308.9}$ response of the hydrocarbons in any desired direction.

Discussion and Conclusion

The results suggest that an instrument based on the $\Delta I_{308.9}$ method should give readings of total hydrocarbon reactivity closely approximating those which can be obtained by measuring each hydrocarbon individually with a gas chromatograph and multiplying its concentration with the appropriate reactivity factor (*5*). Since a $\Delta I_{308.9}$ instrument would, at continuous flow, give a continuous direct reading, far less time and effort would be involved in its use. It should be noted that the $\Delta I_{308.9}$ method gives a zero response to methane and acetylene whereas, strictly speaking, the Dimitriades reactivity ratings (*5*) suggest a finite response. However these ratings define Class I as the class of hydrocarbons that does not require control; a zero methane and acetylene measurement (which was the goal of the present work) appears to be preferred. The method is not restricted to the Dimitriades rating (*5*) since, by increasing nozzle distance (reaction time) and/or [O] the response to n-butane relative to ethylene—i.e., of less reactive hydrocarbons to highly reactive hydrocarbons, can be increased; such a measurement could be preferable in late photochemical smog situations.

A simplification of the present method is possible in situations where acetylene is present in negligible concentrations. Under those conditions measurement of $I_{308.9}$ would suffice and only one PMT would be needed. Since the other hydrocarbons tested all give the same spectral distribution, a larger wavelength region of the $OH(A^2\Sigma - X^2\Pi)$ system could then probably be used with possibly a corresponding increase in sensitivity. No attempts have been made in this work to optimize sensitivity; improved optical design and greater sensitivity of the electrooptical detection system are undoubtedly possible. It would therefore appear attractive to investigate the use of the method for the lower concentrations that are of interest in the measurement of organic pollutants in ambient air. Such pollutants include nonhydrocarbon organic compounds, primarily from solvents (*4*). However, since most of these compounds contain alkyl groups it is quite possible that they could similarly be measured. An improved sensitivity also would have the advantage, for the concentration range of interest in car engine exhaust monitoring, that pure O_2 discharge gas could be used instead of a He (or Ar)–≈10% O_2 mixture; it has been shown that such an approach would only result in about a factor of three decrease in sensitivity under the conditions of our experiments.

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Trace Element Composition in Atmospheric Particulates During 1973 and the Summer of 1974 at Chadron, Neb.

Arthur W. Struempler
Chadron State College, Chadron, Neb. 69337

■ Air was collected continuously on filters in northwestern Nebraska during 1973 and the summer of 1974 and the particulate matter was analyzed for Ag, Al, Cd, Co, Cu, Mn, Pb, Tl, and Zn. Noticeable and consistent seasonal differences were evident in aerosol Al, Mn, and Pb. Those metals found in aerosol particulates are largely soil derived if their concentrations are likewise high in the soil. Conversely, aerosol metals are more likely to be associated with anthropogenic sources if their concentrations are low in the soil. Aerosol Pb appears to be largely derived from the combustion of leaded gasoline, but the aerosol sources of Ag and Cd are more difficult to document. The data will serve to monitor any changes in air quality as additional coal-fired power plants are constructed at upwind locations.

By necessity, more coal must be used in the future to meet our energy needs. Utilization of coal from Wyoming, Colorado, and Montana will certainly increase because it is economically mineable and relatively low in sulfur. Also, because of economics, more coal-fired plants will be constructed near these coal reserves and may alter the aerosol concentrations of some pollutants. Nebraska is located to the east and downwind from these coal reserves. Since aerosol particulates are readily transported by the wind, Chadron's location in northwest Nebraska is ideal for establishing the concentrations of various atmospheric metals before additional coal-fired power plants are constructed in neighboring western states. To obtain this information, air was collected continuously during 1973 and the summer of 1974, and its particulate matter analyzed for aerosol Ag, Al, Cd, Co, Cu, Mn, Pb, Tl, and Zn. Metal concentrations and their variability were evaluated for seasonal trends and sources. The data are of further use in monitoring air quality and assessing any change in metal concentrations.

Experimental

Air was aspirated continuously through filters at the rate of 14 l./min during all of 1973 and from June through September in 1974. Filters were changed each Monday, and the various aerosol metals were analyzed after each season's collections. The air-sampling gear was housed in a greenhouse, and consisted of a vacuum pump which collected outside air through a 37-mm diameter Millipore filter (type AA, 0.8-μm mean pore size) made of mixed esters of cellulose. The filter was located 1¼ m above the earth's surface and was protected from precipitation by a polypropylene lined box. Air collections were made on the southeast corner of the college campus, which is located at the extreme southeast corner of Chadron, Neb., a town with a population of 6000, located in the sparsely populated Northern Plains (42° 50′N, 103° 05′W, 1000 m above sea level). No roads were located within 1 mi of the sampling site within a compass reading of 45 through 270 degrees. A few roads exist in the region beyond 1 mi of the sampling site, within the arc of 45 through 270 degrees, but the region is virtually uninhabited for hundreds of miles. As with most Northern Plains states, the land is relatively flat and is used principally for grazing. Prevailing winds are from the south, west, and north, and it is estimated that surface winds blowing from the northwest and north and over the residential area of Chadron to the sampling site occurred less than 10% of the time. Therefore, most collections represent surface winds from virtually uninhabited areas.

The metals were analyzed with a Model 303 Perkin-

Table I. Metal Concentrations (Ng/M³) of Atmospheric Particulates During 1973 at Chadron, Neb.

Week beginning		Ag	Al	Cd	Co	Cu	Mn	Pb	Tl	Zn
Jan.	1	0.06	40	0.65	4.3	5.0	3.2	20	0.42	16
	8	0.02	50	0.46	2.6	4.6	2.5	14	0.30	11
	15	0.02	690	0.44	4.7	5.0	8.8	69	0.32	21
	22	0.02	90	0.31	4.0	4.5	4.2	56	0.25	19
	29	0.03	250	0.48	2.8	5.5	3.7	59	0.14	16
Feb.	5	0.03	200	0.32	4.1	4.7	3.2	67	0.21	14
	12	0.03	260	0.33	3.7	4.6	3.9	51	0.22	11
	19	0.02	310	0.34	3.4	4.8	4.5	42	0.20	8
	26	0.03	740	0.32	4.3	4.3	7.9	35	0.31	12
Mar.	5	0.03	830	0.56	4.7	3.9	9.6	34	0.23	18
	12	0.03	630	0.58	5.0	4.1	7.1	60	0.26	25
	19	0.03	700	0.27	4.6	4.5	6.7	38	0.35	21
	26	0.03	660	0.31	3.9	4.3	7.7	42	0.22	16
Apr.	2	0.03	310	0.66	2.5	3.6	4.6	34	0.15	23
	9	0.04	1070	0.89	4.1	3.9	10.3	56	0.30	19
	16	0.25	350	0.66	3.7	4.6	3.5	20	0.22	26
	23	0.08	470	0.44	2.9	4.4	5.7	38	0.18	18
	30	0.15	560	0.54	3.2	5.1	5.7	77	0.18	27
May	7	0.18	980	0.91	3.6	5.4	8.2	39	0.22	21
	14	0.36	2230	0.68	4.1	6.6	15.6	36	0.27	22
	21	0.47	640	0.59	2.8	5.7	5.4	18	0.25	26
	28	1.80	400	0.87	2.7	5.5	5.8	20	0.48	12
June	4	0.12	280	0.93	3.0	3.6	3.5	9	0.20	6
	11	0.11	760	0.83	3.9	5.7	6.3	19	0.26	16
	18	0.16	610	0.55	2.8	6.0	4.1	22	0.20	21
	25	0.46	230	0.83	1.6	5.6	3.1	24	0.15	14
July	2	0.07	870	0.84	2.6	5.0	7.1	20	0.16	15
	9	0.03	810	0.99	1.6	5.3	6.3	26	0.14	12
	16	0.04	790	0.52	2.8	5.8	5.0	28	0.32	13
	23	0.40	1000	1.32	4.7	6.7	7.0	38	0.42	16
	30	0.03	610	0.74	3.4	5.5	4.3	26	0.25	9
Aug.	6	0.29	1020	0.46	5.1	5.7	7.6	35	0.28	12
	13	0.09	1000	0.48	3.1	5.9	11.7	24	0.20	9
	20	0.04	740	0.54	3.1	5.9	12.7	36	0.21	26
	27	0.04	540	0.37	4.1	5.5	6.2	35	0.19	14
Sept.	3	0.09	300	0.61	3.0	5.7	6.3	50	0.19	15
	10	0.12	310	0.27	3.0	5.3	5.7	40	0.16	40
	17	0.15	430	0.48	2.9	4.8	6.5	44	0.22	21
	24	0.07	380	0.32	3.5	4.8	3.1	73	0.19	11
Oct.	1	0.23	930	0.67	1.6	7.3	8.2	89	0.07	21
	8	0.21	390	0.67	3.7	5.5	3.7	87	0.23	25
	15	0.22	940	1.07	3.1	6.7	7.3	68	0.26	21
	22	0.05	610	0.53	2.6	6.3	5.8	69	0.15	25
	29	0.17	170	0.36	1.9	5.0	2.4	57	0.13	9
Nov.	5	0.12	140	0.31	3.1	5.5	2.1	73	0.14	18
	12	0.04	430	0.26	2.8	5.1	3.5	39	0.11	3
	19	0.05	250	0.29	2.2	5.1	4.1	62	0.12	4
	26	0.12	300	0.42	2.1	5.1	3.3	52	0.18	4
Dec.	3	0.05	180	0.46	2.8	6.7	2.5	46	0.12	21
	10	0.19	230	0.34	3.2	6.8	3.7	69	0.14	13
	17	0.23	70	0.77	2.7	6.7	1.7	85	0.12	4
	24	0.10	60	0.72	3.0	6.6	3.0	70	0.13	10
$\overline{X}$		0.15	535	0.57	3.3	5.3	5.7	45	0.22	16
σ		0.26	382	0.24	0.9	0.9	2.8	21	0.08	7

Elmer atomic absorption spectrometer, equipped with a HGA-2000 heated graphite atomizer and a deuterium background corrector. The statistics were calculated with a Hewlett-Packard 9810A programming calculator. Container cleaning methods and laboratory procedures have been described previously by Struempler (*1*). Only new 1-oz Nalgene linear polyethylene containers were used for storage or analysis. Any containers with blank solutions with a detectable background of Zn (the most contaminatable metal under study) after the acid soaking and cleaning process were discarded. Extreme care was exercised to minimize metal loss or contamination effects. Only ultrapure acids were used in all instances except in the container washing process. Aerosol particulates were removed from the filter by ultrasonic treatment for 1 hr in 10 ml of ion-free water acidified to 0.2% with HNO_3. Completeness of metal dissolution from the filters was compared by quartering test filters and:

> Dry ashing in Pt crucibles at 300°C for 30 min followed by continued ashing at 500°C for 1 hr and reconstituting the metals in an aqueous solvent containing 1% HNO_3
>
> Dry ashing similar to above, but metals were reconstituted in minimum HF and HNO_3 (1 + 3), followed by evaporation to dryness and appropriately diluting
>
> Wet ashing in minimum HNO_3 with warming until the filter dissolved. Metals were then reconstituted in an aqueous solution

In all cases, blanks were carried through. Both dry and wet ashing procedures proved erratic for some metals and could not be used as the principal technique for metal analysis. Neither could strong acid concentrations be used for dissolution purposes, as this enhanced interference effects. Hence, the ultrasonic treatment method was used for dissolution of metals from the filters. The deuterium background corrector was used for all analyses.

Table II. Metal Concentrations (Ng/M^3) of Atmospheric Particulates During the 1974 Summer Season at Chadron, Neb.

Week beginning		Ag	Al	Cd	Co	Cu	Mn	Pb	Tl	Zn
June	3	0.04	380	0.26	3.5	5.8	3.3	34	0.16	3
	16	0.03	270	0.36	2.6	5.1	2.7	19	0.09	1
	17	0.04	670	0.32	3.4	6.9	7.6	19	0.13	7
	24	0.04	980	0.54	2.8	6.2	10.6	19	0.19	17
July	1	0.04	820	0.39	2.0	5.7	9.3	22	0.14	3
	8	0.04	810	0.20	2.3	6.0	10.9	17	0.19	9
	15	0.05	680	0.21	1.9	6.0	7.0	19	0.14	6
	22	0.04	810	0.26	1.8	6.0	10.4	23	0.16	3
	29	0.03	670	0.18	1.6	5.3	7.6	25	0.14	3
Aug.	5	0.04	520	0.21	2.1	5.8	5.0	16	0.17	4
	12	0.04	750	0.28	1.8	6.5	5.8	20	0.10	11
	19	0.03	740	0.31	2.6	5.9	6.2	21	0.13	6
	26	0.03	590	0.17	1.0	5.6	6.9	21	0.11	1
Sept.	2	0.05	710	0.39	3.0	7.9	7.7	35	0.23	3
	9	0.03	460	0.22	1.2	5.6	5.6	48	0.10	3
	16	0.02	710	0.27	2.8	6.7	7.0	43	0.18	9
	23	0.03	720	0.51	1.8	7.2	8.2	41	0.11	11
$\overline{X}$		0.04	664	0.30	2.2	6.1	7.2	26	0.15	6
σ		0.01	175	0.11	0.7	0.7	2.3	10	0.04	4

Results and Discussion

Table I shows the concentration of nine metals in aerosol particulate matter during 1973. The means and standard deviations are also shown at the bottom of the table. As elsewhere in this report, the concentrations of the tested elements are reported in ng metal/m^3, and means are represented as the arithmetic mean.

Seasonal differences are evident in the data. Silver was found in highest concentrations during the April–July period. Aluminum was noticeably low during December and January. Aerosol Pb increased during the autumn season. The test for standard deviation is based on a normal distribution. Silver exhibited a larger standard deviation than the mean; hence, this test was invalid for Ag. The large Ag concentrations during the summer season account for this deviation. However, if the large Ag value of May 28 is deleted, the mean then becomes 0.12 with a sigma of 0.12. The large aerosol Ag concentrations during the summer months were of particular interest, as no cloud seeding operations with AgI were believed to have occurred within several hundred miles of Chadron during the May–June period.

Mainly to determine if the large aerosol Ag concentration was seasonal, air was again sampled and analyzed for all nine elements during the June–September time period of 1974. Climatic conditions were different during the 1974 season as western Nebraska experienced a drought during the summer of 1974 when only 11.5 cm of rain fell in Chadron during the 17-week 1974 summer season as compared to 21.8 cm during this same time period in 1973 (*2, 3*). The results of the 1974 collection are shown in Table II and a comparison of the means and standard deviations between the two seasons are shown in Table III. Three and one-half times less Ag was detected during the 17-week 1974 summer season as compared to the 1973 summer season. Approximately a 50% decrease in Cd, Co, Tl, and Zn was likewise noted. Little difference in the aerosol concentrations of the other metals was observed between the two summer seasons.

An interesting aspect of the data is the consistent and greater abundance of Al and Mn during both of the 17-week 1973 and 1974 summer seasons as compared to their abundance during the entire 52-week period. Trace elements arising from airborne dust would be in greater concentrations during the drier summer months, and their associated convective storms, than during a snow-covered

Table III. Means and Standard Deviations of Aerosol Metals in Atmospheric Particulates for 1973 and 1974

		Ag	Al	Cd	Co	Cu	Mn	Pb	Tl	Zn
1973 (52 weeks)	$\overline{X}$	0.15	535	0.57	3.3	5.3	5.7	45	0.22	16
	σ	0.26	382	0.24	0.9	0.9	2.8	21	0.08	7
1973 (June–September)	$\overline{X}$	0.14	628	0.65	3.2	5.5	6.3	32	0.22	16
	σ	0.13	271	0.28	0.9	0.7	2.6	15	0.07	8
1974 (June–September)	$\overline{X}$	0.04	664	0.30	2.2	6.1	7.2	26	0.15	6
	σ	0.01	175	0.11	0.7	0.7	2.3	10	0.04	4

Table IV. Aerosol Metal Concentrations at Various Locations (Ng/M³)

Location and year(s) sampled	Ag	Al	Cd	Co	Cu	Mn	Pb	Tl	Zn
Many U.S. urban stations (1964–65)(*4*)			2	<0.5	90	100	790		670
N.W. Indiana, 25 stations (June 11–12, 1969)(*5*)	<1–5	1375–2600		0.47–2.6	26–4000	63–390	400–3700		100–1540
Columbia, Mo. (1971)(*6*)		1520		0.86		30			56
San Francisco, 9 stations (July 23, 1970)(*7*)	0.05–0.2	250–2000		0.46–1.7	27–100	5–34			27–500
Corvallis, Ore., rural (1972)(*8*)		450		<0.1	<35	2.7			
Windward Hawaii (1967) (*9*)		28			55				
North Atlantic sites (1970–72)(*10*)			0.003–0.62		0.12–10		0.10–64		
South Pole (1970)(*11*)		0.6		0.8	36	10	0.6		30
Chadron, Neb. (1973)	0.15	535	0.57	3.3	5.3	5.7	45	0.22	16

Table V. Correlation Coefficients (× 100) Between Metals in Air Particulates During 1973 and Arranged in Order of Decreasing Concentration in Earth's Crust

	Ppm in earth's crust, Mason (*12*)	Al	Mn	Zn	Cu	Co	Pb	Tl	Cd	Ag
Al	81,300	—	86	23	20	30	−17	26	34	8
Mn	950		—	32	7	35	−15	27	19	4
Zn	70			—	4	20	8	8	4	0
Cu	55				—	−26	28	−17	26	24
Co	25					—	−2	58	−7	−13
Pb	13						—	−38	−21	−17
Tl	0.5							—	27	42
Cd	0.2								—	35
Ag	0.07									—

winter season. Of those metals tested, Al and Mn are in highest concentrations in the earth's crust and would appear to be largely dust derived, as only meager or no industrialization exists in the Chadron area. Plausible then is the lower aerosol Al and Mn concentrations during the snow-covered winter season and the higher concentrations during the dustier summer season.

To compare aerosol metal concentrations from other areas, data have been assembled in Table IV showing aerosol metal concentrations from urban, rural and nonpopulated regions. These data indicate that metal concentrations vary widely among regions. Even within a 24-hr collection period at a given collection site, the range may vary up to a factor of 100. Except for perhaps soil-derived metals, Chadron's air in general would be expected to be lower in trace metals than air from urban regions. On the other hand, it contains a greater concentration of trace metals than air from a nonpopulated region. The exception is Co, which appears high in relation to the other studies. No explanation can be given for this higher reading. Little is known regarding aerosol Tl, and our work indicates a concentration of 0.22 ng/m³ of air as an annual mean for 1973.

In an attempt to find a common metal source, correlation coefficients of metal concentrations have been computed between pairs of elements. Table V shows these correlation coefficients between metal pairs for the 52-week period of 1973. A large correlation coefficient value between metal pairs is indicative of a common source and similar type behavior. A more meaningful relationship can be reached by a further comparison of the data with the concentrations of metal in the conterminous U.S.'s earth's crust (in ppm): Al, 81,300; Mn, 950, Zn, 70; Cu, 55; Co, 25; Pb, 13; Tl, 0.5; Cd, 0.2; and Ag, 0.07 by Mason (*12*). Aluminum and Mn exhibit the largest correlation coefficient, namely 0.86, which suggests a common and natural source for these two metal pairs. Undoubtedly, colloidal soil-borne dust particles entrapped on the filters account for the strong relationships between Al and Mn. Lead exhibits a negative correlation value for all metals except Zn 0.08 and Cu 0.28. The data further suggest that either Al or Mn may be used for reference elements in studies of this kind, as their behavior is similar when tested against the other metals.

A further evaluation in the behavior patterns of aerosol metals can be found in Table VI, which shows the correlation coefficients of metal pairs for the 17 summer weeks of 1973 and 1974. Using either reference elements Al or Mn, a consistent increase in correlation coefficient values is noted for Zn, Cd, and Ag during the drier 1974 summer as compared to the wetter 1973 summer season. As drier seasons are more enhanced with dust particulates it seems plausible that these elements are also associated with a crustal source. A further comparison of the correlation coefficients shows that the metal pairs Cu and Co, Cu and Tl, and Cu and Zn appear to have a common source during the summer months, as they exhibit larger correlation coefficients for this time period when compared to their entire 1973 correlation values. Again, this suggests seasonal differences and sources. Cobalt and Tl correlation values remain high and constant under any seasonal comparison.

As dust particles are an obvious source for trace metals in the Northern Plains, a further attempt was made to ascribe the extent of soil-borne metals derived from air to those metals in the earth's crust. An enrichment factor, *EF*, can be calculated as follows according to Zoller (*11*):

$$EF_{\text{crust}} = \frac{(\text{X/Al})\ \text{air}}{(\text{X/Al})\ \text{crust}}$$

(where X/Al_{air} and $\text{X/Al}_{\text{earth's}}$ crust) refers to that ratio of the concentration of element X to a reference element Al (or Mn) in air (Table I) and likewise to that concentration in the earth's crust by Mason (*12*). The earth's crust contains 8.1% Al and 0.095% Mn, and these elements of highest concentrations were chosen for the reference elements.

An enrichment factor near unity for any element is associated with a crustal source, particularly for those elements in largest concentrations in the earth's crust. Even though

Table VI. Correlation Coefficients (x 100) Between Metals in Aerosol Particulates During June–September 1973 and 1974

	Al		Mn		Zn		Cu		Co		Pb		Tl		Cd		Ag	
	1973	1974	1973	1974	1973	1974	1973	1974	1973	1974	1973	1974	1973	1974	1973	1974	1973	1974
Al	—		59	89	−21	64	54	40	40	−3	−24	−20	51	43	26	35	−1	23
Mn			—		19	45	39	29	20	−13	−4	−16	9	45	−10	25	−19	22
Zn					—		20	41	−6	20	21	−4	15	20	−35	54	1	2
Cu							—		28	38	8	33	50	45	12	46	30	29
Co									—		24	−4	67	48	−8	36	15	22
Pb											—		3	0	−45	12	−5	−40
Tl													—		36	12	33	42
Cd															—		39	8
Ag																	—	

Table VII. Enrichment Factors for Aerosol Metals Relative to Earth's Crust with Reference Elements Al and Mn Normalized to Unity

	EF crust			*EF* crust	
Element	Al	Mn	Element	Al	Mn
Al		1.1	Cu	15	16
Mn	0.91		Pb	525	575
Ag	326	355	Tl	67	73
Cd	432	474	Zn	34	37
Co	20	22			

their interpretation must be used with caution, increasing enrichment factors from unity are indicative of anthropogenic sources. As shown in Table VII, either Al or Mn yields similar enrichment values. The data are further suggestive that Al or Mn is largely soil derived. To a lesser degree Cu, Co, and Zn tend to be associated with a natural source. The very large Pb value can be rationalized by the combustion of leaded gasoline which constitutes approximately 98% of total lead emissions (*13*). The large Ag and Cd values are supportive of anthropogenic sources rather than normal soil-weathering processes.

A final evaluation of the data is a linear regressive analysis of the 1973 aerosol metal concentrations (Table I) and a comparison of these results with the *EF* values of the previous table. These results are shown in Table VIII, where Al and Mn are used as the reference (independent variable), and the other metals as the dependent variables according to:

$$Y = a + bX$$

where X = concentrations of either Al or Mn
Y = other metal concentrations
a = intercept
b = slope

An intercept value passing near the origin supports the belief that the metal pairs originate from the same source. Most intercept values are near their mean value which may be expected when the slope is near zero as in the case of Al as the reference element.

Evident from the data is the general inverse relationship between the slope and *EF* values. As the slope becomes zero, or even negative, the *EF* values tend to increase in value, demonstrating another method for evaluating unnatural sources for that element. This observation is particularly true for Al as the reference element.

This analysis further points out that the most concentrated element in similar types of studies should be most useful as a reference element as it is least sensitive to change for a given amount element from unnatural sources.

Summary and Conclusion

Correlation coefficients, enrichment, and linear regression values and their inverse relationships with reference metals Al or Mn, suggest that, in general, those metals in aerosol particulates at Chadron are likely to be soil derived if their concentrations are likewise high in the soil. Conversely, aerosol metals are more associated with unnatural sources if their concentrations are low in the soil. Similar environmental sites would be expected to yield similar atmospheric metal patterns. The source of aerosol Pb is obvious, but less explainable are the anthropogenic Ag and Cd sources. As the mean residence time of aerosol particu-

Table VIII. Linear Regression Coefficients and Intercepts Using Al and Mn as Reference Metals, 1973 Concentrations

			Al			Mn	
Ppm in earth's crust, Mason (*12*)		Ng/m^3 (Table I)	Intercept	Slope	*EF* (Table VII)	Intercept	Slope	*EF* (Table VII)
Al	81 300	535				−129	117	1.1
Mn	950	5.7	2.3	0.0064	0.91			
Zn	70	16	14	0.0044	34	12	0.8192	37
Cu	55	5.3	5.1	0.0005	15	5.2	0.0211	16
Co	25	3.3	2.9	0.0007	20	2.7	0.1070	22
Pb	13	45	50	−0.0090	525	51	−1.0782	575
Tl	0.5	0.22	0.19	0.0005	67	0.17	0.0079	73
Cd	0.2	0.57	0.45	0.0002	432	0.48	0.0163	474
Ag	0.07	0.15	0.12	0.0001	326	0.13	0.0033	355

late matter in the midlatitudes can vary up to four days to a week in the lower troposphere and weeks in the upper troposphere (*14, 15*), any cloud seeding with AgI at some distant location and previous time could have enhanced the Ag aerosol concentrations. Because Cd is the most volatile element under study, its behavioral pattern may result from fossil fuel combustion at some distant time and place.

Seasonal differences, with associated causes, are most pronounced with Al and Mn. The increase in aerosol Pb appears to be related to the return of 2000 students (and associated autos) for the fall semester. Less explainable though are the reasons for the reduced Cd, Co, Tl, and Zn concentrations during the drier and dustier 1974 summer season, unless these elements, too, are at times from anthropogenic sources. Their sources may be difficult to document.

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Performance of Charcoal Tubes in Determination of Vinyl Chloride

John E. Cuddeback*, William R. Burg, and Shelton R. Birch[1]

Department of Environmental Health, University of Cincinnati, Cincinnati, Ohio 45267

■ The adsorption characteristics of airborne vinyl chloride on activated charcoal was examined for use as an analytical sampling device. Data are presented to show that charcoal has a limited yet useful capacity for adsorbing low levels of vinyl chloride. Breakthrough volumes, sampling rates, and storage characteristics are presented that indicate a 100-mg portion of activated charcoal in a sampling tube has a capacity of at least 65 μg of vinyl chloride with a twofold safety factor when sampling air containing 5 ppm of vinyl chloride. Analytical methodology is described that produced a 90% recovery of vinyl chloride even after two weeks of sample storage.

The need for analysis of ambient air for low levels of vinyl chloride monomer (VCM) was recognized January 22, 1974. It was on this day that it was made public that three polymerization reactor cleaning personnel at the B. F. Goodrich Co. plant in Calvert City, Ky., had died of a rare form of liver cancer. The results of this announcement was an immediate implication of VCM as a cancer suspect agent. The ensuing investigation (*1, 2*) indicated the need for an accurate analytical method for low level work.

The Environmental Protection Agency (EPA) and the National Institute of Occupational Safety and Health (NIOSH) were concerned with monitoring personal and environmental exposure to VCM. The EPA was concerned with airborne concentrations of VCM that were transported beyond the plant boundaries into the surrounding community and would be covered under the National Hazardous Pollutant Standards. On the other hand, NIOSH required in-plant exposure data in order to advise the Occupational Safety and Health Administration (OSHA) on safe working standards. After the announcement by B. F. Goodrich Co. there was a flurry of measurement and standards-setting activity; the OSHA standard went from 500 ppm (*3*) to 50 ppm (*4*) to 1 ppm (*5*). As of this writing the EPA has yet to set an emission standard, however, a large amount of data has been obtained from the ambient air in the vicinity of polyvinyl chloride plants (*6*), and this may be the basis for future research.

The general sampling method finally chosen by the EPA and NIOSH was based on absorption of VCM on charcoal followed by desorption by CS_2 and gas chromatographic analysis. The major difference in the methods of the two agencies was the size of the sampling device and amount of charcoal used; the EPA used an 18-in. tube with three 3-in. sections of charcoal (*6*) and NIOSH used a smaller tube with about one inch of charcoal divided into two unequal sections (*7, 8*). The EPA is finalizing a method for air sam-

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[1] Present address, USAF Environmental Health Laboratory, Kelly AFB, Tex.

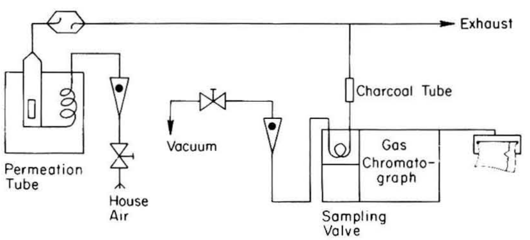

Figure 1. Dynamic dilution system for charcoal tube testing and calibration of gas chromatograph

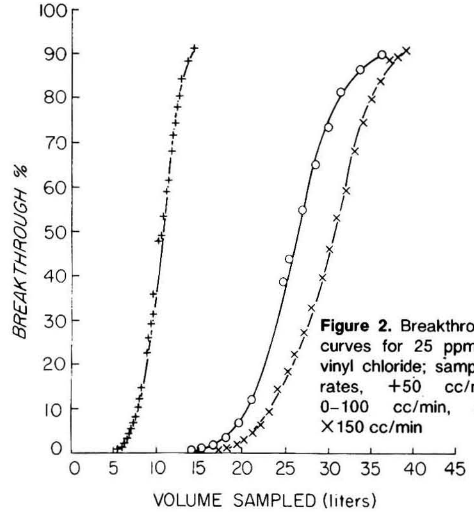

Figure 2. Breakthrough curves for 25 ppm of vinyl chloride; sampling rates, +50 cc/min, ○–100 cc/min, and ×150 cc/min

pling at this time (*9*). The charcoal-filled tubes have been extensively used by both of the agencies for field studies of VCM levels in air; however, there has not been a thorough description of the performance parameters and thus our laboratory undertook an examination of the charcoal tube absorption method for VCM.

Experimental Apparatus and Procedures

Calibration and Standards. Known concentrations of VCM were obtained in the flow dilution system (Figure 1) with a gravimetrically calibrated permeation device made as described previously (*10*). A combination of two different permeation devices and variation of dilution air provided a concentration range of 0.5–50 ppm VCM. Solution standards were also made by injecting known volumes of VCM into volumetric flasks containing measured quantities of carbon disulfide. The flasks were sealed with a silicone rubber septum before injecting the VCM, and adjustment was made for atmospheric conditions assuming ideal gas behavior. Solution standards were made fresh daily as needed. Samples from the dynamic flow dilution system were periodically checked against solution standards so that solution standards were not often needed and served only as a cross-check.

Sampling Equipment. Samples were obtained by drawing a metered stream of air through charcoal tubes obtained from the Mine Safety Appliance Co. The tubes were the small type used for personal monitoring (*8*) and were from a single batch of charcoal. The sampling system is schematically shown in Figure 1. The regulated house vacuum system was used to draw samples through the charcoal tubes thus providing a constant flow. Effluent from the charcoal tube was sampled by means of a stainless steel seven-port sampling valve with a calibrated (*11*) loop system, the loop could be used for direct air sampling when the charcoal tube was not in line.

Table I. Retention Data for Vinyl Chloride on Charcoal Tubes

Vinyl chloride concn, ppm	Sample rate, ml/min	Mass VCM flow rate, μg/min	Retention volume, l^a	Retention time, min^a	Total mass, μg^a
5	50	0.639	10.0	200	127.9
5	100	1.278	9.8	98	125.2
5	150	1.916	29.3	195	373.6
25	50	3.19	7.9	158	504
25	100	6.38	22.8	228	1456
25	150	9.58	20.5	137	1312
50	50	6.38	9.0	180	1285
50	100	12.78	18.1	181	2311
50	150	19.16	14.8	98.7	1891

^{a} At 10% breakthrough from front section of tube.

Analytical Equipment. Analysis of flow system gases was performed directly using a Tracor MT 160 chromatograph equipped with a flame ionization detector. The operating conditions were as follows: column 6 ft × ⅛ in. stainless steel, column packing Poropak Q, column temperature 135°C, inlet temperature 150°C, detector temperature 175°C, carrier gas flow rate 30 cc/min of nitrogen. Peak areas were computed by means of a Disc Integrator. The detection limit for VCM was 1 ng.

Sample Analysis. Analyses of air samples were made directly using the calibrated gas-sampling loop. Air was drawn through the sampling loop for 30 sec at 100 cc/min before injection to achieve reproducible results. The detection limit was less than 0.1 ppm VCM when using a 3.81-ml sample volume. A charcoal tube was placed in series with the sample loop and the effluent analyzed when determining sampling efficiencies. The charcoal tubes were analyzed for VCM by placing the charcoal in a 2-ml glass vial and sealing the vial with a silicone rubber septum. The vial was then cooled to dry ice temperatures for several minutes before injecting 0.5 ml of room temperature carbon disulfide through the septum. The vial was removed from the dry ice when the bubbling produced by the mixing of the carbon disulfide and charcoal ceased. The vial was allowed to stand at room temperature for 5 min before removing 5 μl of the solution from the sealed vial for injection into the chromatograph.

Results and Discussion

Sample Capacity. Testing of the charcoal tubes was undertaken to determine their capacity for vinyl chloride. In these tests only the front portion of the two-section charcoal tube was used. Figure 2 illustrates a set of breakthrough curves obtained when sampling from a 25-ppm VCM in dry air (less than 20% r.h.). The general sigmoid shape of the breakthrough curves remained the same for 5- and 50-ppm samples. Data for three concentrations of vinyl chloride are presented in Table I. There is not a definite trend with sample concentration and breakthrough volume nor is there a firm trend with sampling rate and breakthrough volume. It is apparent, however, that the 50-cc/min sample rate had a 10% breakthrough volume that was lower than when sampling at higher flow rates in all cases.

Table II gives packing data for the front section of charcoal tubes from two manufacturers. As can be seen there is considerable variation both in total content and how effectively the charcoal has been packed. The variations in the packing of the charcoal tubes may explain lack of consistency between the 100- and 150-cc/min sample rates as noted in Table I, however, this does not explain the consistently lower retention volume for the 50-cc/min flow rate. One further point should be made concerning the possible differences when used in the field with a reciprocating piston-type pump: The flow in the system used in our experiments was a constant vacuum source and did not have the pulsed flow observed with the small personal pumps. The pumping system may radically alter the retention characteristics and give more consistent results between the high flows and the low flows.

The variability of charcoal in absorbing VCM can be readily seen in Table III which presents data on respirators as well as charcoal tubes. Respirator data were obtained by NIOSH (*12*) on commercially available charcoal scrubbers used in respirators. The major feature of interest is the difference in capacity of the charcoal in the three situations examined. Again the difference must be explained as a combination of flow rate and packing characteristics. The data obtained on the charcoal tubes were taken at a much lower relative humidity which may explain the appreciably greater capacity of the tubes.

Recovery of VCM. Desorption of a substance from charcoal is dependent on variables such as compound to be desorbed, solvent, charcoal source, temperature, and sample age. Table IV presents the recovery data for charcoal tubes stored for up to two weeks. The recovery figures indicate an average initial recovery of vinyl chloride of about 87.5% which diminishes somewhat with age, about 7% in one week. Additional storage beyond one week apparently has little effect on the higher concentration sample. However, if only the two variables, storage time and concentration, are considered, a 16% decrease in recovered vinyl chloride was noted for the low concentration samples after 14 days.

During sample storage there was migration of the vinyl chloride from the front section to the back section of the tubes and this made analysis of both sections mandatory in order to determine total VCM. The tubes were stored at room temperature and the migration could have been minimized by storing under refrigeration. This migration may explain the slight decrease in the average sample recovery upon storage if it is assumed that the charcoal retains a certain fraction of vinyl chloride. Thus, there is an added amount of charcoal that must be considered after migration. A straightforward linear approach indicates that the amount retained would be 1.5 times greater than if all of the vinyl chloride were on the front section—i.e., the total amount of charcoal would be 150 mg instead of 100 mg on front only. As shown in Table III, the average loss with no storage is 13% and increases to an average of 19% for 7 days and 24% for 14 days whereas a linear approximation would predict 19.5% average loss due to the additional charcoal.

Table II. Packing Variations in Charcoal Tubes

Supplier		Front section packed length, mm	Front section wt. of packing, mg	Wt, g/mm
MSA[a]		18.2	103.1	5.66
MSA[a]		14.6	92.8	6.36
MSA		16.6	103.2	6.22
	Av	16.5	99.7	6.08
	% rel. std. deviation	10.9%	6.0%	6.1%
SKC[b]		15.1	85.0	5.63
SKC		15.2	82.4	5.42
SKC		14.1	86.2	6.11
SKC		16.6	87.3	5.26
SKC		17.0	90.5	5.32
SKC		17.2	85.9	4.99
	Av	15.9	86.2	5.45
	% rel. std. deviation	7.8%	3.1%	7.0%

[a] Mine Safety Appliance Co. [b] SKC, Inc.

Table III. Ten Percent Breakthrough Capacity of Charcoal Absorbers

Cartridges,[a] sample capacity		Canisters,[b] sample capacity		Charcoal tubes,[c] sample capacity	
Air, l/g charcoal	VCM, mg/g charcoal	Air, l/g charcoal	VCM, mg/g charcoal	Air, l/g charcoal	VCM, mg/g charcoal
44.9	5.7	48.9	12.5	148	18.9
36.6	4.7	53.5	13.3	181	23.1
41.1	5.2	35.8	9.1	90	12.8
40.0	5.1	40.1	10.2		

[a] Flow rate, 30 l/min at 50 ppm and 50% rel. humidity (Ref. 12).
[b] Flow rate, 60 l/min at 100 ppm and 50% rel. humidity (Ref. 12).
[c] Amounts of 50–100, and 150 cc/min at less than 20% relative humidity.

Table IV. Partition of VCM Upon Storage

Storage time, days	Vinyl chloride sampled, μg	Vinyl chloride recovered, %[a]	Recovered sample in front, %	Recovered sample in back section, %
0	2.55	85	100	0
0	31.9	89	100	0
7	2.55	83	84	16
7	31.9	79	86	14
14	2.55	71	84	16
14	31.9	81	79	21

[a] Average for six tubes at each storage time except for zero storage in which case only one tube was used.

Migration was observed between the sections of the charcoal tube and led to the examination of the effects of temperature plus the possibility of losses by migration out of the tube to ambient air. To examine variations in migration with temperature and losses from the tubes, a series of tubes were stored at 43°, 22°, and 4°C, sealed by ordinary plastic caps supplied with the tubes or fused closed by means of a torch. Table V presents the data from 24 samples. There is one immediately apparent factor: storage at 4°C limits migration severely during the seven-day storage period. Even at the end of 15 days the migration of vinyl chloride between the two sections was appreciably hindered. Thus, there is a definite effect of storage temperature on the migration of vinyl chloride throughout the tube; however, this migration did not affect the total recovery of the vinyl chloride.

A multivariant analysis was performed on the data displayed. In Table V the four variables, storage temperature, time, quantity of VCM, and sealing method, were examined for effect on recovery of the VCM. The multivariant analysis included two additional variables not included in the result indicated in Table IV—storage temperature and method of sealing the tubes. The hypothesis that each of the indicated variables had no effect was tested at the 0.01 level and in none of the cases was this hypothesis rejected. The effect of the above variables on partition of the VCM between the sections of the tubes was also tested and as might be expected, temperature had an effect on the partition; however, the storage time and quantity of VCM ab-

Table V. Charcoal Tube Performance Under Various Conditions

		High concentration, 31.9 μg						Low concentration, 2.6 μg					
		Capped tubes, °C			Fused tubes, °C			Capped tubes, °C			Fused tubes, °C		
Storage days		43	22	4	43	22	4	43	22	4	43	22	4
7	Recovery, %	91	71	87	69	79	79	87	84	77	72	86	90
	Total recovered in back section, %	22	14	3	19	21	3	23	14	0	27	27	10
15	Recovery, %	78	98	85	60	81	85	76	67	81	64	69	69
	Total recovered in back section, %	28	20	11	28	23	15	28	18	6	22	19	1

sorbed also affected the degree of partition. The only factor that did not influence the VCM partition was the method of sealing the tubes.

Analytical Methodology. From the data presented above, it can be seen that the charcoal tubes must be refrigerated if any information is to be gained from a separate analysis of the rear section of the tube. The function of the additional section is to determine breakthrough of VCM during sampling. To achieve this additional bit of information, it is necessary to refrigerate the tubes, preferably at dry ice temperatures, in the interim between sampling and analysis. If the tubes have not been refrigerated during the interim, the analytical procedure should be modified and the tube sections should be analyzed as a combined sample. When the tube sections were combined, the recovery was enhanced considerably over separate analysis. Ten identical VCM samples were obtained, and the charcoal tubes stored at ambient temperature for two weeks. Five of the tubes were analyzed as a unit by combining the front and rear sections before analysis, and the remaining five were analyzed separately. The average total recovery was 90.8% (std dev 5.5%) for the combined section analysis and 78.0% (std dev 4.5%) for the tubes which had each section analyzed separately. Thus, there was a 14% decrease in recovery when analyzing the tube sections separately and this could be significant at low concentrations.

The sample losses upon immediate analysis of the charcoal tubes, or when analyzing the combined sections of tubes stored for a period preceding analysis, amounted to approximately 10%. An examination of the head-space gas in sealed 2-ml vials containing standard solutions indicated that VCM was distributed between the gas phase and the carbon disulfide such that the head-space gas should not be neglected. Comparison of solutions of carbon disulfide originally containing 30.1 μg/ml of VCM and the head-space gas above the solution provided an approximate value for the Henry's law constant; the value determined was 8.1 atm. When we use this value and apply Henry's law to the analysis procedure described previously, head-space gas losses would be expected to be on the order of 6% when the head space was 1.5 ml. The remaining losses of VCM can be attributed to irreversible absorption on the charcoal. The Henry's law constant can be used to show typical losses when making-up standards in a 25-ml volumetric flask are on the order of 1% which may be decreased by limiting the head space.

Conclusions

A small charcoal tube is adequate for sampling vinyl chloride if well-controlled conditions are maintained. From the data given above, the recommended sampling procedure is as follows: sample rate, 100 cc/min; maximum sample volume, 5 l; and low-temperature storage, if breakthrough is thought to be a problem. The conditions given above provide a safe limit under most circumstances such that variabilities in temperature and relative humidity will not pose a problem. The analysis of tube contents should be performed on the combined contents of the charcoal tube unless the tubes have been stored at −20°C or less, in the interim between sampling and analysis and the head-space gas over the desorbing reagent, CS_2, should be minimized for highest recovery efficiencies. For accurate determination of recoveries, each charcoal tube batch should be examined by random selection of charcoal tubes from the same batch followed by a performance check using a dynamic flow system to absorb known concentrations on the charcoal. The dynamic system should be used to avoid sample losses that might occur when using a standard vinyl chloride solution in ethyl acetate as previously done (7) for other compounds. Recovery data should be determined over the same time interval as anticipated storage time.

Thus, while the charcoal tube method appears adequate for concentrations of VCM on the order of 1–50 ppm or more, there should be great care taken when using the method for very low levels, such as might be found around the perimeter of a polyvinyl chloride plant. As the concentration of VCM decreases, the scatter in the data and sample losses become a greater factor in analytical accuracy.

Acknowledgment

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Comparison of Manual and Automated Analysis Methods for Sulfur Dioxide in Manually Impinged Ambient Air Samples

Oliver John Logsdon II* and Mark J. Carter

Central Regional Laboratory, Environmental Protection Agency, 1819 West Pershing Road, Chicago, Ill. 60609

■ Data were compared from the analysis of manually impinged 24-hr ambient air samples for sulfur dioxide by two commonly used automated methods and the Environmental Protection Agency reference method. The automated analytical methods, both adaptations of the West-Gaeke pararosanaline method to Technicon AutoAnalyzer systems, yielded results that were not significantly biased from and were more precise than the reference method.

The Environmental Protection Agency (EPA) has promulgated a manual analytical procedure as the reference method for the determination of sulfur dioxide in manually impinged ambient air samples (*1*). Many air pollution control agencies that analyze large numbers of samples find the reference method tedious and slow when compared to available automated methods and therefore routinely use the automated analysis techniques.

Also, there is no SAROAD (Storage and Retrieval of Aerometric Data) method code number for data generated by automated analysis of manually impinged samples so these data have been processed and stored under the reference method code number (*2*). Once in the data bank, data from both manual and automated methods are indistinguishable and therefore used interchangeably. If biases exist in the methods used to analyze manually impinged samples for sulfur dioxide, then erroneous conclusions may inadvertently be drawn from the data.

This report compares analytical data from the analysis of manually impinged ambient air samples by the three pararosanaline methods in common use. The EPA manual reference method is compared to the West-Gaeke (*3*) method adapted to a Technicon AutoAnalyzer I system (*4*) and to a Technicon AutoAnalyzer II system (*5*). The automated methods were modified to use the reference-method absorbing solution (*6*).

Analytical Methods

Reference Method. This method of analysis of manually impinged sulfur dioxide samples was used as described in the *Federal Register* (*1*). Briefly, 5 ml of SO_2 absorbed in potassium tetrachloromercurate (TCM) are placed in a 25-ml volumetric flask. One ml of 0.6% sulfamic acid in distilled water is added and the solution allowed to stand for 10 min. Two ml of 0.2% formaldehyde in distilled water and 5 ml of 0.016% purified pararosanaline in 0.3 *M* phosphoric acid are pipetted in. The solution is diluted to volume with distilled water and the absorbance read against a distilled water blank at 548 nm with 1-cm cells after 30 min.

Automated I Pararosaniline Method. This automated system is the West-Gaeke method adapted to a Technicon AutoAnalyzer I and was used as described in Reference 4. The manifold diagram in Figure 1 shows the analysis scheme.

The pararosaniline is 0.016% purified (99–100%) pararosaniline in 11.8 *M* phosphoric acid. The formaldehyde solution was prepared by diluting 5 ml of 40% formaldehyde to 1 l. with distilled water. The sulfamic acid solution was prepared by dissolving 2.0 g of sulfumic acid in distilled water and diluting to 1 l. The sulfamic acid solution used here is 0.2%. Reference 4 uses 0.17%. This difference was not considered significant.

Automated II Pararosaniline Method. This automated system is a modification of the West-Gaeke method (*2*). The method is adapted to a Technicon AutoAnalyzer II and was used as described in Reference 5. Figure 2 shows the manifold diagram.

The pararosaniline solution used in this procedure is 0.016% pararosaniline in 1.84 *M* phosphoric acid. Formaldehyde solution was prepared by diluting 5 ml of 40% formaldehyde to 1 l. with distilled water and adding 0.5 ml of Aerosol 22 wetting agent. The Aerosol 22 smooths the flow of the solution through the manifold and colorimeter flow cell and does not affect the analysis. Two-tenths percent sulfamic acid solution was prepared by dissolving 2 g of sulfamic acid in distilled water and diluting to 1 l.

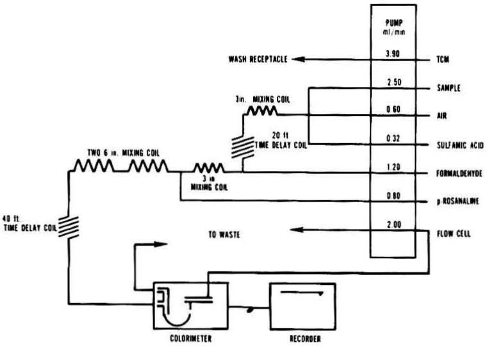

Figure 1. Automated I sulfur dioxide manifold diagram. Compatible with AutoAnalyzer I components and equipment

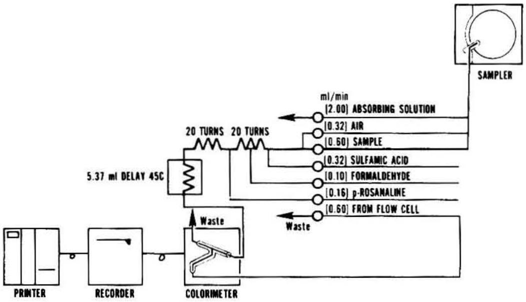

Figure 2. Automated II sulfur dioxide manifold diagram. Assembled from AutoAnalyzer II components and equipment

Table I. Comparison of the Analysis Solutions at the Time the Sample Absorption Is Determined

Method	Reference method	Automated I	Automated II
TCM, *M*	0.016	0.020	0.020
Sulfamic acid, %	0.024	0.011	0.054
Formaldehyde, %	0.008	0.014	0.017
Pararosanaline, %	0.0032	0.0027	0.0022
pH	1.56	0.85	1.11
λ max, nm	547	580	560
Extinction coefficient,[a] × 10^4	5.13	4.06	4.8
Solution detection limit,[b] μg/ml	0.075	0.030	0.021
Air detection limit,[c] μg/m³	13	5	4

[a] Expressed as absorbance liters/centimeter mole determined from the difference of the sample and blank absorbance. [b] Determined from two standard deviations of the blank. [c] Assuming 300 l of air sampled.

Methods Comparison

In all of the analytical procedures, sulfur dioxide in absorbing reagent is determined as sulfite ion by the addition of formaldehyde and acid bleached pararosaniline to form a colored species, pararosaniline methyl sulfonic acid (*7, 8*). The absorbance of the colored solution is determined at some point between 540 and 570 nm. Scaringelli et al. have shown that the λ max is pH dependent (*7*). Figure 3 shows the absorption spectra of a reagent blank and a sample containing sulfur dioxide as determined by each method.

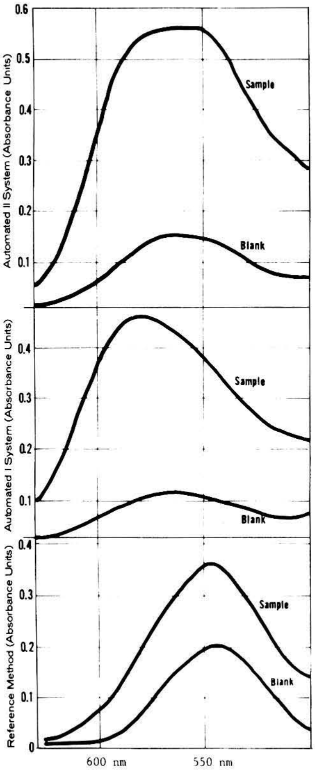

Figure 3. Absorption spectra of the analysis solutions from each method. The sample contained approximately 1 μg SO_2/ml

Thirty-six samples for the comparison of the reference method and the Automated II method were collected. Most were 24-hr ambient air samples collected using reference-method sampling procedures (*1, 9*). These samples were collected from National Air Surveillance Network monitoring sites in Illinois, Indiana, Michigan, Minnesota, Ohio, and Wisconsin where the average ambient sulfur dioxide concentration is generally less than 80 μg per cubic meter (less than 0.5 μg of sulfur dioxide per milliliter (μg SO_2/ml) in absorbing reagent). To broaden the range of available sample concentrations, four samples from the field were spiked with SO_2 in absorbing reagent and two samples were collected from test atmospheres generated with a permeation tube apparatus (*1, 10*). In addition, 17 similar samples were collected for comparison of the Automated I method to the Automated II method. A number of samples were analyzed in duplicate to determine the precision of each method.

Results and Discussion

Table I shows the concentrations of the reagents added for each method in the analysis solution at the time the absorbance is determined. The apparent higher sensitivity of the automated methods in Figure 3 is due to the use of 2.5 times more sample than in the reference method. The extinction coefficients in Table I show that the reference method is most sensitive in fact. The detection limits based on twice the standard deviation of the blank are also shown. The Automated II method has the highest sulfamic acid concentration (used to reduce interferences from nitrogen oxides) of the three methods. However, the analytical results indicated no significant differences between methods due to this. The nitrogen dioxide (NO_2) concentrations corresponding to each sample were between 5 and 150 μg NO_2/m^3, and each method appears able to cope with these levels. Nitric oxide (NO) concentrations were not determined.

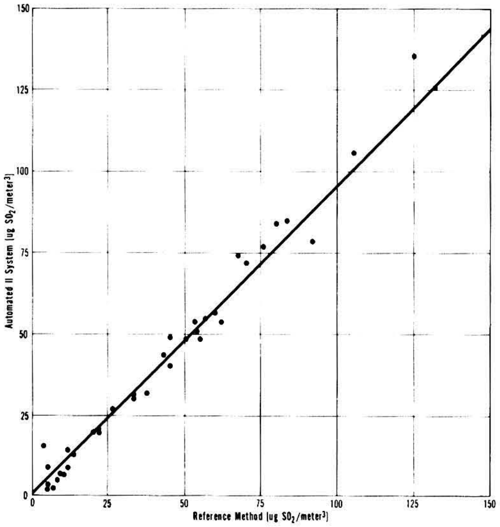

Figure 4. Plot of comparison data for the reference and Automated II methods

Equation of the line: $y = 0.959\ X + 0.002$

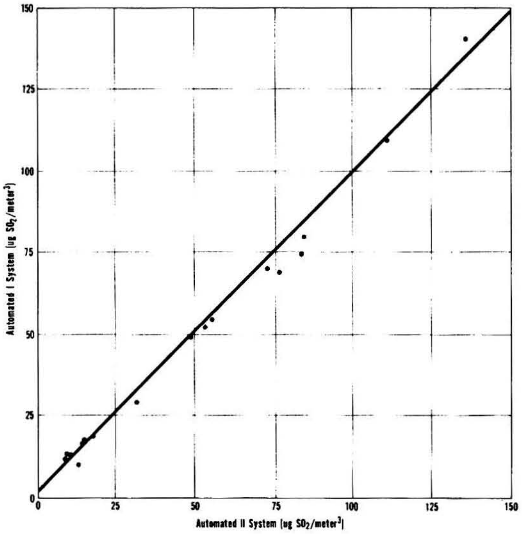

Figure 5. Plot of comparison data for the Automated II and Automated I methods

Equation of the line: $y = 0.972 \times + 0.013$

Each method contains sufficient formaldehyde and pararosaniline and gives linear plots of absorbance vs. concentration for samples in the range of 0–1 μg SO_2/ml (0–167 μg/m^3). Any samples higher than 1 μg/ml are routinely diluted with absorbing reagent.

Figure 4 shows the data plot from the reference method and the Automated II procedure comparison. The slope was calculated to be 0.96 ± 0.03, which is not significantly different from 1.0 (t-test $\alpha = 0.05$); the correlation coefficient was 0.992. The analysis of duplicate samples yielded standard deviations of 0.037 μg SO_2/ml (N = 7, mean concentration = 0.26 μg SO_2/ml) and 0.013 μg SO_2/ml (N = 16, mean concentration = 0.42 μg SO_2/ml) for the reference and Automated II methods respectively. An F-test showed the variance of the Automated II system to be significantly less than that of the reference method.

The data from samples analyzed with the Automated I and Automated II systems are plotted in Figure 5. The slope of 0.97 ± 0.02 is not significantly different from 1.0 and the correlation coefficient is 0.998. Duplicate analyses with the Automated I system yielded a standard deviation of 0.023 μg SO_2/1. (N = 17, mean concentration = 0.50 μg SO_2/ml) which is significantly greater than that of the Automated II procedure. This precision is, however, better than the reference method.

The results from the Automated II system were on the average 0.012 μg SO_2/ml (2 μg/m^3) higher than the reference method results. The Automated I system results were on the average 0.006 μg SO_2/ml (1 μg/m^3) higher than the Automated II system results or 0.018 μg SO_2/ml (3 μg/m^3) higher than the reference method. These biases are not significant when considering the variations in duplicate analysis by each method.

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Received for review May 5, 1975. Accepted October 1, 1975. Mention of commercial products is for identification only and does not constitute endorsement by the Environmental Protection Agency of the U.S. Government.

Correction

B. J. Dowty, D. R. Carlisle, and J. L. Laseter point out an error in their paper, "New Orleans Drinking Water Sources Tested by Gas Chromatography–Mass Spectrometry. Occurrence and Origin of Aromatics and Halogenated Aliphatic Hydrocarbons" [*Environ. Sci. Technol.*, **9** (8), 762–5 (1975)]:

"Closer examination of the spectrum of compound number 58, reported in Table I as (2- or 1-Napthyl)dichloromethane, reveals this compound to be dichloroiodomethane. Although both of these compounds share common spectral features such as their isotope ratios of the molecular ion and the presence of the —$CHCl_2$ fragment, comparison of the spectrum of our compound with that of the recently synthesized dichloroiodomethane reveals our initial interpretation to be in error. Spectrum of the dichloroiodomethane was furnished by Robert Kleopfer, USEPA, Region VII."

Analysis of Air Pollutants Using Sampling Tubes and Gas Chromatography

John W. Russell

Analytical Laboratories, Dow Chemical Co., Midland, Mich. 48640

■ Sampling tubes filled with gas chromatographic packings were excellent for concentrating organic pollutants from air. The collected pollutants were thermally desorbed into a gas chromatograph and quantitated using flame ionization or flame photometric detection. Advantages of the technique are ppb sensitivity and quantitative recovery, as well as superior sample stability and sampling convenience. The suitability of various sampling tube packings for collecting specific compounds was shown by determination of breakthrough volumes and recovery values.

A frequent problem in air quality analysis involves the collection of a representative and stable sample. The collection technique must ensure that pollutants be quantitatively recoverable and sufficiently concentrated to provide the necessary sensitivity. Current sampling techniques involving gas bags, evacuated bulbs, cold-trapping, or solution trapping suffer from various drawbacks, such as surface adsorption of pollutants, water or solvent interference, inconvenience, or poor sensitivity resulting from inability to concentrate pollutants.

The use of sampling tubes packed with gas chromatographic adsorbents circumvents these difficulties. A known volume of air is passed through a tube at a controlled rate. The pollutants collected on the packing are thermally desorbed directly into a gas chromatograph for analysis. The technique has been previously used to collect 2-chloro-2-bromo-1,1,1-trifluoroethane on Porapak P, Porapak Q, and Apiezon K packings (*1*). Urine metabolites collected on Tenax-GC porous polymer (*2*) and bis(chloromethyl)ether collected on Chromosorb 101 porous polymer (*3*) have been determined using gas chromatography–mass spectrometry. To extend the usefulness of this technique, different adsorbents for packing tubes and the effects of air flow rate and pollutant concentration have been systematically investigated. Gas chromatographic procedures for determination of a number of organic compounds using the tubes are also reported. Particular attention was directed toward determination of the "breakthrough volume," the sampled air volume at which the compound being collected begins to elute from the tube. The breakthrough volume is dependent upon the gas chromatographic retention time of the compound at ambient temperature using the adsorbent as the stationary phase. Since this volume represents the maximum volume of air that may be sampled before losses of the pollutant can occur, it was determined for each pollutant to be quantitated. In addition, recovery of the pollutant was determined by comparing the quantity of pollutant recovered from a sampling tube to the quantity introduced to the air stream that had flowed through the tube.

Experimental

Breakthrough volumes were determined using two sampling tubes in series. An aliquot of a standard solution of the pollutant of interest was injected into an air stream flowing through the tubes at a known rate, usually 100 ml/min. Since the presence of water can reduce breakthrough volumes, the air stream was nearly saturated by passing the air through two water-filled bubblers to simulate the most disadvantageous humidity conditions. The injector was heated to appropriate temperatures to ensure volatilization. After a known volume of air had passed through the sampling tubes at ambient temperature, the second tube was analyzed to determine whether the compound had eluted from the first tube, indicating breakthrough. If none eluted (less than 1% of the quantity injected), the tube was reconnected in series, more air was passed through, and the second sample tube was reanalyzed. This procedure was repeated until the breakthrough volume (or an arbitrary limiting volume) was reached. Breakthrough volumes from 1–10 l. were generally determined, since <1 l. suggested that the sampling tube did not possess adequate retention and 10 l. usually allowed sufficient sensitivity.

Recovery was determined by injecting an aliquot of standard solution into an air stream flowing at 100 ml/min into a single sampling tube. After a volume of air less than the breakthrough volume had passed, the quantity of pollutant subsequently desorbed from the tube was compared with that of an aliquot of the standard injected into the gas chromatograph.

Apparatus

The collected pollutants were determined by mounting the tube on the injection port of a Tracor 550 gas chroma-

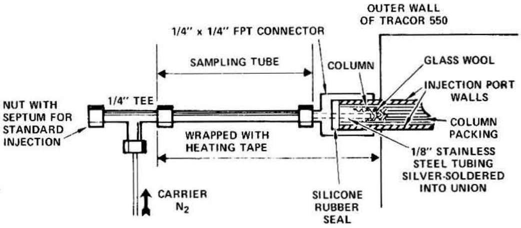

Figure 1. Schematic of sampling tube apparatus attached to Tracor 550 gas chromatograph

Table I. Compounds Concentrated from Air Using Tenax–GC Porous Polymer

Compound	Breakthrough vol, l.
Benzene	3
Chlorobenzene	>10
o-Dichlorobenzene	>10
1,2,4-Trichlorobenzene	>10
1,2,3,5-Tetrachlorobenzene	>10
Pentachlorobenzene	>10
Hexachlorobenzene	>10
Bromoform	>10
1,2-Dibromoethane	>10
Phenol	>10
p-Chlorophenol	>10
2,4,6-Trichlorophenol	>10
Diphenyl oxide	>10
o-Phenyl phenol	>10
Pentachlorophenol	>10

Table II. Compounds Concentrated from Air Using Porapak N Porous Polymer

Compound	Breakthrough vol, l.
Acetaldehyde	0.5
Methanol	1
Diethyl ether	3–5
Acetone	3–5
n-Butanol	>10
Methyl isobutyl ketone	>10
Acetic acid	10
Acetonitrile	2
Acrylonitrile	3–5
Propylene oxide	1.5
Methyl acetate	3
Vinyl bromide	1
Ethyl bromide	2–3

Table III. Compounds Concentrated from Air Using Carbosieve B Adsorbent

Compound	Breakthrough vol, l.
Methyl chloride	1.3
Dimethyl ether	3
Vinyl chloride	4
iso-Butane	>10
Vinylidene chloride	>10

tograph with carrier gas flow introduced through the tube (Figure 1). The tube was heated to a fixed temperature by wrapping with heating tape controlled by a variable transformer. The desorbed pollutants were collected on the front of a gas chromatographic column selected to retain the pollutants at low temperatures (e.g., 60°), and thus prevent peak spreading during the desorption procedure. The column was then temperature programmed to elute the pollutants.

Sampling Tube Construction

Sampling tubes of 0.25 in o.d., 0.19 in. i.d. stainless steel tubing with Swagelok fittings were filled with adsorbents using gentle tapping. Glass wool plugs of approximately 0.4 in. length were placed in each end such that a 4-in. sampling tube contained approximately 3.2 in. of adsorbent. The tube was conditioned by heating overnight at the upper temperature limit of the adsorbent with a nitrogen flow of 30 ml/min. The tube was reconditioned after each use.

Calibration

A standard of the pollutant was prepared by diluting an appropriate quantity of the compound in a solvent that would not interfere with the gas chromatographic analysis. The concentration of the standard solution was such that a 5 μl. aliquot corresponded to 1–5 ppm of the pollutant in air, assuming a 1-l. air sample.

The chromatograph was calibrated by injecting 5 μl. of the standard solution into a heated, unpacked sampling tube mounted on the instrument. The column was then temperature programmed. Alternatively, the standard could be injected into a packed tube and thermally desorbed and analyzed in the same manner as the samples. However, some high-boiling compounds would not elute completely from the packed sampling tube during desorption unless the tube was reversed to allow back flushing into the injection port. For this reason, all sampling tubes should be mounted with the end where air entered during sampling attached to the port.

Applications

The following stationary phases were useful as sampling tube packings. Tables I–III list the potential pollutants studied and the determined breakthrough volumes. The gas chromatographic conditions used with the various packings are shown in Table IV. The recovery in every instance for the compounds listed in the tables was determined to be 100 ± 3%. Representative chromatograms are shown in Figures 2 and 3. The start of the chromatograms (0 min) coincides with the commencement of sampling tube heating.

Tenax-GC. Tenax-GC porous polymer (Applied Science Laboratories, Inc., State College, Pa.) was most useful for general-purpose air sampling. It has excellent retention, exemplified by the 3-l. breakthrough volume for benzene. The high upper temperature limit (275°C) of this 2,6-di-

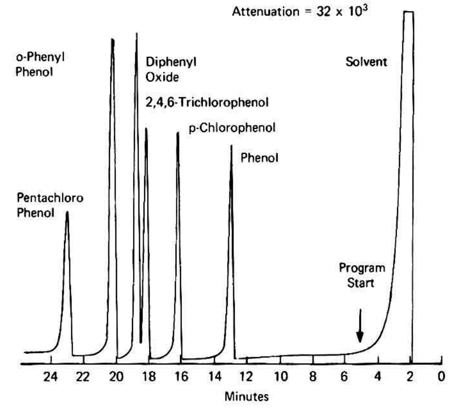

Figure 2. Chromatogram of phenolics and diphenyl oxide desorbed from Tenax-GC porous polymer sampling tube
Quantities equivalent to 5 ppm each in one liter air

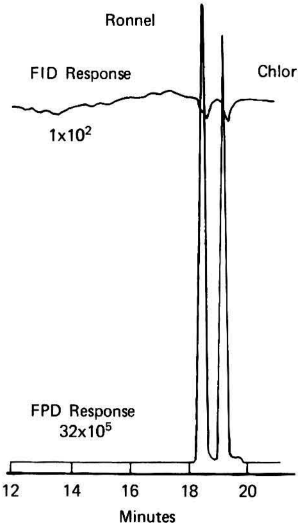

Figure 3. Chromatogram of ronnel and chlorpyrifos desorbed from 20% DC-200 silicone oil sampling tube
Quantities equivalent to 8 ppb each in one liter air

phenyl-p-phenylene oxide porous polymer facilitates desorption of such high-boilers as hexachlorobenzene and pentachlorophenol, and also minimizes potentially interfering packing bleed from the tube during desorption.

Porapak N. This porous polymer (Waters Associates, Framingham, Mass.) is characterized by long retention times (*4*) and thus appreciable breakthrough volumes. It was very useful for collecting low-boiling organic compounds, such as many of the more common solvents. However, in the case of many of the compounds collected, varying the amount of water on the sampling tube altered peak width and retention time during the gas chromatographic analysis. Thus, higher humidity air may cause peak broadening and somewhat shorter retention times. This effect, which concerns the chromatographic column and not the sampling tube, may be compensated for by using mass spectrometric detection or by spiking a sampling tube with a standard to aid in peak identification.

Carbosieve B. Carbosieve B carbon molecular sieve (Supelco, Inc., Bellefonte, Pa.) has the ability to reversely adsorb many organic compounds that have boiling points below ambient temperature. Although unusual in its ability to retain such compounds, Carbosieve B requires high desorption temperatures that may cause some organic compounds to chemically react on the catalytic surface of the packing. Ethylene oxide adsorbed in Carbosieve B polymerizes when the tube is heated above 200°C. Methyl bromide appears to exchange a Br atom for a Cl atom (present as an impurity in the adsorbent) during thermal desorption from Carbosieve B. Thus, peaks for both methyl bromide and methyl chloride appear in the chromatogram. Because of such reaction phenomena, care should be taken in using Carbosieve B adsorbent to ensure that compounds being determined are not altered during desorption.

Porapak R. Porapak R porous polymer (Waters Associates, Framingham, Mass.) was suitable for concentrating trimethylamine from air. The breakthrough volume and recovery determined were >10 l. and 95%, respectively.

20% DC-200. Sampling tubes packed with 20% DC-200 silicone oil (Dow Corning Corp., Midland, Mich.) were effective for concentrating chlorpyrifos [*O,O*-diethyl-*O*-(3,5,6-trichloro-2-pyridyl)phosphorothioate] and ronnel [*O,O*-dimethyl-O-(2,4,5-trichlorophenyl)phosphorothioate] from air. The breakthrough volumes for both compounds were >10 l. Recovery of chlorpyrifos was 100 ± 3%. However, small amounts of ronnel were lost during the sampling process, due perhaps to hydrolysis. Thus, when 1 l. of high-humidity air was passed through a sampling tube containing the equivalent of 1 ppm (v/v) ronnel, recovery was 95 ± 3%. At the 8-ppb level and 1 l. of air, recovery was 90 ± 3%. Ronnel appears to be stable in a sealed tube after sampling has ceased, since the recovery did not decrease when a sampling tube was spiked with ronnel, stored, and analyzed 24 hr later.

Discussion

Since minor variations may occur in gas chromatographic packings, sampling tube packing techniques, and sampling conditions, the recommended maximum sampling volume is 50–70% of the breakthrough volume. Breakthrough volumes can be increased by using longer sampling tubes, which, however, will result in higher back pressure and may require longer heating cycles for desorption.

The data were compiled at 25°C. Higher temperature would significantly decrease pollutant retention.

The air flow rate during sampling may also be critical since insufficient time of contact between pollutant molecules and packing may result in some of the pollutant passing through the tube without ever being adsorbed. This problem is especially apparent with low surface area adsorbents such as Chromosorb 101. At a flow rate of 100 ml/min, adsorption of benzene on Chromosorb 101 (4-in. sampling tube) is incomplete but is quantitative at 25 ml/min. All data presented here were obtained using a 100-ml/min air flow rate. Higher flow rates may be permissible in many cases, but should be proved by experiment. Porapak R quantitatively adsorbed trimethylamine even at a flow rate of 1 l./min.

The quantity of the compound of interest collected affects the breakthrough volume only slightly. A pollutant present at 20 ppm will breakthrough at a slightly smaller volume than when at 1 ppm. This difference is insignificant if a margin of error is allowed as noted above. If the sampling tube approached saturation, loss of the compound would occur, regardless of the breakthrough volume. However, concentrations of this magnitude (and considerably

Table IV. GC Conditions Used with Sampling Tubes

Sampling tube	4-In. Tenax-GC porous polymer, 60/80	4-In. Porapak N porous polymer 80/100	2-In. Carbosieve B adsorbent, 100/120	4-In. Porapak R porous polymer, 80/100	2-In. 20% DC-200 silicone oil on C.W., H.P. support 100/120
Sampling tube desorption	5 Min at 260°C	5 Min at 200°C	5 Min at 270°C	5 Min at 200°C	5 Min at 230°C
Column	8 Ft × 0.25 in. s.s. 10% OV-17 silicone oil on Gas Chrom Q support, 60/80	4 Ft × 0.125 in. s.s., Porapak N porous polymer, 80/100	2 Ft × 0.125 in. s.s., Carbosieve B adsorbent, 100/120	6 Ft × 0.25 in. glass, Chromosorb 103 porous polymer, 80/100	6 Ft × 0.25 in. glass, 10% OV-17 silicone oil on Gas Chrom Q support, 100/120
Column temp.	5 Min at 60°C program 15°C/min to 280°C and hold	5 Min at 60°C program 15°C/min to 200°C and hold	5 Min at 80°C program 20°C/min to 290°C and hold	5 Min at 25°C, program 15°C/min to 200°C and hold	5 Min at 90°C program 15°C/min to 260°C and hold
Injection port temp.	220°C	120°C	80°C	170°C	200°C
Detector temp.	FID, 280°C	FID, 280°C	FID, 280°C	FID, 240°C	FPD (525 nm filter P specific), 230°C
Carrier gas flow, ml N_2/min	30	20	20	20	20

less) will overload gas chromatographic detectors. The sampling tube technique is most appropriate for low concentrations, <100 ppm in 1 l. of air sample, when flame ionization detection is used. The presence of high concentrations of compounds other than the compound of interest may have an effect on breakthrough volume which must be determined experimentally.

Recoveries of compounds from sampling tubes stored for several days after sampling have been excellent. Tubes packed with 20% DC-200 silicone oil were spiked with the equivalent of 2 ppb and 12 ppb chlorpyrifos in 1 l. of air and sent to a sampling location several thousand miles away where 1 l. of chlorpyrifos-free air was passed through them. Recoveries of the spikes were 100% (2 ppb) and 104% (12 ppb) after the tubes were returned and analyzed three weeks later. Quantitative recoveries have been the rule for sampling tubes spiked with many compounds analyzed 24 hr later. Stability of samples concentrated using sampling tubes is thus considered excellent.

The sensitivity of the technique is approximately 1 ppb when concentrating a 1-l. air sample and using flame ionization detection. At low ppb, interference may be encountered unless more specific detectors are used. The flame photometric detector was especially useful for phosphorus- or sulfur-containing compounds. Other detectors that could eliminate interference owing to their specificity are electron capture for halogenated compounds, thermionic for nitrogen compounds, and mass spectrometric for m/e of individual compounds.

Conclusions

The high sensitivity, recoverability, and wide applicability of the sampling tube technique are apparent. Porapak N and Tenax-GC porous polymers were suitable packings for general usage in air sampling. Most organic compounds boiling between 20–100°C can be concentrated and recovered using Porapak N, while higher-boiling compounds may be collected and determined using Tenax-GC.

A compound for which sampling techniques and breakthrough volumes have not been determined can probably be sampled using the same sampling tube as given herein for a compound of similar boiling point and functional group. An indication of the suitability of a sampling tube packing for collecting a compound may be obtained by using an analytical column containing the same packing as the tube. If similar gas chromatographic retention times are found for two compounds, one of which can be collected using the packing in the column, then the other compound probably can also be collected. Likewise, an approximation of the breakthrough volume of a compound may be obtained by comparison of retention times. If the retention time of the compound is bracketed between retention times of two compounds of known breakthrough volume, then the breakthrough volume of the first compound lies between those breakthrough volumes.

It is expected that the sampling tube technique will be extended to other compounds and that it should prove to be superior for sampling traces of most organic pollutants in air.

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NOTES

Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmosphere

Donald Mackay* and Paul J. Leinonen

Department of Chemical Engineering and Applied Chemistry and The Institute for Environmental Studies,
University of Toronto, Toronto, Ont., Canada. M5S 1A4

■ The equations presented here can be used to predict the approximate rates of evaporative loss of low-solubility contaminants in an air–water system; however, it is very desirable to obtain specific mass transfer rates for that system, particularly the coefficient for the controlling phase.

In a recent paper Mackay and Wolkoff (*1*) discussed the rate at which low solubility compounds, such as pesticides, polychlorinated biphenyls, or hydrocarbons, evaporate from water bodies to the atmosphere. They showed that the very high activity coefficients of these compounds in aqueous solution result in high equilibrium vapor partial pressures and thus surprisingly high evaporation rates. A stated assumption in that paper was that diffusion or mixing in the water phase is sufficiently fast that the concentration of the contaminant at the water–air interface is close to that in the bulk of the water. The validity of this assumption depends on the relative rates of evaporation and liquid diffusion or mixing, the slower process controlling the overall rate.

Liss and Slater (*2*) have recently reviewed mass transfer rates between the ocean and the atmosphere in terms of liquid and vapor phase mass transfer coefficients and have suggested that liquid and vapor phase mass transfer coefficients are typically 20 cm/hr and 3000 cm/hr respectively. They showed that the mass transfer rate for most low-solubility gases is liquid phase controlled, whereas for more soluble gases, such as SO_2, the vapor phase may control. As noted by Mackay and Wolkoff the very short calculated half-lives of some compounds in aqueous solution (essentially from the vapor phase coefficient only) clearly indicate liquid phase control.

The purpose of this note is to extend the previous analysis to include the liquid phase rates of Liss and Slater, thus leading to a more realistic estimate of the rate of the total evaporation process of low-solubility compounds from the bulk of a water body to the atmosphere. The original analysis applied only to the evaporation rate from the surface.

In deriving the rate equations it is convenient to consider a column of water 1 m^2 in cross section of depth L m containing L m^3 of water. If the concentration C_i mol/m^3 of the evaporating compound, i, in the column is uniform, then the amount of i in the column is C_iL moles. Mackay and Wolkoff showed that a convenient expression for the equilibrium partial pressure of the compound in the vapor, P_i, as a function of its concentration in an aqueous solution, is

$$P_i = C_iP_{is}/C_{is}$$

where P_{is} and C_{is} are the compound's vapor pressure (atm) and solubility in water (mol/m^3). The group (P_{is}/C_{is}) is effectively a Henry's law constant, H_i (atm m^3/mol).

The rate of mass transfer across a phase boundary can be expressed in terms of an overall mass transfer coefficient obtained by combining two individual phase or film mass transfer coefficients k_{iG} and k_{iL} (m/hr). These equations have been given by Liss and Slater and in mass transfer texts, e.g. Treybal (3). Here it is convenient to use an overall liquid coefficient K_{iL} (m/hr) given by

$$1/K_{iL} = 1/k_{iL} + 1/(H_ik_{iG}/RT)$$

where T is the absolute temperature (K) and R the gas constant (8.2×10^{-5} m^3 atm/mol K).

The mass flux N_i across the phase boundary can then be given in terms of the bulk liquid concentration and the partial pressure in the atmosphere P_i (atm).

$$N_i = K_{iL}(C_i - P_i/H_i) \text{ mol/m}^2 \text{ hr} \qquad (1)$$

Combining this with a mass balance equation in an unsteady state model (and assuming no other methods of loss) leads to the differential Equation 2 which can be integrated to express the concentration of the compound as a function of time as in Equation 3, where C_i is the concentration at time t and C_{i0} the concentration at zero time

$$dC_i/dt = -K_{iL}(C_i - P_i/H_i)/L \qquad (2)$$

$$C_i = P_i/H_i + (C_{i0} - P_i/H_i) \exp(-K_{iL}t/L) \qquad (3)$$

If P_i is negligible—i.e., the background atmospheric level of the contaminant is low compared to the local level, then Equation 3 simplifies to

$$C_i = C_{i0} \exp(-K_{iL}t/L) \qquad (4)$$

A half-life τ_i may then be defined from Equation 4 as the time required for the concentration to drop to half its original value.

$$\tau_i = 0.69\, L/K_{iL}$$

A steady state model can also be set up in which it is assumed that the evaporation rate of the contaminant is exactly balanced by its influx from other sources. The concentration C_i then adjusts to a value such that these rates are equal. This model represents a situation, for example, of a lake with fairly constant influx whereas the unsteady state model represents either a pulse injection of contaminant as from a spill, or a river with a point source of contaminant.

If the influx rate is I_i mol/m^2 hr then, equating this to N_i, the steady state model yields

$$C_i = I_i/K_{iL} + P_i/H_i \qquad (5)$$

The mean residence time of i in the volume is then C_iL/I_i which can be shown to be $L[1 + P_i/(C_iH_i - P_i)]/K_{iL}$ hr. This reduces to L/K_{iG} when P_i is negligible and is only different by a factor of 0.69 from the unsteady state model half-life.

The physical model that these equations represent is of well-mixed air and water phases separated by an interface with near stagnant films of air and water on either side. Most of the resistance to mass transfer (and hence most of the concentration gradient) lies in these films. This is probably the most simple but realistic model of mass transfer between the near surface regions of water bodies and the atmosphere. Other rate-limiting diffusion processes at depths in water bodies, for example, through thermoclines, are not considered here. Equation 3 represents a situation in which a water body becomes depleted of a compound introduced at a point in time for example from an accidental spill. Equation 1 may be used to predict the steady state exchange rate of a compound between the atmosphere and a water body assuming that there is a constant rate of supply of material to one phase and removal from the other.

Table I gives evaporation parameters and rates for vari-

Table I. Calculated Evaporation Parameters and Rates at 25° C

Compound	Solubility, mg/l.	Vapor pressure, mm Hg	H, atm m^3/mol	K_L, m/hr	Resistance in liquid phase, %	τ for L = 1 m, hr
n-Octane	0.66	14.1	3.21	0.124	>99.9	5.55
2,2,4-Trimethylpentane	2.44	49.3	3.04	0.124	>99.9	5.55
Benzene	1780	95.2	5.5×10^{-3}	0.144	95.6	4.81
Benzene at 10° C	1750	45.5	2.67×10^{-3}	0.137	91.3	5.03
Toluene	515	28.4	6.68×10^{-3}	0.133	96.3	5.18
o-Xylene	175	6.6	5.27×10^{-3}	0.123	95.4	5.61
Cumene	50	4.6	1.46×10^{-2}	0.119	98.3	5.79
Naphthalene	33	0.23	1.18×10^{-3}	0.096	82.2	7.15
Biphenyl	7.48	0.057	1.55×10^{-3}	0.092	85.5	7.52
DDT	1.2×10^{-3}	1×10^{-7}	3.89×10^{-5}	9.34×10^{-3}	13.2	73.9
Lindane	7.3	9.4×10^{-6}	4.93×10^{-7}	1.5×10^{-4}	0.19	4 590
Dieldrin	0.25	1×10^{-7}	2.00×10^{-7}	5.33×10^{-5}	0.078	12 940
Aldrin	0.2	6×10^{-6}	1.44×10^{-5}	3.72×10^{-3}	5.4	185
Aroclor 1242	0.24	4.06×10^{-4}	5.73×10^{-4}	0.057	69.2	12.1
Aroclor 1248	5.4×10^{-2}	4.94×10^{-4}	3.51×10^{-3}	0.072	93.2	9.53
Aroclor 1254	1.2×10^{-2}	7.71×10^{-5}	2.76×10^{-3}	0.067	91.6	10.3
Aroclor 1260	2.7×10^{-3}	4.05×10^{-5}	7.13×10^{-3}	0.067	96.6	10.2
Mercury	3×10^{-2}	1.3×10^{-3}	1.14×10^{-2}	0.092	97.8	7.53

ous compounds at 25°C in the same form as Mackay and Wolkoff (*1*). The values of k_{iG} and k_{iL} used are those of Liss and Slater (2) corrected, as they suggest, for the molecular weights of the compound diffusing. The relative magnitudes of the liquid and vapor resistances are $1/k_{iL}$ and $RT/H_i k_{iG}$ respectively. It is interesting to consider which resistance dominates by examining the percentage of the resistance lying in the liquid phase. In all cases except the pesticides, which have very low vapor pressures, the liquid phase resistance dominates.

For substances such as alkanes with high Henry's law constants—i.e. the vapor pressure to solubility ratio is high, the rate of evaporation is controlled by the small concentration difference driving forces for diffusion attainable in the liquid phase, and the rate of evaporation is controlled by the liquid phase coefficient k_{iL}. Conversely, for substances with low values of H_i the evaporation rate is controlled by concentration gradient in the vapor. The phase resistances are approximately equal for a H_i of 1.6×10^{-4} atm m^3/mol.

The half-lives for a water depth of 1 m show that most of these compounds evaporate rapidly from solution. In situations where the water body is turbulent with frequent exchange between the surface water layer and the bulk, for example in a fast-flowing shallow river, or during whitecapping on a lake or ocean, the liquid phase mass transfer coefficient may be considerably increased and the evaporation rate increased correspondingly. For depths greater than 1 m the half-life is correspondingly increased, assuming that the rate of eddy diffusion is substantial.

The vapor phase mass transfer coefficient used here is higher than the value used by Mackay and Wolkoff that was based on a mean water evaporation rate of 1000 mm/year. At 10°C and 30% relative humidity, the k_g value of 3000 cm/hr yields an evaporation rate of 1730 mm/year. Since the object of the present note is to give only approximate rates and indicate the factors controlling these rates, the difference is relatively small and is attributable to uncertainty in evaporation rates and conditions.

Average environmental conditions are usually closer than 10°C than 25°C; thus it is interesting to consider the effect of temperature on the rates. The mass transfer coefficients and aqueous solubilities are relatively temperature insensitive, the principal effect being on the vapor pressure, P_{is}. This only affects the rate significantly if the system is vapor phase controlled; thus for most of the compounds in Table I the rates and half-lives are insensitive to temperature as illustrated by the data for benzene.

Literature Cited

(1) Mackay, D., Wolkoff, A. W., *Environ. Sci. Technol.* **7**, 611–14 (1973).

(2) Liss, P. S., Slater, P. G., *Nature*, **247**, 181–4 (1974).

(3) Treybal, R. E., "Mass Transfer Operations," 2nd ed., McGraw-Hill, New York, N.Y., 1968.

Received for review November 1, 1974. Accepted August 18, 1975.

CORRESPONDENCE

SIR: In their article dealing with organic matter in New Orleans drinking water, Dowty et al. [*Environ. Sci. Technol.*, **9**, 762 (1975)] presented data on the content of organics in Mississippi River water before and after treatment. One of the treatment procedures they used involved a commercial activated carbon–ion-exchange system for removal of organic matter and dissolved salts. While the data on the organic content of the water from this system were presented only as "preliminary data", I question whether any significance can be given to them based on what is known about the activated carbon in the treatment unit and the process operating parameters.

As is well known, removal of organic compounds by carbon beds depends upon the detention time of the water within the bed as well as on the previous operation history of the bed. No information on the depth of carbon or the rate of application of water is given, let alone information on the types and amounts of organic compounds previously adsorbed by the carbon, if any. If carbon beds are designed and operated properly they can do a good job of removing many organic compounds, but careful monitoring of the process and regeneration of the carbon at the proper time are required. Because adsorption in many cases is reversible, it is possible for previously adsorbed compounds to appear in the effluent from the carbon bed thus illustrating the need for careful process control. I agree that further studies are needed to determine optimum procedures for operating carbon beds, but it is important to note that much is already known which should be taken into account, even when collecting preliminary data on the efficiency of removal of certain compounds.

Vernon L. Snoeyink

Associate Professor of Sanitary Engineering
University of Illinois at Urbana-Champaign
Department of Civil Engineering
Urbana, Ill. 61801

SIR: We are in agreement with Dr. Snoeyink in that the efficient use of carbon in filtering devices is a complex and delicate process requiring careful monitoring. Since the release of recent findings about dissolved organics in tap water (*1, 2*), many consumers have started purchasing bottled water and commercial filtering devices for home use.

Many types of filtering devices are available to consumers of which most have not received as much testing or monitoring of performance as needed. The device we used in our study is manufactured by a well-established company which services a large portion of the scientific community and is available for home use and therefore possibly representative of such devices.

Further, we share with Dr. Snoeyink his concern about the importance of the pretreatment of the charcoal. Thus our statement, "These compounds could have originated from the plastics used somewhere in the preparation or storage of the ion-exchange resins or charcoal." Because of the inherent problems associated with charcoal filtering and the need to evaluate such devices, it seems that some federal or state agency should assume the responsibility of seeing that the claims made to the consumer are indeed met by the devices on the market.

Literature Cited

(1) Draft Analytical Report New Orleans Area Water Supply, prepared and submitted by the Lower Mississippi River Facility, Slidell, La., Surveillance and Analysis Division, Region VI, U.S. Environmental Protection Agency, Dallas, Tex., November 1974.

(2) Dowty, B., Carlisle, D., Laseter, J. L., *Science*, **187**, 75–7 (1975).

John L. Laseter

Chairman and Professor
Department of Biological Sciences
University of New Orleans
New Orleans, La. 70122

INDUSTRY TRENDS

Emcon Associates (San Jose, Calif.), an environmental consulting firm, has opened a new branch office at Oak Brook, Ill., to serve East Coast and Midwest clients.

ERCO Industries Ltd., a Canadian component of Envirotech, announced that Great Lakes Paper Co. (Thunder Bay, Ont.) will use ERCO's salt-recovery process as a step to eliminate bleached kraft pulp mill water pollution.

Fisher-Klosterman has installed a special system to collect glass and enamel dust from resistor manufacturing at the Ohmite Manufacturing Co. Division of North American Philips, Inc. (Nashua, N.H.).

Davis Water & Waste Industries, Inc. (Thomasville, Ga.) has consolidated its Davco Division (Thomasville) and Defiance Division (Tallevast, Fla.)

Research-Cottrell, Inc. has received an order in excess of $15 million from American Electric Power System for design and materials for three electrostatic precipitators.

Peabody Galion Corp.'s subsidiary, **Peabody Engineered Systems,** has a $20 million air pollution control order for flue gas desulfurization from Alabama Electric Cooperative Inc.

Camp Dresser & McKee International Inc. will prepare long-range development programs for water supply, wastewater facilities, and drainage systems for the city of Surabaja, Indonesia.

Dames & Moore (Los Angeles, Calif.) is preparing an environmental report on the continued operation maintenance of the existing Muskingum River (Ohio) Basin flood control system for the U.S. Army Corps of Engineers.

Environmental Measurement Systems (Seattle, Wash.) announced that 24 of its ultrasonic manhole monitor units, for wastewater monitoring in sewer lines, were purchased by the District of Columbia.

The Manufacturing Chemists Association (Washington, D.C.) has let $500,000 worth of contracts to do research into impacts, if any, of fluorocarbons on the earth's atmosphere.

Hercules Inc. (Wilmington, Del.) will market chitins and chitosan, a cationic polymer from crustacean shells, for Marine Commodities International (MCI, Brownsville, Tex.) worldwide. Hercules also has an option to buy all of MCI's stock. Chitins are used as flocculents and thickeners.

International Ecology Systems Corp. (Chicago, Ill.) has purchased the assets and work in progress of Freeman Laboratories, Inc. Freeman makes pollution monitors.

A **Salem Corp.** subsidiary, **Wilputte Corp.** (Murray Hill, N.J.) has a multi-million dollar contract to rehabilitate the No. 4 coke battery at Allied Chemical's Ashland, Ky., coke plant.

Olson Laboratories (Anaheim, Calif.) has received a $140,000, 8-mo contract from EPA to develop exhaust emission data from light-duty vehicles (model years 1972–1975).

Betz Environmental Engineers, Inc. has a 1-yr EPA contract to evaluate the current worldwide technology for controlling emissions from blast furnace cast houses.

The Minges Associates, Inc. (Farmington, Conn.) has done a value analysis/engineering test study of a $7.5 million advanced wastewater treatment plant at Plainville, Conn., for EPA, and has identified cost savings.

Koppers Co., Inc. (Pittsburgh, Pa.) has recently completed the second phase of a combined water and wastewater facility at Palm Beach County, Fla. That phase added 1.5 mgd for waste treatment, and 6 mgd for water.

Andco Inc. has a sublicensing agreement with AB Svenska Maskinverken (Kalhäll, Sweden) giving the Swedish firm rights to market the Andco-Torrax municipal waste conversion process in Denmark, Finland, Iceland, Norway, and Sweden.

SF Air Control, Inc. (Old Greenwich, Conn.) is U.S. marketer for a new type municipal solid waste conveying system developed by AB Svenska Flaktfabriken. The system is being installed in two of Stockholm's suburbs, and uses pneumatic conveyance.

Stanley Consultants, Inc. is providing full engineering services to alleviate pollution and flood control problems for Lake Chicot, Ark. The U.S. Army Corps of Engineers (Vicksburg, Miss.) is directing the project.

Corning Glass Works (Corning, N.Y.) has shifted solar energy research emphasis to finding a cost-effective solar collector, and will not produce collectors unless they contribute data necessary to the research program.

Frost & Sullivan, Inc. (New York, N.Y.) foresees solar heating and cooling as a $1.25 billion industry by 1980; and as a $10 billion industry by 1985.

NEW PRODUCTS

Aerator
Because of its design the unit may be used effectively in shallow water. It finds application in sewage treatment plants, industrial sewage lagoons, and farm waste ponds. Aeroflot Industries **101**

Ion, gas analyzer
Instrument gives direct digital display of concentration in ppm, moles/liter or other units with the use of ion-selective or gas-sensing electrodes. After calibration, the analyzer can be left unattended to perform continuous or automatic monitoring. Lazaar Research Laboratories, Inc. **102**

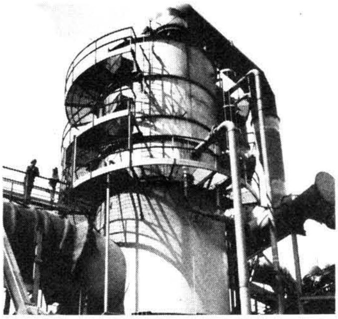
Tape recording system
Cassette tape recording system provides four channels of FM and direct signal record and playback. The system can be used in machine vibration analysis. It operates on batteries or on external power. Dallas Instruments, Inc. **103**

Computerized spectrophotometer
The atomic absorption spectrophotometer can analyze up to 70 elements with accuracy to six significant figures. Set up time is about 2 min. The unit has pre-programming capability. Fisher Scientific Co. **104**

Data logger/alarm scanner option
The software option to the basic system will permit the establishment of up to 4000 individual alarm setpoints in a 1000 point scanning system. Designed for the chemical, petrochemical and synthetic fiber plants. Doric Scientific/ Emerson Electric Co. **105**

Ammonia electrode/ion meter
The meter, standardized to known concentrations of ammonia (as free NH_3), will read concentrations directly in any of several common units. The electrode is designed to be used in effluents or sewage, and can read ammonia concentrations in a range of 0.017–17,000 ppm. Orion Research Inc. **106**

Hopper switch
Designed especially to control material flow in small hoppers, cyclones, packaging machinery and loading equipment common to the plastics and chemical industries. When the hopper is in operation, there is no live seal between the actuating probe and the drive mechanism. Monitoring Manufacturing, Inc. **107**



Scrubber-cooler
The six-stage scrubber removes particulate matter from the SO_2-rich copper converter gases; the gases are then cooled as required in the production of sulfuric acid. Gas throughput rates may range from 70,000–304,000 acfm at 700°F. Swemco Inc. **108**

CO analyzer
The battery or a.c. operated direct reading unit is calibrated directly from a pressurized span gas cylinder; no sample bag is needed. The unit is available in a variety of range combinations. interscan corp. **109**

Fire starter
Smokeless, oxygen-rich fire source for burning agricultural, forest and other wastes without contributing to air pollution. The blocks are lightweight. Cleanweld Products, Inc. **110**

Transducer indicator
When operated with the transducer, the indicator unit displays displacements directly in engineering units (inches, degrees). The unit has an auxiliary analog output to signal other instruments. Trans-Tek, Inc. **111**

Mass flowmeter
The non-linear flowmeter measures low flow rates and is stable within 2% from 0.1 psia to 250 psig. No correction is required over wide ranges of temperature and pressure. The unit has a d.c. output signal for recording. Teledyne, Hastings-Raydist **112**

Pesticide
The concentrated insecticide is compounded of pyrethrins, piperonyl butoxide and other non-toxic ingredients. It is recommended for use in institutions, public buildings and homes. Hadco Corp. **113**

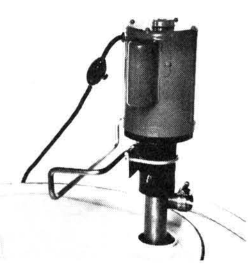
Processing unit
Can be used for dispersion, homogenization, emulsification, deaeration or defoaming of liquids of varying viscosities and under a wide range of temperatures. Cornell Machine Co. **114**

Indoor composting toilet
Using the principle of humification, the process requires circulating air, heating coils and a handful of peat moss to initiate the decomposition process. Comparable in size to the flush toilet, the unit is made of polystyrene plastic. Recreation Ecology Conservation of United States, Inc. **115**

Dust collector transport
A new technique converts the dust collector to a semi-trailer for transport to the job site. The low-boy trailer is eliminated, larger bags can be used, and hopper assembly follows on another trailer; field erection is complete in 2 days. Aeropulse, Inc. **116**

Water consumption monitor
The device will restrict water flow, aerate the water and serve as a syphon breaker to permit incoming water to be introduced below the rinse tank operatihg level. Aqualogic, Inc. **117**

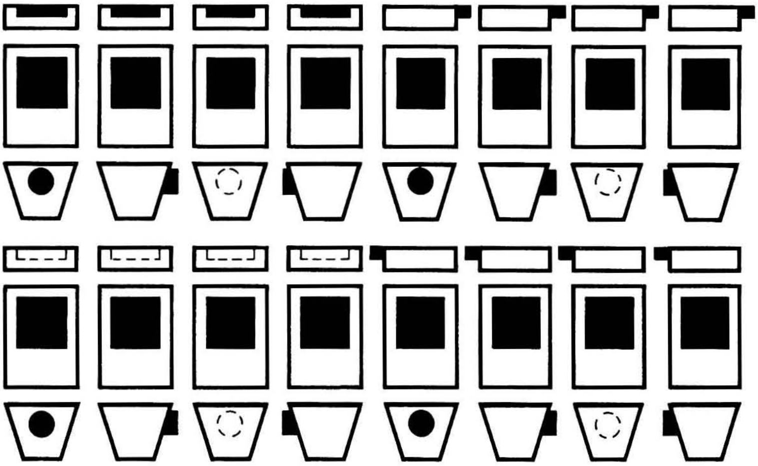
Industrial fiber
The product finds application in the manufacture of filter bags. The polyacrylonitrile fiber is heat, acid and moisture resistant. Dow Badische Co. **118**



Barrel pump
The electrical pump is self-priming, and features double ball bearings, hardened drive pin and quick disconnect between motor and suction tube. It will dispense about 25 gpm from 55, 30 and 15 gal drums and 13 gal acid carboys. Devon Products, Inc. **119**

(continued on page 1184)

How to get 16 baghouse designs from just 3 parts.



PF^2 Baghouse For Air Pollution Control

The idea: a custom baghouse with an off-the-shelf price.

Our PF^2 is your lowest cost way to meet EPA standards with a baghouse. You save about 15-20% over a regular baghouse of the same capacity.

How come?

The answer is in our square design. The unit is fully prefabricated, but comes in three easy to bolt together sections. Because all sides are the same, the top and bottom can be set on any which way. Need an inlet on the south side and an outlet on the north? You've got it. Or any other way — up to 16 combinations.

It's a custom feature at an off-the-shelf price.

The square shape, plus our 4½″ diameter bags, also means you get maximum filter surface per cubic foot. No waste. And more savings.

The same goes for overhead room. "Square" presents a low profile and so fits where other baghouses won't.

The trade-off

You **don't** get top bag access that on our other models makes changing bags easier. And a regular, taller rectangular shape such as our standard PF-60 can deliver more filter area per square foot of floor space... if you have the head room.

But you're not paying for these things, either. So what you **do** get is a top quality WP unit with the maximum filtering efficiency of our Pulseflo™ system at a totally new price.

How fast can we deliver?

Quick. Zip. PF^2 is a stock item. But even if we don't have the specific model you need on hand, it doesn't take that long to put one together.

FEATURES:
- Capacities from 1,000 to 20,000 CFM
- From 30″ square on up
- All welded seams
- Shipped fully assembled
- Available immediately

Write us for details and a quotation.

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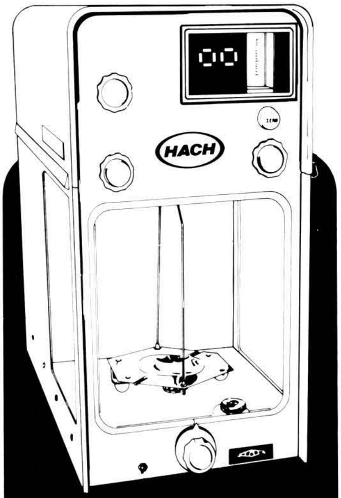
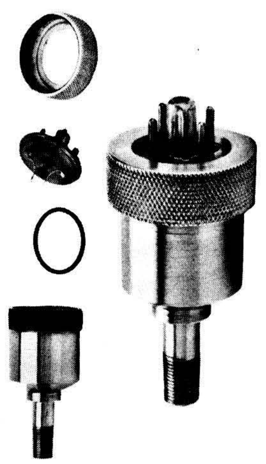
259

Name: ____________________ Title: __________
Company: ____________________
Address: ____________________
City: ____________________
State: ____________________ Zip: __________

CIRCLE 20 ON READER SERVICE CARD



Flare tip
The 54-in. diameter flare tip allows the efficient disposal of up to 2.3 million lb/hr of waste gases. Peripheral baffles protect the flare tip against high winds, while the 54 in. fluidic seal within the tip provides high resistance to air entry into the stock. National Airoil Burner Co. **120**



Vacuum sensor tube
The stainless steel casing and interchangeable octal-type pin header with gasket makes the sensor resistant to corrosive gases. The tube senses pressures from atmosphere through 10^{-3} Torr. CVC Products, Inc. **121**

Pit liner
The prefabricated, thermoplastic membrane lines a pit to form a container for transformer dielectric coolant. Oil released during a tank rupture is contained within the membrane area; water accumulation within the pit is prevented by the use of a sump pump. Environetics, Inc. **122**

Flow metering pump
Electronic pressure-feedback operation provides either constant flow or constant pressure that is virtually pulseless. The pump delivers unlimited solvent quantities at 0–28 ml/min to 3000 psi. Altex Scientific, Inc. **123**

Portable stack gas analyzer
The non-dispersive infrared analyzer can be used to test power plant or industrial stack gases. It is designed to measure a particular gas or a combination of gases. Horiba Instruments, Inc. **124**

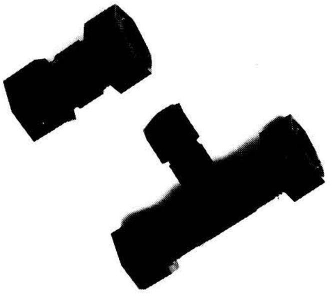
Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

Power supply for arc lamps
The power supply for deuterium and hydrogen arc lamps regulates line voltage and current ripple. The lamps find application in spectrofluorometry/photometry, reflectometry and chromatography. Schoeffel Instrument Corp. **125**

Unbreakable electrodes
Made from high-impact epoxy the combination, pH measuring and reference electrodes are unbreakable. Electrode features include a removable safeguard tip and the option of a refillable or sealed electrode. They are compatible with all pH meters. Tudor Scientific Glass Co. **126**

Phosphate-free detergent
The all-purpose detergent contains no phosphates, NTA, chromates or enzymes. The detergent with a pH of 6.7 does not harm the skin or etch glassware. M.D. Industries, Inc. **127**

Purge assembly
It may be connected directly to the cylinder or panel-mounted in the line between the cylinder and regulator. The assembly combines diffusion resistance with high pressure operation. It permits purging of possible toxic and/or flammable gases from a system prior to opening the system to the atmosphere. Union Carbide Corp. **128**



Flexible piping system
The pipe, available in ¼ in., ½ in. and ¾ in. sizes, is made of polybutylene plastic; fittings are made of an acetal copolymer. The system is non-corrosive and is highly resistant to scale build-up. All materials are nontoxic. Celanese Plastics Co. **129**

Low-velocity sensors
Designed to sense very low flow velocities of gases and liquids. The sensors have process and pollution control applications. Monitoring of process and effluent streams is possible even when the temperature exceeds 1000°F. Flui-Dynamic Devices Limited **130**

Gas chromatograph
The automated, modular model is designed to do head space analysis of samples such as vinyl chloride monomers, other residual monomers and air and water pollution determinations. Sampling module accepts 30 samples. Perkin-Elmer Corp. **131**

NEW LITERATURE

Coatings. Brochure describes Dimetcote 3 coatings that resist marine corrosion on structures, as well as temperatures from −100° F to 600° F. Ameron **151**

Microscopes. Catalog lists microscopes and related products for many aspects of medicine, pollution science, biology, and biochemistry. Graf-Apsco of Illinois Inc. **152**

Amplifiers. Brochure describes application, theory, and selection of single and multichannel amplifiers for power plant monitors, medicine, and electrochemical processes. Specifications are given. Analog Devices **153**

Liquid Level monitors. Literature describing liquid level monitors for sewage treatment, nuclear power plants, and many other applications is now available. WESMAR **154**

OSHA compliance log. Simple booklet acts as log to make record keeping easier in order to comply with regulations governing hazardous vapors. Matheson Safety Products **155**

Industrial safety equipment. Condensed catalog lists a full line of safety equipment for personal protection, environmental surveillance, hazard control, and emergency care. Ask for Bulletin 2600-1. Mine Safety Appliances Co. **156**

Air monitors. Literature describes full product line of ozone, hydrocarbon, and other monitors, and analysis instruments. Analytical Instrument Development, Inc. **157**

Pollution control projects. Booklet, "Excellence in Environmental Engineering," lists the company's accomplishments in pollution control programs. Air, water, solid waste, and oil and chemical recovery work is described. The Firestone Tire & Rubber Co. **158**

Pipeline rehabilitation. Brochure describes contractor's technique for rehabilitating old sewers that have begun to deteriorate. Complete service is provided. National Power Rodding Corp. **159**

Ozone/sonic water treatment. News kit provides technical literature and papers concerning sewage treatment with ozone and ultrasonics. Plant at Indiantown, Fla., is fully described. Telecommunications Industries, Inc. **160**

Analytical instruments. Catalog contains information on columns and supplies needed to operate and maintain the company's analytical instrumentation. Hewlett-Packard **161**

Stack gas analyzers. Data sheet 07-01-02 describes stack gas analyzers for controlling processes, determining air pollution compliance, or monitoring combustion efficiency. Mine Safety Appliances Co. **162**

Water clarification. Product Data Sheets PYM-DS-26, 27, and 28 describe AMERFLOC coagulants that are resistant to chlorine and have EPA approval for potable water usage. Drew Chemical Corp. **163**

Trap strainer. Brochure describes a new sanitary trap strainer for dairy,

(continued on page 1186)

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

food, pharmaceutical, and beverage processing. Time spent changing and cleaning filter media is saved. Newark Wire Cloth Co. **164**

OSHA noise guidelines. Semi-technical article sets forth basic guidelines for firms undertaking noise measurements and analysis in efforts to comply with OSHA regulations. B&K Instruments, Inc. **165**

Water monitoring. Brochure describes the CLAM family of self-cleaning instruments that monitor effluents from mixed liquors to sludges with up to 10% solids. An application guide is provided. Biospherics Inc. **166**

Wastewater reclamation. Bulletin tells how a combination of powdered activated carbon regeneration by wet air oxidation and biophysical wastewater reclamation can be adapted to an existing sludge plant. Zimpro Inc. **167**

SO_x removal. Brochure 75DL01 describes Thiosorbic lime, which is specially adapted to flue gas desulfurization at power plants. Dravo Lime Co. **168**

Automatic valving. Technical Bulletin No. 0105 describes line of analytical gas chromatographs featuring automatic valving and multicolumn systems for specific applications. Carle Instruments, Inc. **169**

Engineering services. Brochure describes engineering services that include water and wastewater, pipelines, transportation, utility and communications, and other fields. Michael Baker, Jr., Inc. **170**

Conversion factors. Booklet, "Conversion Factors," provides factors for hundreds of industrial and scientific measurement units. It comes in very handy in many fields. Engelhard **171**

Fuel saving. Fuel Saver Fact Sheet No. 3 gives four methods to increase boiler efficiency and tells how each method can be enhanced to cut heating costs. Fuel Efficiency, Inc. **172**

Computerized burner control. Bulletin tells how a low-excess-air burner cuts fuel costs by thousands of dollars annually and improves boiler performance. CEA Combustion, Inc. **173**

Explosion-proof controls. Bulletin F975 describes an extensive line of explosion-proof control stations, buttons, and switches developed to meet OSHA and industry standards. Adalet Division, The Scott & Fetzer Co. **174**

Butterfly valves. Bulletin 45.00-1 gives complete information on high-pressure butterfly valves, actuators, and accessories. Corrosion resistance is a feature. DeZURIK **175**

Pumps. Bulletin describes the company's line of Varistaltic pumps, including peristaltic, oscillating, sealless, and other pumps. Manostat Corp. **176**

Low particulate burner. Brochure describes an advanced air pressure recovery (APR) burner of high performance and low particulate emissions. Peabody Engineering **177**

Sludge press. Bulletin 5595 describes the "MRP-36," an advanced design multiroll sludge press now available. Capacity is increased. The Permutit Co. **178**

Plastic pipe. Brochure describes Super-Flex 160 plastic pipe, so called because it withstands 160 psi and is used with pumps submersible to 265 ft. Goodall Rubber Co. **179**

Pressure gauges. Catalog describes line of low-differential air and gas pressure gauges, combustion test instruments, flowmeters, and related equipment. Dwyer Instruments, Inc. **180**

Flow controls. Literature describes new flow transducer that can be operated by compressed air, gas, or steam, and needs no electricity. Sizes from 130 to 9000 scfm. Union Flonetics Corp. **181**

Sludge conditioning. Brochure describes sludge conditioner that will work on raw sewage, even with rags, paper, wood chunks, plastics, and chemical and petrochemical wastes. Franklin Miller, Inc. **182**

Dust collectors. Catalog F-1812 describes high-efficiency multitubular dust collectors—10-in. tube units usable in single or multiple sections for a wide capacity range. American-Standard Industrial Products Division **183**

Engineering consulting. Brochures describe the company's capabilities in engineering and testing for air, water, noise, waste, energy, and OSHA. Rossnagel & Associates, Inc. **184**

Biological freeze-drying. Bulletin 657-A describes the company's modular designed biological freeze dryers. Stokes Division, Pennwalt Corp. **185**

Liquid level switches. Catalog No. 7504 shows a complete line of liquid level control switches for operating relays, alarms, valves, computer inputs, and other equipment. Fluid Products, Inc. **186**

Pipe railing. Bulletin 881-B contains full engineering, design, and installation information for "Connectorail" pipe railing that meets or exceeds OSHA and building code regulations. Julius Blum & Co., Inc. **187**

Clarifier. Bulletin 314-9A2 describes the "rim-flo" clarifier used for settling solids from liquid. Company says that it outperforms center feed clarifiers. Envirex **188**

Trace element analysis. Catalog 750 lists reagents useful to the environmental analyst requiring verified reference accuracy. Many elements and other parameters can be determined. J. T. Baker Chemical Co. **189**

Trichloroethylene regulations. Bulletins review trichloroethylene control regulations in Massachusetts and California. Dow Chemical U.S.A., Inquiry Services, 1703 S. Saginaw Rd., Midland, Mich. 48460 (write direct).

Training programs. Brochures describe training program for water and wastewater systems personnel. Washington State Coordinator, Green River Community College, 12401 S.E. 320th St., Auburn, Wash. 98002 (write direct).

Computer programs. Report describes computer programs for water quality data. Inland Waters Directorate Report Series No. 38. Enquiry Centre, Environment Canada, Ottawa, Ont. K1A OH3, Canada (write direct).

Geological data. *Pennsylvania Geology* describes what is happening geologically in the Commonwealth. Bi-monthly. Topographic and Geologic Survey, Dept. of Environmental Resources, Harrisburg, Pa. 17120 (write direct).

ASTM publications. Single copies of the 1975–1976 list of ASTM publications are now available. ASTM, 1916 Race St., Philadelphia, Pa. 19103, Attn: Mr. A. L. Batik (write direct).

Odor pollution assessment. Article describes techniques used in France. C-1-75-100, "The Fundamentals of Industrial Olfactometry (1)," by Paul Sigli, et al. Embassy of France, Commercial Counselor, Suite 620, 1100 Connecticut Ave., N.W., Washington, D.C. 20036, Attn: M. Bernard Renard (write direct).

Air pollution publications. Brochure, "Publications of APCA," is available. Publications Dept., Air Pollution Control Association, 4400 Fifth Ave., Pittsburgh, Pa. 15203 (write direct).

"Meet the Gypsy Moth." Information Services, Northeastern Forest Experiment Station, 6816 Market St., Upper Darby, Pa. 19082 (write direct).

Outer Continental Shelf management. Title of report is, "Mineral Resource Management of the Outer Continental Shelf." U.S. Geological Survey, National Center, Reston, Va. 22092 (write direct).

"The Sun is Red." Film on environmental pollution available on a loan basis. Danish Information Office, Royal Danish Consulate General, 280 Park Ave., New York, N.Y. 10017 (write direct).

BOOKS

Landscape Assessment: Values, Perceptions, and Resources. Ervin H. Zube, et al., Eds. xii + 367 pages. Halsted Press, 605 Third Ave., New York, N.Y. 10016. 1975. $35, hard cover.

From scenes like the Grand Canyon to the neighborhood auto junkyard, landscape has its impact on people. However, it is the non-spectacular landscape in which most Americans spend their lives. The assessment of this landscape was discussed at a conference held at Amherst, Mass., in 1973, in which improved methods of landscape management were sought.

Lead, Vol. 2. Frederick Coulston and Friedhelm Korte, Eds. 299 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1975. $24.50, hard cover.

What is the fate of lead, one of the more toxic elements known? This book examines origins of lead in the environment, its uptake by animals, children, and adult humans, and its effects. It also looks at lead levels in air and populations, and describes what happens when lead gets into blood. The controversy of leaded gasoline is also discussed.

The Food in Your Future Steps to Abundance. Keith C. Barrons. vii + 180 pages. Van Nostrand Reinhold Co., 450 W. 33rd St., New York, N.Y. 10001. 1975. $7.95, hard cover.

"Could the world really get along without pesticides?" This book asks that question, and goes on to describe how ecologically sound land management and judicious use of chemicals increase, rather than deplete fertility of the limited amount of food-producing land. The author is an agricultural technologist with Dow Chemical U.S.A. (Midland, Mich.).

Ecological Modeling in a Resource Management Framework. Clifford S. Russell, Ed. xi + 394 pages. The Johns Hopkins University Press, Baltimore, Md. 21218. 1975. $6, paper.

Here, ecological modeling mainly involves the aquatic environment. This volume is based on a symposium on the subject of aquatic resource management, held at the Brookings Institution (Washington, D.C.) in September 1974. Both the symposium and the book grew out of plans for the Marine Ecosystem Analysis (MESA) project of NOAA, which is presently active in the New York Bight.

OSHA and Accident Control Through Training. C. Richard Anderson. 250 pages. American Society for Metals, 9333 Kinsman Road, Metals Park, Ohio 44073. 1975. $17.50, hard cover.

This book offers a sound training program in industrial accident and health control. Such a program is important for insuring compliance with OSHA regulations. How-to-do-it information and data on setting up and applying programs that lead to sound safety practice are provided.

Papers Presented Before The Second Symposium on Coal Utilization. iv + 351 pages. National Coal Association, 1130 17th St., N.W., Washington, D.C. 20036. 1975. $7, paper.

The papers were given at the symposium held at Louisville, Ky., in October. They cover air pollution and control problems and approaches, fuel-grade methanol, desulfurization systems, fate of trace elements, and other factors affecting the environment. Economic considerations are also fully discussed.

Water Resources of the World. Frits van der Leeden. 560 pages. Water Information Center, Inc., 44 Sintsink Drive East, Port Washington, N.Y. 11050. 1975. $32.50, hard cover.

This reference work covers water resources in 138 countries and territories. Data on streamflow, runoff, ground water, water use, industrial requirements, and similar information, are given. Also covered are financing of water projects, water supply in developing countries, and data concerning the world's major rivers and water bodies, including lakes and reservoirs. Tables, maps, and charts are provided.

Pollution Control in the Asbestos, Cement, Glass and Allied Mineral Industries. Marshall Sittig. ix + 333 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, N.J. 07656. 1975. $36, hard cover.

The industries mentioned in this book's title have to contend not only with air and water pollution problems, but with health hazards, as well. Solid waste disposal is also a factor. What countermeasures are being taken to date? This book offers a complete discussion of the state-of-the-art in control of pollution from these industries.

Water Quality Parameters—STP 573. 590 pages. American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103. 1975. $29.50 (less 20% to ASTM members), hard cover.

This book presents nearly 50 papers on inorganic analysis, organic analysis, continuous monitoring, and remote sensing. Biological analysis, and quality control of water are also covered. The volume is important to those concerned with water pollution. Publication Code No. 04-573000-16.

Environmental Education: A Guide to Information Sources. William B. Stapp, Ed. 225 pages. Gale Research Co., Book Tower, Detroit, Mich. 48226. 1975. $18.

This reference work brings together a diverse set of information sources that focus on methods of communicating environmental awareness. It is an annotated bibliography for educators in formal and informal settings. Included are U.S. Government services, sources of funding, and many other important items of basic information. The editor is chief of the Environmental Education Unit of UNESCO.

Cases and Materials on Environmental Law (Second Edition, 1973). 1975 Supplement. Oscar S. Gray. 408 pages. BNA Books, the Bureau of National Affairs, Inc., 1231 25th St., N.W., Washington, D.C. 20037. 1975. $7.50, paper.

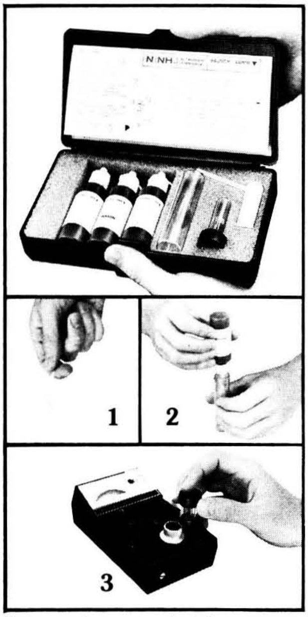
This cumulative supplement covers decisions among which are Supreme Court cases on NEPA, circuit court decisions concerning Clean Air Act implementation, oil spill cases, class actions, cases construing the NEPA, and many other decisions. Texts of the Energy Supply and Coordination Act of 1974 and other laws and guidelines are included.

Solar Energy in Building Design. Bruce Anderson. 1300 pages. Total Environmental Action, Church Hill, Harrisville, N.H. 03450. 1975. $28, unbound manuscript.

This work contains nearly all information on solar energy in buildings, with over 500 photos, charts, graphs, and illustrations. Bibliographies, lists of component manufacturers, and material on heat theory, wind, and methane, solar cooling, and weather are provided. Past and present solar projects, buildings as solar collectors, low-impact solutions, hot water heating, and related matters are exhaustively discussed.

Mining in the Outer Continental Shelf and in the Deep Ocean. 119 pages. Printing and Publishing Office, National Academy of Sciences, 2101 Constitution Ave., N.W., Washington, D.C. 20418. 1975. $6.25, paper.

Continental shelf and deep ocean mining offers the U.S. "enormous potential" to develop alternate mineral



sources and protect itself against embargoes, price increases, and the like. This report evaluates the state of technology of marine mining, and also examines environmental implications, as well as regulatory requirements and education and manpower needs.

Physiological Limnology—An Approach to the Physiology of Lake Ecosystems. H. L. Golterman. xiv + 490 pages. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N.Y. 10017. 1975. $51.95.

This volume describes relations between the abiotic environment and the smaller organisms in open water of lakes. It discusses many aspects of algal growth, trace elements, and organic chemistry. Eutrophication, bacterial physiology, and difficulties in food chain research, as well as sewage effects are also covered.

Land Use in Advancing Agriculture. A.P.A. Vink. x + 394 pages. Springer-Verlag New York, Inc., 175 Fifth Ave., New York, N.Y. 10010. 1975. $25.80, hard cover.

As agriculture advances, rational land use must be increasingly taken into account. This book gives a complete explanation of land use, as well as landscape ecology and land conditions. Land degradation, land use limitations, and conservation of nature and wildlife are also discussed. Research sources included farmers and agricultural experts from many countries.

Principles of Waste Management. N. Y. Kirov. 150 pages. The Secretary, Dept. of Fuel Technology, School of Chemical Engineering, University of New South Wales, Box 1, P.O., Kensington, Sydney, Australia. 1975. $12.50.

This book answers a need for a realistic assessment of the present state of waste management technology. Its first part covers unit operations, and its second part discusses disposal and reutilization processes. Liquid and gaseous wastes, as well as solid wastes, are covered.

The U.S. Energy Problem. 3 vols., 1500 pages. The National Technical Information Service, U.S. Department of Commerce, Springfield, Va. 22161. 1975. $35, entire set.

These volumes explain in detail why there is and will continue to be an energy and power crisis, how alternatives must be analyzed, and what the technological variables are. It also explains how $100 billion can be saved if the breeder reactor is developed by 1985, rather than 1990. Other energy alternatives and R&D needs are discussed. The report was prepared for the National Science Foundation by InterTechnology Corp.

MEETING GUIDE

January 12–13 Newark, Del.
Eighth Mid-Atlantic Industrial Waste Conference. University of Delaware

Write: Mid-Atlantic Industrial Waste Conference, Dept. of Civil Engineering, University of Delaware, Newark, Del. 19711

January 12–13 Philadelphia, Pa.
Safe Transportation of Hazardous Materials. Manufacturing Chemists Association (MCA)

Write: William H. Butterbaugh, MCA, 1825 Connecticut Ave., N.W., Washington, D.C. 20009

January 13–14 Orlando, Fla.
Meeting of the Committee on Spill Control Systems. American Society for Testing and Materials (ASTM)

Write: Sam Bowman, ASTM, 1916 Race St., Philadelphia, Pa. 19103

January 16 Washington, D.C.
Meeting of the Committee for the Study of Environmental Manpower

Write: Dr. Stanton J. Ware, study director, Committee for the Study of Environmental Manpower, National Research Council, 2101 Constitution Ave., N.W., Washington, D.C. 20418

January 19–21 Houston, Tex.
1976 Annual Meeting. Cooling Tower Institute (CTI)

Write: Dorothy Garrison, Executive Secretary, CTI, 3003 Yale St., Houston, Tex. 77018

January 19–23 Washington, D.C.
55th Annual Meeting. National Academy of Sciences–National Research Council

Write: Transportation Research Board, National Academy of Sciences–National Research Council, 2101 Constitution Ave., N.W., Washington, D.C. 20418

January 20–23 Atlanta, Ga.
Resolving Corrosion Problems in Air Pollution Control Equipment. Air Pollution Control Association, the Industrial Gas Cleaning Institute and the National Association of Corrosion Engineers

Write: Dale Miller, National Association of Corrosion Engineers, P.O. Box 1499, Houston Tex. 77001

January 24–28 Los Angeles, Calif.
Solar Heating and Cooling Workshop and Exhibit. Solar Energy Industries Association (SEIA)

Write: SEIA, 1001 Connecticut Ave., N.W., Suite 632, Washington, D.C. 20036

January 28–30 Austin, Tex.
Twelfth Air Pollution and Industrial Hygiene Conference. Universtiy of Texas at Austin

Theme is "Air Quality Management in the Electric Power Industry." *Write:* Engineering Institutes of the College of Engineering, Cockrell Hall 2.102, The University of Texas at Austin, Austin, Tex. 78712

January 29–30 Madison, Wis.
8th Annual Noise Control in Internal Combustion Engines. The University of Wisconsin—Extension

Write: John M. Leaman, Dept. of Engineering, University of Wisconsin—Extension, 929 North Sixth St., Milwaukee, Wis. 53203

January 29–February 1 Boca Raton, Fla.
1976 Annual Industry Convention. The Soap and Detergent Association

Write: The Soap and Detergent Association, 475 Park Ave. South, New York, N.Y. 10016

Courses

January 5–6 Newark, N.J.
Air Pollution Control and Design Update. New Jersey Institute of Technology

Fee: $120. *Write:* Director, Continuing Education, New Jersey Institute of Technology, 323 High St., Newark, N.J. 07102

January 5–9 Pacific Grove, Calif.
Applications of Stormwater Management Models. U.S. Environmental Protection Agency in cooperation with the University of Massachusetts–Amherst

Fee: $125. *Write:* Dr. Francis A. DiGiano, Dept. of Civil Engineering, Universtiy of Massachusetts, Amherst, Mass. 01002

January 5–9 Golden, Colo.
Shale Oil—Its Production, Properties, and Utilization. Colorado School of Mines

Fee: $350. *Write:* Dr. P. F. Dickson, Colorado School of Mines, Golden, Colo. 80401

January 7–8 Newark, N.J.
Wastewater Treatment. New Jersey Institute of Technology

Fee: $120. *Write:* Director, Continuing Education, New Jersey Institute of Technology, 323 High St., Newark, N.J. 07102

January 7–9 Washington, D.C.
Energy/Resource Conservation Through Recycling. George Washington University

Fee: $305. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

January 7–9 Marietta, Ga.
Gas Chromatography. Varian Instruments

Fee: $160. *Write:* Varian Instruments, Training Dept.—D-430, 611 Hansen Way, Palo Alto, Calif. 94303

January 19–23 Philadelphia, Pa.
Recognition of Occupational Health Hazards. American Industrial Hygiene Association and the National Institute of Occupational Safety and Health

Limited to 50. Fee: $250. *Write:* American Industrial Hygiene Association, 66 S. Miller Rd., Akron, Ohio 44313

January 19–23 Madison, Wis.
Solar Energy Thermal Processes. University of Wisconsin—Extension

Fee: $350. *Write:* Robert C. Lutton, P.E., University of Wisconsin—Extension, Engineering Dept., 432 N. Lake St., Madison, Wis. 53706

January 19–30 Research Triangle Park, N.C.
Gas Chromatographic Analysis of Air Pollutants, Course No. 429. Air Pollution Training Institute

Fee: $500. *Write:* Registrar, Air Pollution Training Institute MD 17, National Environmental Research Center, Research Triangle Park, N.C. 27711

January 24–28 Los Angeles, Calif.
Solar Heating and Cooling Workshops and Product Exhibit. The Solar Energy Industries Association, Federal Energy Administration, and the Energy Research and Development Administration

Fee: $75. *Write:* Solar Energy Industries Association, Western Regional Workshops, 1001 Connecticut Ave., N.W., Suite 632, Washington, D.C. 20036

January 26–30 Cincinnati, Ohio
Orientation to Wastewater Treatment Operation, Course No. 173. U.S. Environmental Protection Agency

Fee: $110. *Write:* Registrar, National Training Center, MPOD, OWPO, WHM, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268

Call for Papers

December 15 deadline
1976 Intersociety Conference on Transportation. American Society of Mechanical Engineers (ASME)

Conference will be held on July 18–24, 1976 in Los Angeles, Calif. *Write:* J. F. Courtney, Vought Systems Division, LTV Aerospace Division, P.O. Box 5907, Dallas, Tex. 75222

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Volume 9, Number 13
December 1975

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NAMES INDEX. This index contains the names of *ES&T* research and feature authors and of people mentioned in staff-written parts of *ES&T*. Authors are designated by boldface page numbers.

SUBJECT INDEX. Under the basic subject categories are listed the titles of papers and articles, arranged alphabetically.
All parts of *ES&T* have been indexed, with the exception of letters, currents, industry trends, new products, new literature, books and meeting guide.

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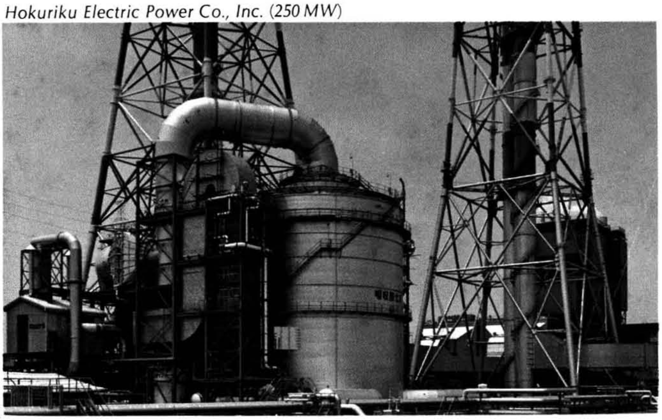

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Fuji Kosan	98,000	Oil-Fired Boiler and Claus Sulfur Plant	Kainan
Mitsubishi Rayon	56,000 (30)	Oil-Fired Boiler	Otake
Tohoku Oil	8,800	Claus Sulfur Plant	Sendai
Hokuriku Electric Power	467,000 (250)	Oil-Fired Boiler	Toyama
Mitsubishi Petrochemical	435,000 (230)	Oil-Fired Boiler	Yokkaichi
Daicel	65,200 (33)	Oil-Fired Boiler	Aboshi
Amagasaki Cokes	15,500	Industrial Incinerator	Hyogo
Mitsubishi Chemical Industries	250,000 (135)	Oil-Fired Boiler	Yokkaichi
Mitsubishi Petrochemical	94,000 (49)	Oil-Fired Boiler	Yokkaichi
Hokuriku Electric Power	652,000 (350)	Oil-Fired Boiler	Fukui
Gulf Power	53,000 (23)	Coal-Fired Boiler	Florida
Denki Kagaku Kogyo	76,000 (40)	Oil-Fired Boiler	Chiba

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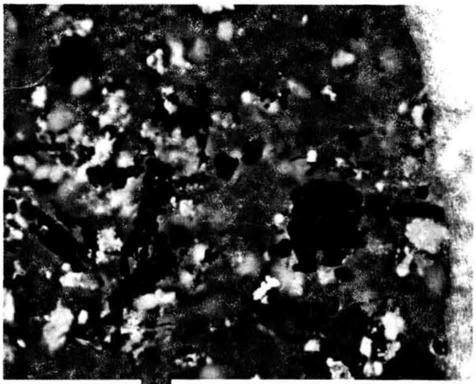

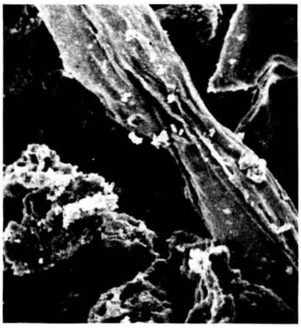

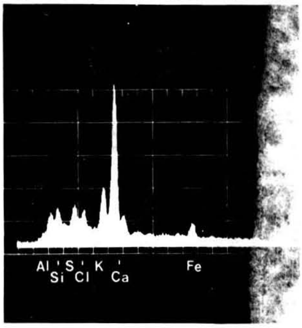
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