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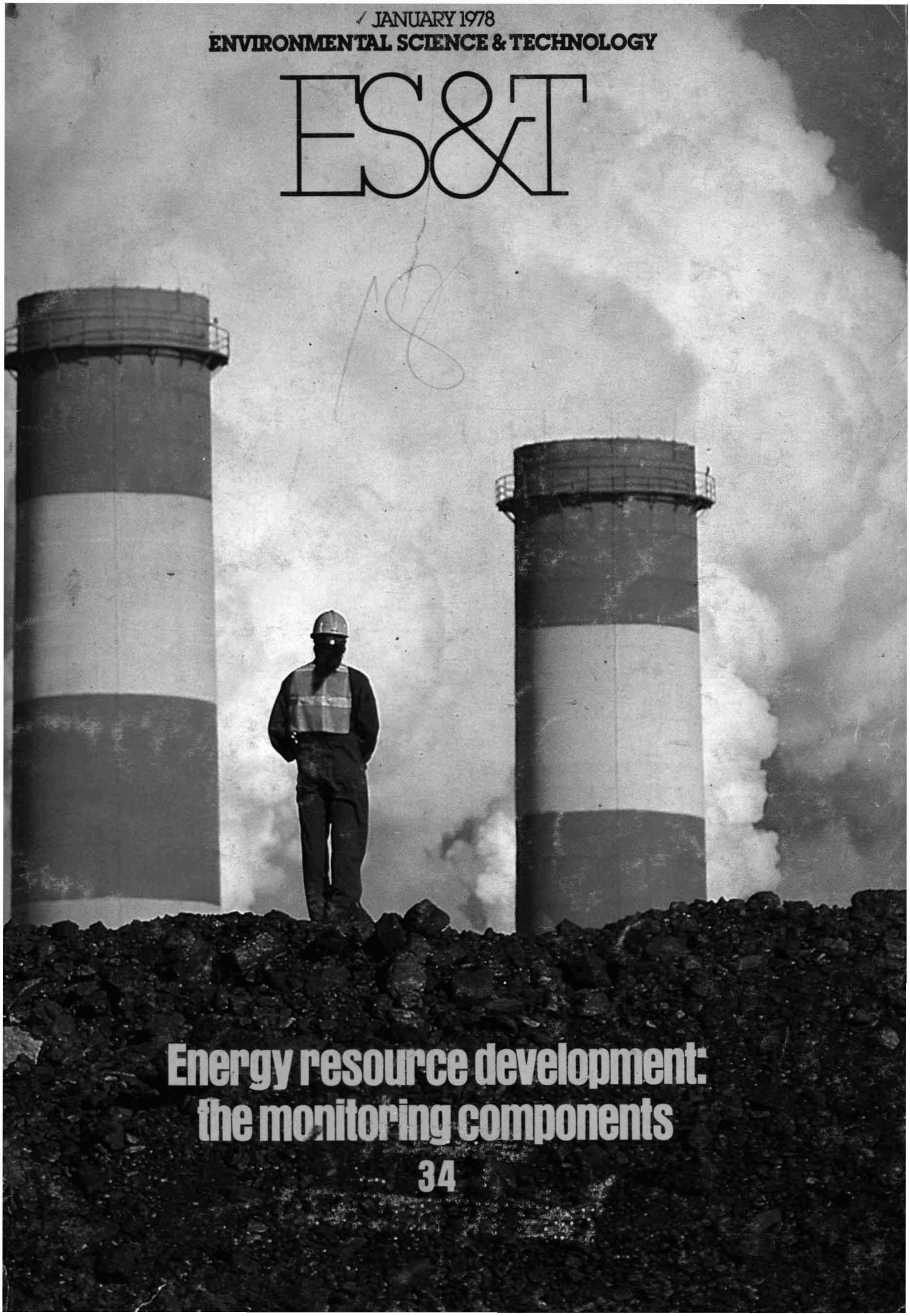

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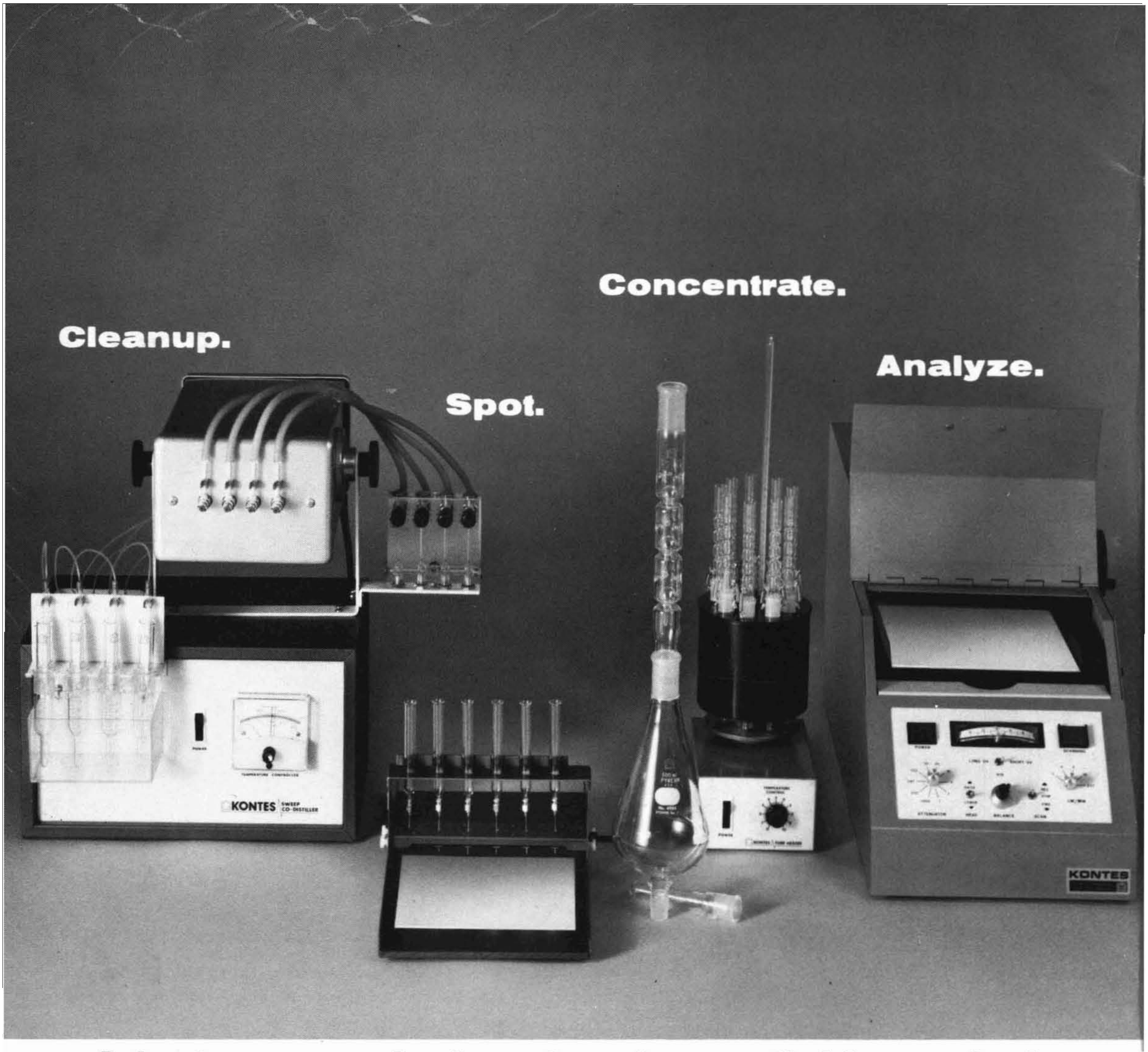

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†Pesticide Analytical Manual, Volume I, U.S. Dept. HEW, Rev. January 1968 232.2-29 • Analytical Methods for Pesticides and Plant Growth Regulators, Volume VI; Zweig, G., and Sherma, J.; Academic Press, N.Y. 1972-193

††Patent #3,562,539

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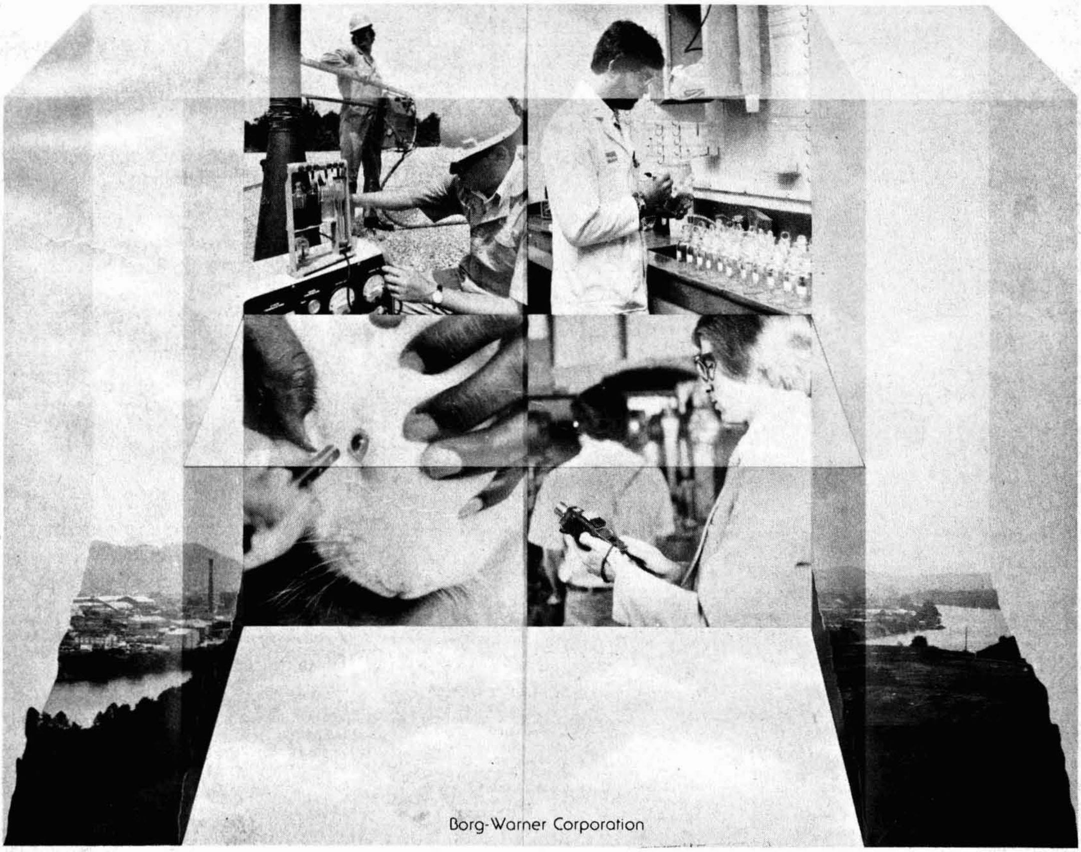

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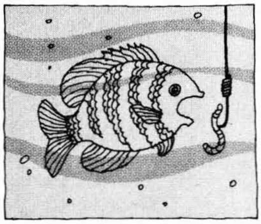

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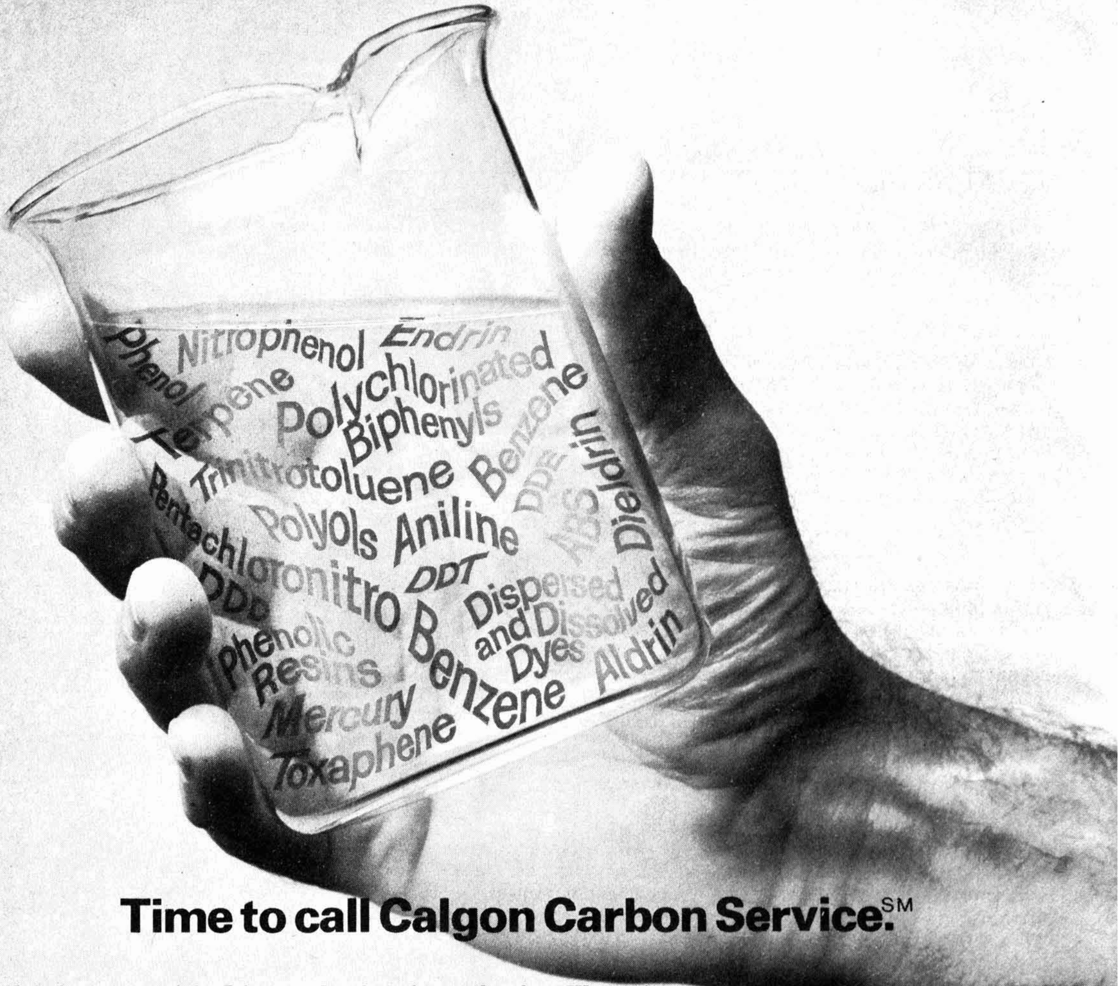
Concerned about toxic organics in plant wastewater?



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GUEST EDITORIAL

Research in water reuse

The reclamation of wastewaters for reuse has moved to center stage—stimulated by the increasing demand for water and by the excellent quality of effluents that are too valuable to discard.

Yet the direct reuse of wastewaters for water supply is hardly new. Effluents have been used for industrial purposes at a Bethlehem Steel plant in Baltimore and for lawn watering and toilet flushing at Grand Canyon Village for 40 years, and hundreds of other reuse projects are serving a wide variety of *nonpotable* uses throughout the country. What is new is the push for direct reuse for *potable* purposes. This has culminated in a bill in Congress, HR5101, which would *require* EPA to use almost 10% of its $263 million 1978 research budget for the development and demonstration of the feasibility of *direct* reuse of wastewaters for drinking.

Such an effort is misguided.

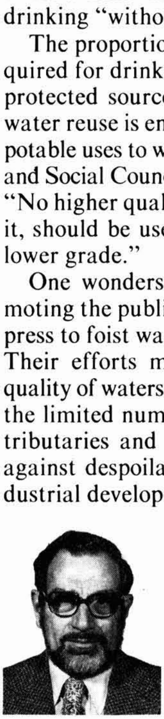
Research into the *indirect* reuse of wastewaters for drinking deserves a far higher priority, as it would be of immediate benefit to the many millions of people who are now obliged to ingest waters drawn from polluted rivers, where water-treatment facilities are not now designed to remove the myriad synthetic organic chemicals that are the contaminants at issue. Such research would reveal their presence and concentration, would develop monitoring and analytical protocols, would establish the efficacy of treatment processes to remove these contaminants, and would attempt to identify the health significance of exposure to these chemicals as we seek to reduce this exposure.

Research on direct reuse for drinking would do none of these. A specific urban wastewater that is used to demonstrate the feasibility of its conversion to drinking water is likely to contain only a few of the hundreds of chemicals that are troublesome, and a demonstration that they can be removed would not be applicable to other urban situations. Furthermore, the standards against which to measure the performance of the demonstration plant are not yet established, nor are they likely to be available soon. Also, the fact that a wastewater can be made to meet the "Drinking Water Standards" is misleading, as the standards were established on the assumption that the most desirable sources would be used, not wastewater treatment plant effluent.

The latency period for the diseases that are attributable to chemical contaminants is on the order of decades. A demonstration plant that would expose a population needlessly is unconscionable. Meanwhile it is unacceptable to conclude, as did the Corps of Engineers in recommending that New York City obtain additional water supply from the Hudson, that communities have already used the Hudson for drinking "without ill-effects".

The proportion of our total water needs that is required for drinking is small. If sufficient water from protected sources is not available for all purposes, water reuse is entirely appropriate for the many nonpotable uses to which water is put. The UN Economic and Social Council stated this philosophy well in 1958: "No higher quality water, unless there is a surplus of it, should be used for a purpose that can tolerate a lower grade."

One wonders why agencies responsible for promoting the public health, such as EPA and AWWA, press to foist wastewaters on the public for drinking. Their efforts might better address improving the quality of waters now being consumed, and identifying the limited number of unpolluted sources in upland tributaries and underground, and protecting them against despoilation by uncontrolled urban and industrial development.



Daniel A. Okun

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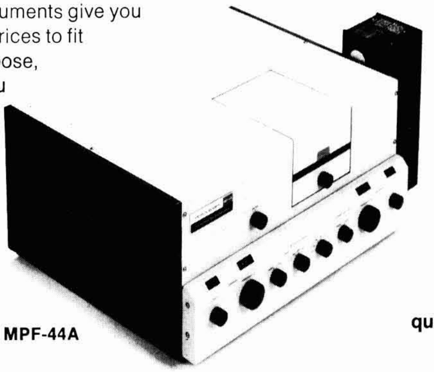
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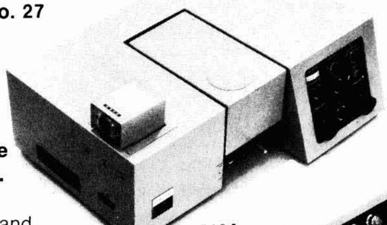
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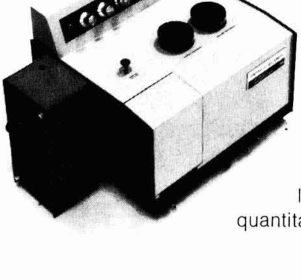
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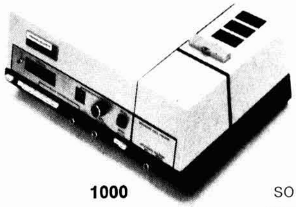
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ES&T CURRENTS

INTERNATIONAL

"The hotter the sun, the cooler the house," Gershon Grossman of the Technion (Haifa, Israel) proves with a new, spherical solar energy device. The spherical device, unlike many flat plates, essentially tracks the sun, and heats a fluid to 200 °C. Grossman and his coworker, the University of Colorado's Frank Kreith, say that the collector can provide enough energy for space heating and Rankine cycle air conditioning, and even to operate some home appliances. It is made of steel, sprayed with polyurethane, and machined into its shape. Hot water is stored in a pressure tank. The device works best in a sunny climate, and can be installed for $1200, on a mass-produced basis, in a 3-bedroom home.

WASHINGTON

Toxic or carcinogenic chemicals have been found in 14 major river basins. The EPA findings, reported in "Monitoring to Detect Previously Unrecognized Pollutants in Surface Waters," are the results of 204 water sample analyses. The samples were taken from industrialized river basins including the Illinois, Delaware, Mississippi, Tennessee and Willamette; and from the Great Lakes and San Francisco Bay. Among the organic chemicals found, in concentrations generally less than 1 ppb, were benzene, acetone, toluene and dichloromethane.

New amendments (P.L. 95-190) to the Safe Drinking Water Act were passed last month. Two significant regulations are being considered by the EPA. One would set the upper limit on trihalomethanes at 100 ppb for communities with populations over 75 000. Communities with populations between 25 000–75 000 would be required to monitor their potable water sources for trihalomethanes. The second regulation would, for the first time, require that communities with populations over 75 000 modify their plants to include removal treatments such as carbon beds. If, however, a city could show that its potable water supply contained no organics, it could apply for a variance.

The EPA has issued new regulations implementing sections of the 1977 Clean Air Act Amendments. Each state must classify clean air areas as Class I (air quality remains unchanged), Class II (moderate industrial growth is allowed) or Class III (intensive industrial growth is allowed). One final rule designates certain areas—basically national parks and wilderness areas—as Class I areas that cannot be redesignated into the other two classes. Of the proposed rules, one would require a preconstruction permit for any of 28 major pollution source categories; another rule would require that a new source use the best available pollution control technology to obtain a construction permit. The fifth report in EPA's series on air quality in the U.S. is now available. The shortened title is "Air Quality Data—1975 Annual Statistics . . ." EPA/450/2-77-002.

OTA director Peterson

Russell W. Peterson becomes the second director of the Congressional Office of Technology Assessment this month. Peterson will relinquish his responsibilities as president of New Directions, a citizen's lobby concerned with global issues. Prior to assuming the presidency of the 2-year-old lobbying group, Peterson was chairman of the President's Council on Environmental Quality, and Governor of Delaware.

During fiscal 1978, TVA will invest more than $600 million in construction of water and air pollution control projects at 12 of the Tennessee Valley Authority's coal-burning power plants. Construction plans call for the upgrading of existing control systems for water discharges at coal-burning plants and cooling towers to reduce heated water discharges at new nuclear power plants. Air pollution control measures call for the use of high-efficiency electrostatic precipitators for fly ash control and other equipment to meet sulfur dioxide emission standards. TVA plans to implement a demonstration project for fluidized-bed combustion of coal.

A new molecule, dioxirane, may play a role in smog formation says NBS scientists, discoverers of this three-membered ring compound ($H_2\overset{\frown}{COO}$). This simplest member of a new class of organic compounds was detected by NBS physicists using low-temperature microwave spectroscopy, and confirmed by NBS chemists using low-temperature mass spectrometry. Dioxirane is formed as an intermediate in the reaction between ozone and ethylene, a key reaction in the chemistry of photochemical smog formation.

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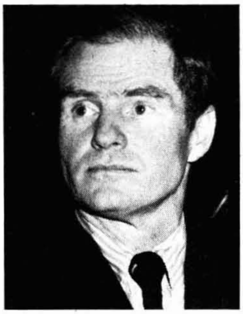
The NSF has awarded $527 100 to a utility to study the use of thermal wastes from power plants as an energy source in raising aquatic foodstuff. The grant from the National Science Foundation to Public Service Electric and Gas Co. is one of the largest grants awarded under the foundation's Research Applied to National Needs.

STATES

Colorado has new drinking water regulations that are modeled after federal regulations. Most of the state's new regulations apply to only 800 community water systems. Among the new provisions is one requiring that drinking water not only be disinfected with chlorine but also filtered to remove Giardia lamblia cysts. The new regulations set limits for mercury and nitrate and surface water quality limits for several pesticides. All community water systems must begin to sample their water, at least twice a month, for microbiological contamination; communities that get their supply from surface sources must test for turbidity daily. Annual analyses for inorganic chemicals and triennal analyses for organic chemicals must be performed by communities using surface-water sources.

Washington's 1977 Voluntary Vehicle Emission Checks found that 46% of the automobiles tested failed to meet the standards set for carbon monoxide and hydrocarbon emissions. Some 907 cars were tested in Seattle and Spokane. In both cities, four-cylinder cars made a better showing than six- and eight-cylinder vehicles; and new cars were found to fail at about the same rate as older models because these new cars must meet stricter emissions standards. These voluntary checks are part of the state's Dept. of Ecology's program to educate the driving public to obtain improved vehicle performance and reduce air pollution.

Virginia and the City of Hopewell received $5.25 million from Allied Chemical Corp. in payment for damages resulting from the Kepone disaster. The state's share, $4.6 million, will be used to assess the feasibility of burning Kepone wastes, and for designing the necessary incinerator. Hopewell's share, $650 000, will help defray the costs of repairs to the city's sewage collector and treatment system. Virginia's toxic substance inventory reporting program went into effect this month; the program was the state's response to the Kepone disaster. Virginia's program requires reporting from a broader range of companies than does the federal reporting rules being drawn up under the Toxic Substances Control Act. Inventory reports, with provisions for confidentiality, will be stored in a computer to permit 16 different state agencies access to the information.



N.J. governor Bryne

Newark, N.J., is the site of the state's first resource recovery facility. The site was dedicated in November by Gov. Brendan T. Byrne and Newark Mayor Kenneth A. Gibson. The facility, valued at $40–80 million, will initially process 1000 tpd of solid waste. The facility will be owned and operated by CEA/OXY Resource Recovery Associates, a joint venture of Combustion Equipment Associates (N.Y.) and Occidental Petroleum Corp. (Calif.). Under the terms of a 20-y contract with Newark, CEA/OXY will recover ferrous metals; non-ferrous metals and glass as markets for these materials develop; and a low-sulfur refuse-derived fuel called ECO-FUEL® II developed by CEA and Arthur D. Little. Under a separate 20-y contract, Public Service Electric and Gas Co. will purchase the fossil-fuel substitute produced at the Newark facility.

What is New York's hydroelectric potential? To find out, the state's Energy Research and Development Authority is conducting a 1-y, $168 000 study to evaluate the potential for small hydropower plants at old and new sites, where production potential is between 50–15 000 kW. Up to 20 sites with the potential for rapid development will be selected; these sites will be selected after all economic, institutional and environmental factors are considered.

Kentucky's most acute environmental problem according to Robert Bell, secretary of the state's Dept. of Natural Resources and Environmental Protection, is the lack of "sufficient technically qualified, highly motivated staff professionals" to enforce federal and state environmental laws. Bell said that his department would seek the necessary financial support to hire these professionals.

MONITORING

An early warning and organic materials detection network is being set up on the Ohio River under a $100 000 EPA grant to the Ohio River Valley Sanitation Commission (ORSANCO). The Early Organics Detection system, as the network is called, is an adjunct to ORSANCO's ongoing monitoring programs. The initial system will consist of weekday monitoring for several organic substances at seven sites on the Ohio River and its tributaries. The Commission and the EPA are seeking additional funds to increase the monitoring sites to 11—the minimum number considered necessary for early detection—and to extend monitoring to a daily basis. The system is to begin operating late this month under the direction of Bill G. Razor.

Groundwater supply/pollution can easily be traced with bromide ion (Br^-). According to William Jester of The Pennsylvania State Univ., Br^- does not, itself, pollute. It stays with the water to which it is added, and is not removed by soil. It can easily and cheaply be detected by neutron irradiation.

Particulate emissions' molecular identify at oil-fired power plant stacks can be ascertained through Raman spectra after collection on sapphire substrates, according to the National Bureau of Standards. Fly ash composition can be determined, as can the presence of toxic substances, such as vanadium pentoxide.

Measurement accuracy of a chlorine gas analyzer is maintained by heat exchanger. Measurements made by the Du Pont 400 photo-

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metric analyzer help to control chlorination reactions in several ways—measurement of the partial pressure of chlorine in off-gas from the reactor; measurement of concentrations of dissolved chlorine in the reaction mass or of one of the reaction products. "If sample cell temperature fluctuates more than 10 °C, as much as 10% error can be introduced in differential gas concentration measurements and the entire reaction process suffers," says Du Pont Instruments' Glenn Apple. "The spiral tube steam heat exchanger easily maintains the sample cell chamber to within ±2 °C to help keep the analyzer's readings on target."

TECHNOLOGY

A 90% overall reduction in dust emissions from grain elevators is achieved with rotary-screw air compressors made by Ingersoll-Rand (Woodcliff Lake, N.J.). These compressors are part of a dust control system at the Saskatchewan Wheat Pool (Thunder Bay, Ont., Canada). Essential to the cleanup operation is a reliable supply of compressed air, "cloth" filters, and properly-shaped fan blades. Dust cakes on the outside of the filters, blown off for collection in hoppers, and conveyed away. The collected dust is made into animal food pellets.

Cooking with hydrogen gas

A home can be run on hydrogen (H_2) instead of natural gas. To prove this, Billings Energy Corp. (Provo, Utah), The Tappan Co. (Mansfield, Ohio), and other firms cooperated in building a 6000-ft^2, 25-room, $200 000 home that was dedicated in November. All normally gas-fired appliances are run on hydrogen stored in an iron-titanium hydride alloy, and extracted through solar heat. The storage is rechargeable. With the house is an H_2/gasoline dual-fuel Cadillac, an H_2-fueled mini-bus, and H_2-fueled tractor. The bus can carry 21 people. Initially, the hydrogen will be made by breakdown of water by electricity.

Air pollution-free sludge incineration is accomplished at a wastewater plant in Louisville, Ky. Sludge-burning ash at 600–800 °F must be cooled below 400 °F to meet baghouse tolerances. This is done with clinker grinders and holding hoppers that are water-cooled. The water does not touch the ash; hence, no water pollution occurs.

Solar energy may be useful for certain industrial process heat supplies. But current costs are presently too high for widespread use, Elton Hall of Battelle Columbus Laboratories (Ohio), noted. Solar energy can cut some industrial fuel bills, but system costs must be reduced, or incentives for its use must be established. Capital costs must be reduced, in order to provide a short payback period. Also, for example, fuel costs are tax-deductible, whereas solar energy systems are deductible only under specified depreciation schedules. Thus, fossil fuel remains more economical for industry at this time, in general.

INDUSTRY

Recycling 100 lb of aluminum can save 200–300 gal of gasoline; the aluminum is from the average new U.S. car; the "gas" saved is over the car's lifetime. This is the view of the Aluminum Association (Washington, D.C.), which also says that if, by 1985, aluminum content rises to 325 lb/car, each new car driver would save almost 1000 gal of "gas." The recycling of aluminum, itself, saves much energy over smelting of aluminum from ore, as the report, "Energy and the Aluminum Industry," points out.

The paper industry's capital outlays were $564 million for environmental improvement in 1976. This represented 29% of all such expenditures, Isaiah Gellman, executive vice president of the National Council of the Paper Industry for Air and Stream Improvement (NCASI, New York City), said. For the same purposes, fixed administrative/research costs are estimated at $828 million for that year, and tax-exempt bonds financed 44% of the environmental protection capital construction programs, Gellman noted. That was a decline from the 54% level reported for 1975. A survey of primary paper plants generated these figures for NCASI.

Ecodyne's Nowlin

Recently-passed federal drinking water standards could raise the average family's water bill to $1185/y, especially in a small town, Duane Nowlin, of Ecodyne Corp.'s Lindsay Division (St. Paul, Minn.), warned. Nowlin believes the crux of the problem to be the requirement that all municipal water must meet this standard. He questioned the need for water, say for toilets, or fire fighting, to meet tight drinking water standards, and suggested that it would be far cheaper to have home purification units to treat that water which is to be used for drinking, cooking or bath water. Nowlin feels that much of the cost for upgrading water could then be sharply cut.

The U.S. chemical wastes management industry is running at only half capacity, while more than 3 million tons of such wastes are being dumped in inadequate disposal sites. This view was expressed by Charles Johnson, technical director of the National Solid Wastes Management Association (NSWMA, Washington, D.C.). Johnson said that the industry has the capacity to take care of all chemical wastes, but noted that it cannot compete in price with environmentally hazardous open dumps, and non-secure landfills. But he expects that tougher laws on hazardous wastes will force proper disposal, and reduce improper landfilling, ocean dumping, and perhaps, deep-well injection.

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. . . *Advisory board*

Dr. Christman has appointed two new members and reappointed a third member to the *Environmental Science & Technology* advisory board. Members of the board are normally appointed to a three-year term. Dates (end of year of service) of the full board are shown in the table. Biographical information of earlier board members appeared in the January 1977 *ES&T, pages 16–17.*

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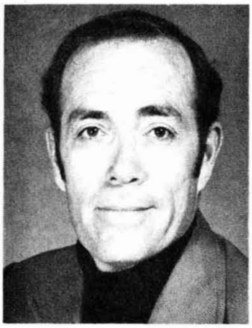
Levin	*1978*	*Trussell*	*1980*
Minear	*1979*	*Tuesday*	*1980*
Morel	*1980*	*Wilson*	*1979*
Orem	*1978*		

The members are drawn from the ranks of those active in the fields of environmental science and technology. They represent a wide variety of disciplines and interests, and lend the benefit of their experience to the continuing effort of *ES&T* to serve its readers in the most competent fashion.

Through formal meetings once or twice a year, and informal communication via the telephone and mails, the board members serve to advise the editor on content and subject matter and to assist, when requested, in solving problems that arise.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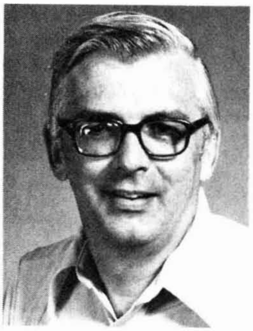
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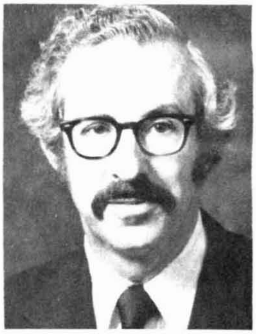
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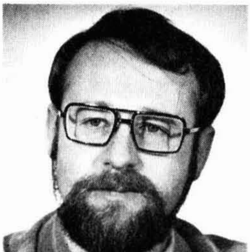
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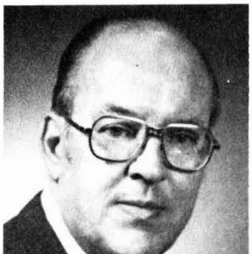
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Dr. François M. M. Morel, associate professor of civil engineering at the Massachusetts Institute of Technology (MIT), received his Licence-es-Sciences (1966) from the Université de Grenoble (France), and his M.S. (1968) and Ph.D. (1971) from the California Institute of Technology. He joined the MIT faculty in 1973, and was appointed to his present position in 1976.

Dr. Morel was the recipient of the Doherty Professorship in Ocean Utilization at MIT from 1974–77. He is a member of the ACS, AAAS and the American Society of Limnologists and Oceanographers.

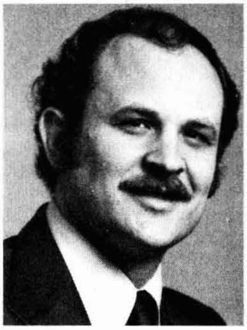
Dr. Morel has authored numerous technical papers and reports. He is especially interested in the interactions between chemical pollutants and microbiota in aquatic systems.

Morel

Dr. R. Rhodes Trussell, vice president of James M. Montgomery, Consulting Engineers, Inc. (Pasadena, Calif.), received his B.S. (1966), M.S. (1967) and Ph.D. (1972) in sanitary engineering from the University of California at Berkeley. He joined JMM in 1972 and was appointed to his present position in 1977.

Dr. Trussell is active in the AWWA Standard Methods Committee, and is preparing a chapter on disinfection for the new AWWA **Water Treatment Plant Design Manual.** Included among his areas of special interest are the control of microbiota in water and the behavior of trace organics in water.

He is the author of 28 articles, and a member of ACS, AAAS, IAWPR, AWWA, WPCF, NACE, AIChE and Sigma Xi.



Trussell

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associate editor

Lois R. Ember
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Biographical information on the Washington editorial staff appeared in the January 1977 *ES&T,* pages 17–18.

. . . Manuscript reviewing staff

Katherine Biggs
manager

Sheila M. Kennedy, an editorial assistant for *ES&T,* joined the manuscript reviewing staff in March 1977. She earned her B.A. degree in chemistry and English from the University of San Diego, San Diego, Calif. Ms. Kennedy is also an editorial assistant for the *Journal of Agricultural and Food Chemistry,* and the *Journal of Chemical and Engineering Data.*

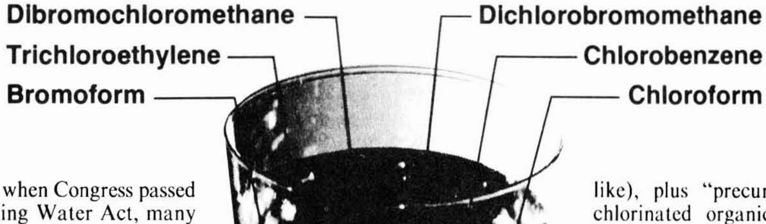
Biographical information on Katherine Biggs appeared in the January 1977 *ES&T,* page 18.

Kennedy

ES&T
OUTLOOK

The chlorination quandary

On the one hand, water must be disinfected;
on the other hand, undesirable products can result.
How to resolve this dilemma was discussed in Tennessee



In late 1974, when Congress passed the Safe Drinking Water Act, many expected that then-President Gerald Ford would veto it. But then came the news from New Orleans, La., that the city's drinking water contained pesticides, halogenated organics, and other such compounds, some of which were suspected to be powerful carcinogens. The rest is history.

Against the risk of those compounds, however, one must weigh the much greater risk of failure to disinfect water altogether. As Guillermo H. Davila of the Washington, D.C., office of the World Health Organization (WHO) reminded a dinner session of the Conference on Water Chlorination: Environmental Impact and Health Effects, chlorination is still the most known and accepted technology. Davila also noted that this technology is, at present, the best for the developing countries, where disinfection is a major need.

The conference was held in early November at Gatlinburg, Tenn., and was jointly sponsored by (DOE) and Oak Ridge National Laboratory (ORNL, operated by Union Carbide for DOE), and hosted some 300 attendees. One of the principal organizers, ORNL's Robert Jolley, told *ES&T* that an aim was to present results of research efforts accomplished since the previous conference (*ES&T*, January 1976, p 20). Another was to shed more light on new problems. These include getting a better "handle" on carcinogenicity/mutagenicity of chlorination trace by-products, such as trihalomethanes (THM), and to define other health and bioaccumulation effects more completely. Jolley also said that facts must be gathered concerning effects of heavier molecular-weight halogenated organics (halocarbons), as well as THM, in the environment.

In the foreseeable future, nationwide regulations concerning abatement of undesirable halocarbons will increasingly be on the books. But before any rational regulations *can* be drafted, the production, fate, and effects of these undesirables must be far better understood than they are at present, Jolley pointed out.

How they're made

The chemistry of THM and other halocarbon production is complex. But to "boil things down," one can say that chlorine (or hypochlorites, and the like), plus "precursors" will yield chlorinated organics, for example. Typical precursors could be naturally occurring humic acids, such as parahydroxybenzoic acid or vanillic acid, or they could be various industrial waste components.

Whatever the precursors are, the halogenated products that are formed occur in parts-per-million (ppm), and even much smaller, though detectable quantities. They can be determined by gas chromatography/mass spectrometry (GC/MS), or similar advanced methods. In this regard, M. Sonneborn of the Federal Health Office (West Berlin, Germany) told the conference that in his experience, chloroform is the THM in the largest concentration in drinking water, but that fluorinated, brominated, and iodinated species also occur. These latter, Sonneborn said, may originate from impurities in chlorine used for disinfection, and from organic precursors in raw water.

Chlorine used as a cooling tower biocide, which then may go out with the "drift", or with effluent discharge, might lead to trace halocarbon formation. ORNL's Jolley explained how some of these showed up in cooling tower, and certain other waters in Tennessee near a TVA power plant. Among compounds found were chloroform, bromodichloromethane, and bromoform.

However, more of the brominated compounds may be found in a marine area. Indeed, they seem to be what was turned up by the University of Miami's Rosenstiel School of Marine and Atmospheric Science (Fla.), where James Carpenter and his colleagues came across these chemicals in Miami's Biscayne Bay. For instance, bromoform was found in concentrations of about 360 ppb by GC/MS techniques. The chlorine that reacted with natural and sewage-borne precursors, and halogen ions in the water, is believed to originate at nearby power plants.

Actual quantification of waterborne halocarbons is in its infancy. But progress is being made. For example, James Symons of the U.S. EPA (Cincinnati, Ohio) observed that in West Germany, there is now a classification of "total organic chlorine" (TOCl). He gave an example from the Ruhr River, in which "TOCl" of 168 ppm was found in one analysis, of which only 14 ppm consisted of THM.

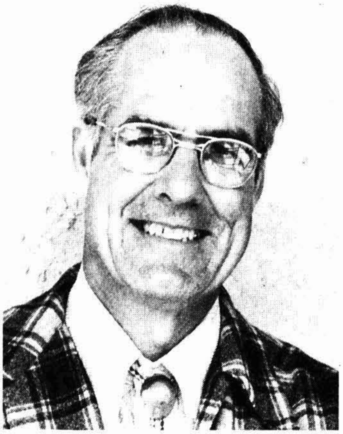
"So what!?"

"So what!?", one asks. "Why worry about chemicals that exist in such seemingly infinitesimal amounts?" Why, indeed? Because these "trace amounts" do some interesting things. Just for openers, they may show mutagenic properties.

Vincent Simmon of SRI International (Menlo Park, Calif.) told how certain halocarbons—in this case, alkyl halides—in trace quantities were "Ames tested" at 37 °C on a special strain of the bacterium, *Salmonella typhimurium*. This strain was dependent upon histidine in order to live. If the Salmonella reverted to a natural, non-histidine-dependent form at an accelerated pace, the compound tested was deemed to be mutagenic, and a candidate for animal, or even human autopsy tissue tests.

WHO's Davila
"One must weigh risks"

Bromoform, dibromochloromethane, and vinyl chloride, for instance, were found to be mutagenic to the Salmonella. Interestingly enough, by contrast, chloroform and carbon tetrachloride were essentially not—this could give rise to some arguments, perhaps! But those compounds—and Simmon listed many—which were mutagenic should be considered "90% effective in proving to be carcinogenic," he warned.



ORNL's Jolley
a better "handle" on by-products

What, then, can be done to mitigate the halocarbon situation? Robert Hoehn of Virginia Polytechnic Institute (Blacksburg) described experiments being done with powder-activated carbon (PAC) as a possible adsorbent for these compounds. Others told the conference about granular-activated carbon (GAC), as well as PAC; synthetic resins; and combinations of resins, GAC, and PAC. But more data are needed, especially with regard to the capacities of carbon and resins to trap and hold the various offending compounds, and whether absorption of certain compounds will cause desorption of others.

Hoehn's data indicated that coagulation, flocculation, and sedimentation, followed by measured doses of activated carbon, show promise for effective precursor removal. And precursor removal prior to chlorination is probably the best way to reduce THM and other halocarbon content in drinking water or waste effluents.

On the other hand, Stephen Hubbs of the Louisville (Ky.) Water Co., said that his company's work shows substantial THM reduction by presettling prior to chlorination. Hubbs also said that post-ammoniation helped to cut THM by about 20% in the distribution system, but that "excessive coagulation" does not reduce THM production significantly. As for active carbon, higher activity and smaller pore size distribution enhanced THM removal efficiency, Hubbs noted.

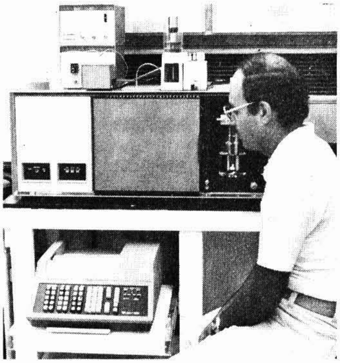
Alternatives

What about getting away from the halocarbon problem by disinfecting with a substance other than chlorine or hypochlorites? EPA's Symons said that such a substance must

- be a good biocide; that is, knock out bacteria, viruses, protozoa and their cysts, and other pathogens
- be cost-effective
- produce fewer hazardous by-products than chlorine produces
- provide an easily measurable residual.

Among chemical alternatives discussed are ozone (O_3), which is coming into increasing use; chlorine dioxide (ClO_2); and, more recently, bromine chloride ($BrCl$).

Ozone has been covered frequently in *ES&T*, and appears to be the most immediately promising alternative so far. ClO_2, from results of pilot-scale work, seems to have good disinfection potential without leaving possibly harmful residues. And, according to Ethyl Corp., BrCl disinfects rapidly—more so than does chlorine—is safer to handle, and easier to store. But BrCl is in the very earliest of experimentation and development stages at this time.



Analysis. *Determining trace halocarbons*

However, alternatives may not be problem-free. For instance, Louisville's Hubbs noted that although O_3 will reduce precursors in raw water, it is not as effective on precursors after coagulation. And he said that after significant contact time, ClO_2 converted some existing non-precursors into precursors.

For a long time, yet

Nevertheless, in many areas, as the WHO's Davila pointed out, the risk of epidemic far outweighs the halocarbon risk. And those areas' countries do not have the time or funds to develop alternatives to chlorine, or precursor-handling systems; moreover, they need disinfection *now*. Thus, good old-fashioned chlorination will be around for a long time, yet, for that reason alone.

That is not to say that halocarbon problems and alternatives to chlorine will always be ignored. On the contrary, Davila said, these things will come as world economic development progresses.

But there is quite a way to go. For instance, in many areas, water quality surveillance is well-nigh non-existent. There is no trained technician help (*ES&T*, September 1977, p 851), community participation, or competent management for drinking water, or wastewater treatment.

However, attention is being given to problems of safe drinking water in more areas of the world, Davila observed. Eventually, removal of unsafe trace substances, and innovative ways to treat water, will become practice in many different countries. But one should not expect fast action in this regard when, even in a country as developed as the U.S., knowledge of environmental/health effects of chlorination, and experience with many disinfectants other than chlorine, need further development. JJ

SO_x scrubbing: clearing the air

A Florida symposium covered numerous FGD technologies. But future emphasis may be on recoverable materials and salable by-products, as well as air cleanup

Some praise the Clean Air Act and its subsequent amendments. Others condemn it. But all can agree that the Act is a technology-pushing, if not technology-forcing statute. That statute is one stimulus for flue gas desulfurization (FGD) scrubber development and evolution.

As of now, quite a variety of scrubbers is developing. Some, for example, do not regenerate the SO_x reactant; others aim at doing so. Some will generate hopefully marketable by-products; others will not. A common scrubber by-product is gypsum whose manufacture by this means is not deemed to be cost-effective in the U.S. By contrast, FGD was a prime gypsum source in Japan until recently, when the market became glutted. The matter of gypsum as a product of SO_x abatement was one topic discussed at the Fourth Symposium on Flue Gas Desulfurization, sponsored by EPA's Industrial Environmental Research Laboratory (Research Triangle Park, N.C.). It was held at Hollywood, Fla., last November, and drew more than 800 attendees.

Third option

ES&T readers will recall the mention of three options with respect to the firing of coal in a "clean" manner (August 1977, p 750). Option No. 1 involves pre-cleaning of coal. Option No. 2 comprises fluidized-bed combustion (FBC). And Option No. 3 calls for FGD scrubbers, which the EPA says—with a weather eye on the other two options—is still the most promising technology, at least for the near term, for meeting present and forthcoming clean air regulations.

Enforcement of these regulations for existing and, especially, new stationary sources "will not be timid," the keynote speaker, David Hutchins, EPA's assistant administrator for air and waste management, announced. He characterized the Clean Air Act Amendments of 1977 as a "mid-course reaffirmation," rather than "correction" of the clean air program. He noted that Congress "did not intend that energy and economic problems should be allowed to degrade air quality."

EPA's Hutchins
enforcement will be bold

Hawkins said that by three years after the federal authorities declare that mandated air quality standards have been generally attained, all plants that were previously granted extensions must be in compliance with SO_x and particulate guidelines. However, up to five years would be allowed for facilities working on, and installing "innovative technology." He warned that no extensions would be allowed for "convenience," and that EPA "will have the weapons to deprive violators of all economic advantages that noncompliance might otherwise bestow." The standards that will have to be met are under draft, pursuant to the new law. Hawkins reminded the symposium that applicable regulations must be finalized by August.

Hawkins also said that with some of the new source performance standards (NSPS) and "best available control technology" (BACT) regulations envisaged, even scrubbers might not help to meet performance standards in the case of high-sulfur coals. He noted, however, that pre-cleaning of these coals could mitigate such a situation. Hawkins defined "new source" as a facility that has not commenced construction as of the date of publication of *proposed* regulations.

Megawattage

As of August, 29 FGD units to service 8914 MW were on line, and 28 more (11 810 MW) under construction, Timothy Devitt and Bernard Laseke of PEDCo Environmental, Inc. (Cincinnati, Ohio), said. In addition.

ES&T

READERS' COMMENTS

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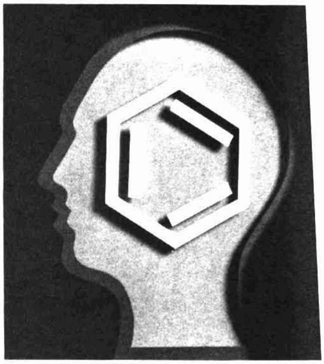

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68 systems (32 628 MW) were in various stages of planning. These numbers were 3291, 6777, and 27 768 MW, respectively, in 1974. PEDCo spokesmen estimated that while FGD in 1975 constituted about 3% of coal-fired capacity, it was close to 4% today, and could be 15% by 1980.

By contrast, in Japan, there are almost 1000 FGD plants (about 31 000 MW equivalent) of all sizes, which also make marketable, mainly gypsum, by-products, Jumpei Ando of Chuo University (Tokyo) pointed out. Ando does not foresee too many more FGD plants' being built in Japan because stringent ambient or performance SO_x regulations are "almost attained," and by-products are in oversupply.

On the other hand, a new air cleanup effort—simultaneous SO_x/NO_x removal— is being undertaken in Japan, at about 40 plants. A catalytic ammonia (NH_3) process is presently considered "most promising," with 85-95% flue gas NO_x removal with an NH_3/NO_x mole ratio of 1/1.2 at 300-400 °C. Nitrogen and water are the products.

Meanwhile, the federal authorities in West Germany (*ES&T*, PAT report, March 1977, p 226) are "postulating" the equivalent of 0.3 lb $SO_2/10^6$ Btu, presumably for new sources, initially. Some engineers consider this standard to be "prohibitive." Rolf Holighaus of KFA-PLE (Jülich) proposed a two-pronged attack on this severe technological problem—advanced FGD development, and FBC as alternatives.

Forward progress

In any case, FGD technology is making strides. For example, at the Scholz Electric Generating Station (Chattahoochee, Fla.) of Gulf Power Co., of the Southern electric system, two existing 40-MW Babcock & Wilcox pulverized coal-fired boilers were retrofitted with three prototype FGD processes. These include:

- a concentrated-mode lime-regeneration sodium/calcium dual alkali process (Combustion Equipment Associates, Inc., and Arthur D. Little, Inc.); SO_x is removed by sodium contact, and hydrated lime regenerates the sodium. The system operated for more than 17 months.
- an iron (III)-catalyzed process (Chiyoda "Thoroughbred 101") with limestone, that leads to formation of high-grade gypsum
- a dry-adsorption process, using activated carbon pellets, known as FW/BF, supplied by Foster Wheeler Energy Corp., and producing concentrated off-gases, and sulfur.

These system have been undergoing rigorous testing since 1975 by Southern Co. Services, Inc. (Birmingham, Ala.).

In the "regenerables" processes, Northern Indiana Public Service Co. (NIPSCO) completed acceptance testing with 12 days at 320 000 acfm, or 92 MWe; and 83 h at 390 000 acfm, or 110 MWe of a Davy Powergas, Inc. (Wellman-Lord)/Allied Chemical SO_2 reduction process in September, at Gary, Ind. A one-year long-term reliability test commenced that month. The process by-produces sulfur with a 99.9%—reagent grade—purity. Removal efficiency comes to 91%; particle emissions to 0.04 lb/10^6 Btu; steam/electricity/gas cost to \$43/h; and sodium carbonate makeup to 6.2 tpd. In all cases, these figures bettered performance criteria. The Allied Chemical SO_2 reduction process has even operated well for smelter applications, according to NIPSCO and the EPA, which shared costs.

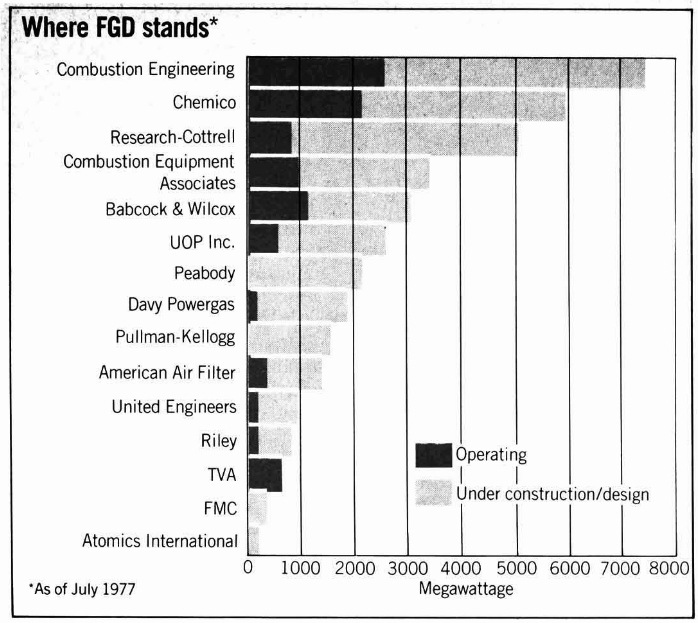
Base metal smelters, incidentally, have a very heavy SO_x emissions problem. Thus, at one, in Kellogg, Idaho, Morrison-Kundsen Co., and St. Joe Minerals Corp. tested (100 scfm) a citrate FGD process first developed by the U.S. Bureau of Mines. Pilot operation has shown more than 99% SO_2 removal. Sulfur was produced, and less than 1.5% of the SO_2 was converted to sulfate. The system reacts SO_2 and H_2S in an aqueous citrate medium.

In addition to sulfur, sulfuric acid—less than 1.5%— is formed. This is converted to sodium sulfate, which can be used as a secondary chemical feedstock, or disposed. Since the process can apply to very high-sulfur coal, demonstration at St. Joe's G.F. Weaton electric station near Pittsburgh, Pa., at 156 000 scfm, is scheduled.

Bottom-line costs for a system are estimated at less than \$73 million (capital), with a 2.73 mills/kWh operating cost at 1000 MWe, use of 2.5%-S coal, a midwest location, and 1977 dollars. Gross energy consumption is put at 3.8%.

Other developments involve scrubbers with other than lime or limestone. For example, the Philadelphia Electric Co. has been testing out a regenerable magnesium oxide (MgO) system that the company says is 93% efficient in SO_2 removal, and produces a marketable 98% sulfuric acid. MgO is regenerated by fluidized-bed recalcining of dried magnesium sulfite. However, availability problems must be overcome.

At an Air Products and Chemicals,



Where FGD stands*

*As of July 1977

Inc., plant at Calvert City, Ky., a 4000-cfm Catalytic, Inc. (Philadelphia, Pa.) pilot ammonia scrubber for a 20-MW boiler is in use to handle 2.3%-S coal. A by-product of the scrubber's open-loop ammonia-sulfur-brine system can be used as fertilizer.

Sludge or no sludge

There are ways to handle scrubber sludge. For instance, IU Conversion Systems, Inc. (Philadelphia) told *ES&T* that the firm now has 10 contracts with electric utilities for its proprietary sludge stabilization process. On the other hand, at Saarbrücken, W. Germany, Saarberg-Hölter Umwelttechnik GmbH (SHU), the Hölter process aims at getting away from the sludge problem entirely by making high-grade gypsum.

Michael Esche, SHU copresident, says that his company's system's availability, in terms of boiler operating time, has been as high as 97.8% since April 1976. A working 700-MW (1.67 million scfm) system is to start up in Germany early next year. It may have to handle 5000–6500 ppm of SO_2, with 90–95% capture.

The plant uses lime/limestone, but the scrubber reactant liquid is clear because of a proprietary process that uses a catalyst, and converts the liquid to calcium chloride solution. An intermediate SO_2 reaction product is calcium bisulfite, which is readily oxidized to marketable, or safely disposable gypsum. SHU estimates capital costs for a turn-key plant at $70–75/kW for a commercial-scale plant, but notes that problems of sulfite sludge, plugging/scaling, and the like, are "abolished."

More advances

Further advances in FGD technology will probably bring about a trend to more marketable by-products, such as gypsum or sulfur, regenerable reactants, and perhaps deliberate SO_2 concentration. NO_x and trace pollutant problems will also have to be increasingly addressed. Indeed, the "Advanced Processes Session" of the symposium pointed up a coming acceleration of this trend. These advances, as well as those in coal precleaning and FBC will be very necessary if the U.S. is to convert to more coal use, as President Carter wants, and, at the same time, "clear the air."

JJ

Monitoring update

A report from the 4th Joint Conference on Sensing of Environmental Pollutants

At the outset, when monitoring came into vogue several years ago, it was media specific. Data were acquired and analyzed for air pollutants such as sulfur dioxide and water pollutants such as BOD. Now, there is a perceptible move toward the acquisition and use of remotely-acquired data from aircraft and satellite.

There is no dearth of data, but there is concern and doubt about the adequacy and interpretation of the data. Overall, most data today are inadequate for their intended use. "Environmental Monitoring," Volume IV of the National Academy of Sciences' study on the EPA decision-making role recognized this inadequacy of data because of the lack of quality assurance.

Until uniform methods are firmly established for quality assurance the data are only marginally useful. Obviously, the continued collection of unreliable data becomes questionable. Their usefulness becomes doubtful.

Nevertheless data are collected at considerable expense:

- Last year, the Federal Government spent $691 million on the collection of data and statistics. It has been estimated that 43% of this expenditure was made in the name of environmental agencies!
- This year, the United Nations will spend $2 million for its Global Environmental Monitoring System.

Held in New Orleans, in November, the 4th conference was supported by a half-dozen technical societies and eight federal agencies. The technical societies include the American Chemical Society, which hosted this conference, the IEEE (The Institute of Electrical and Electronics Engineers), host for the previous session in Las Vegas, Nev. (*ES&T*, December 1975, p 1109), and the American Meteorological Society,

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the upcoming host for the next conference in another two years.

The New Orleans conference drew about 235 technical papers, more than 600 attendees, and 20 exhibitors. The conference proceedings are being published by ACS and should be available in March from ACS Special Issues Sales. Meanwhile, the *ES&T* reprint book, "Environmental Monitoring," also available from Special Issues Sales, covers a collection of articles, books, and news leads on the subject.

The global view

Plenary speaker Leon de Rosen of the UNEP office in Paris told the attendees about the monitoring and information exchange activities of Earthwatch of the United Nations Environment Program. In this global environmental assessment, relevant issues are identified; then necessary data are collected and evaluated to provide a basis for effective environmental management.

De Rosen did not talk about other Earthwatch concerns such as the evaluation of the data; that is, the two-stage process for first, validating the environmental data (a form of quality control), and secondly interpreting the data to recognize significant trends as a basic input to environmental management.

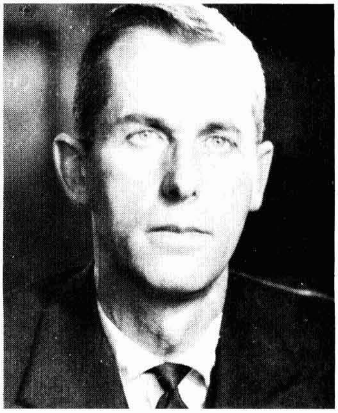
The plenary speaker pointed out that to most people the word monitoring immediately leads them to think of pollution and pollutants. Indeed this was the state of affairs when, in 1974, governments met in Nairobi for an Intergovernmental Meeting on Monitoring. This lead to the formation of the Global Environmental Monitoring System. GEMS is a part of the UNEP Earthwatch program.

For the years 1978 and 1979, Earthwatch will have an operating capital of $8.96 million. Less than half will go to GEMS. This GEMS money, about $2 million each year, is channeled through specialized agencies to encourage national action. For example, with such funding 12 regional stations in 10 developing countries have been equipped with instruments. Indeed, GEMS is considering the establishment of a baseline station at Mount Kenya.

"It is abundantly clear that if the GEMS system is to work properly, national efforts and expenditures will have to be many times the catalytic expenditure of the United Nations" de Rosen said. "One cannot hope to monitor the world with $2 million a year."

Now, he noted, one can look back on this activity with a new eye; one that has seen the Sahel disaster, the energy crisis, and in the technology field the wide applicability of the results of the two Landsat satellites. Today, a balance has been struck between pollutant monitoring and natural resource monitoring.

In de Rosen's view, the Landsat program "gives immense hope to the developing world, especially in their concern for their natural resources—the mainstay of their economics and livelihood." Also, "This satellite monitoring is the means by which vast areas of natural resources in the developing world can be economically monitored."



UNEP's de Rosen
the global view

Information exchange

Another activity of the Earthwatch is the IRS, the Information Referral Service. Its central computer unit is in Nairobi, Kenya, site of the first UN agency in a developing country of the world. Referral is the key—information exchange between those who have the data and those who need the data.

Another aspect of the IRS is decentralization; there are both national and regional focal points in the IRS. To date, IRS partnerships have been established in 76 countries. In the U.S., EPA is the focal point. Carol Alexander heads the IRS activity at EPA headquarters in Washington, D.C.

A main tool of the IRS is an International Directory of Sources that is updated each quarter. The August 1977 edition of this directory contained 3500 sources covering 900 different environmental topics!

Data on chemicals

Although IRPTC (the International Registry of Potentially Toxic Chemicals) started in Nairobi in 1976, it was transferred to the World Health Organization headquarters in Geneva on January 8, 1977. Data are being collected and stored in a computerized data bank, in Geneva, from which data concerning potentially toxic chemicals can be retrieved for dissemination.

Here, there are two noteworthy developments. NIOSH has made available to the IRPTC, free of charge, its complete file on mammalian toxicity of 21 000 chemicals. In addition, a pilot project is underway to collect information on seven groups of chemicals involving more than 300 individual compounds. The purpose of the latter project is to gain experience in the collection, storage, retrieval and eventual dissemination of data on chemicals. IRPTC also plans to publish a newsletter.

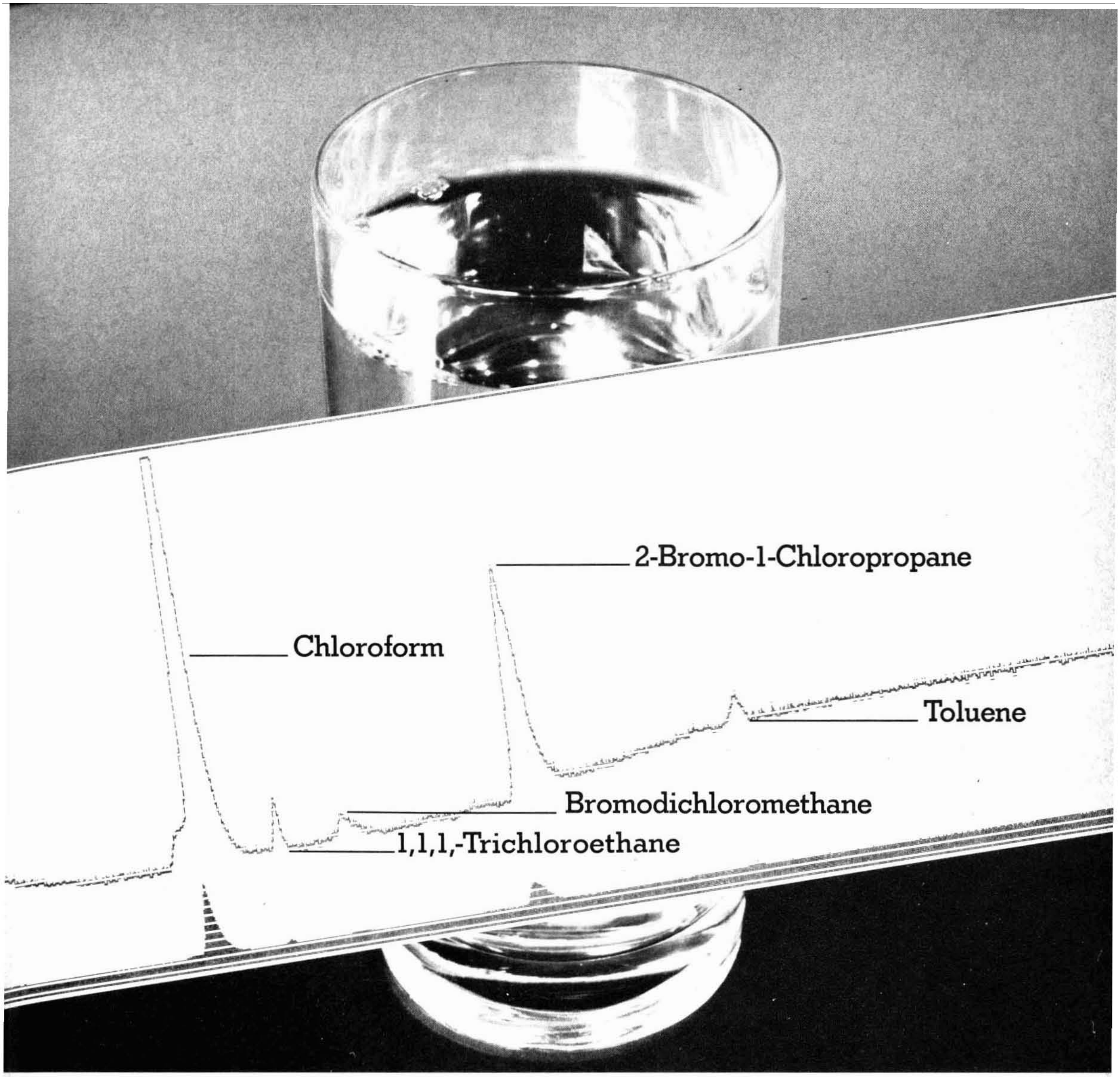
A practical example of pollution monitoring, according to de Rosen, would be the UNEP industry program of pollution monitoring and assessment. In this case the UNEP Governing Council, the intergovernmental body of states that serves as a policymaking and priority-setting mechanism, has directed that each major section of industry be studied in order to assess its impact upon the environment. Then each major industrial sector would evolve appropriate corrective guidelines that might be of help to developing as well as developed countries.

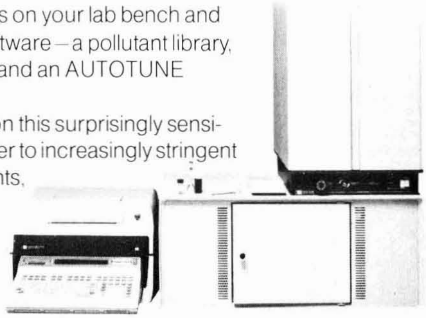
The regional view

The newly appointed EPA Assistant Administrator for R&D, Stephen Gage, a panelist at the Las Vegas Conference, mentioned the new challenges in environmental monitoring. He recognized that the monitoring data are the essential building blocks for environmental management policies.

This EPA spokesman noted that remote sensing from aerial platforms produced useful and promising results. He noted that one of the most cost-effective uses of aerial remote sensing is to locate and screen possible targets for future contact monitoring and compliance inspections. Gage said, "remote sensing techniques will undoubtedly be of increasing importance in the field of environmental sensing." And continued, "Their widespread use should be encouraged to save time and money and to gain perspective. Perspective is critical in understanding the true nature of an environmental problem."

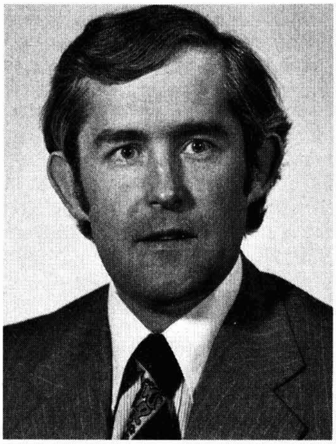
To accomplish this aircraft sensing, small prototype self-contained sensor modules—so-called Enviropods—have


2-Bromo-1-Chloropropane
Chloroform
Toluene
Bromodichloromethane
1,1,1,-Trichloroethane



been developed recently by the U.S. Air Force Avionics Laboratory. As presently configured, the Enviropods contain two identical panoramic cameras. One is mounted in the conventional vertical mode and the second in an oblique mode looking 45° forward of the aircraft, according to Gage.

Gage foresees widespread use of the Enviropods in enforcement, episodic, and emergency monitoring activities of his agency. The Enviropods have been certified by the Federal Aviation Administration for use on light commercial aircraft. Also, they have been successfully demonstrated in the Washington, D.C. area and in the Boston, Atlanta, Philadelphia and New York EPA regions.



EPA's Gage
the regional view

Gage mentioned a number of LIDAR (Light Detection and Ranging) techniques which have been reported earlier (*ES&T*, January 1977, p 36). First used by EPA in 1974, these techniques are especially useful in estimating dispersion coefficients for aerosols, for example.

The use of coal in this country is projected to increase by two-thirds, from a present usage of 700 million tons to 1.2 billion tons by 1985, according to this EPA spokesman. In order to predict the impact of this new energy development, especially in the West, a major monitoring effort has been undertaken to integrate air, water, and land-quality monitoring data. Known as the Western Energy Environmental Monitoring Study, it is described elsewhere in this issue.

Another concern of the EPA, for some time, is the development of an integrated, total system approach to environmental monitoring. EPA is still grappling with a monitoring strategy that will bridge media lines—air, water, and food. This strategy requires a focus on the most important sources and pathways of exposure to critical receptors, where adverse effects appear even at low exposure levels. It also requires the development of models that link the sources, transport, transformations, exposure dose, and effects in quantifiable ways.

The local view

Montana, the fourth largest of the states in land area and 43rd in population, looks forward to the development of its lush coal reserve. One-third of the nation's coal base lies in Montana. With such a resource it is not hard to see why Montanans have been referred to as the "blue-eyed arabs."

Montana lieutenant governor Ted Schwinden said, "In excess of 1.5 million tons of coal are estimated to lie within the Northern Great Plains Region. Of this amount 160 billion tons of coal are mineable and presently represent 37% of the nation's coal reserve basis. These vast quantities, combined with the relatively low cost of its extraction, plus its low sulfur content, are what attracts the coal industry to the West."

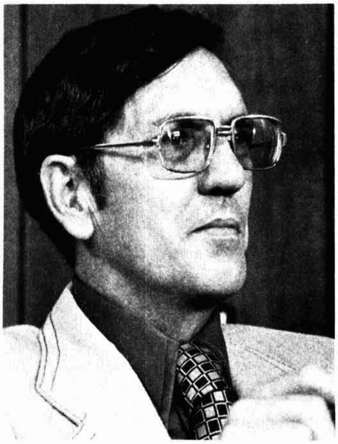
Montana has responded to the environmental ethic. The state has taken steps to protect the environment even though pressured on development. For example, Montana has a strong industrial siting law, mining and reclamation laws, and, as of the meeting time in New Orleans, was the only state to adopt a state NEPA, similar to the federal National Environmental Policy Act, which requires the preparation of environmental impact statements before starting projects.

Schwinden noted that in order for environmental sensing to be useful to policymakers, the sensing procedures must allow an opportunity to coordinate plans for problems before they happen. "The luxury of a leisurely review of the effectiveness of past control procedures is not with us to a great extent any longer," he said.

Schwinden said that a substantial portion of Montana's air quality budget goes toward the operation of highly sophisticated monitoring devices that require expensive, frequent, and difficult maintenance. When breakdowns occur, information on which to base judgments is lost and the way is opened for legal challenge of the entire procedure.

Three years ago, the state Air Quality Bureau gathered some striking mortality statistics that indicated that the Montana death rate for asthma, emphysema, and bronchitis was more than 50% higher than the national rate. The Bureau study also found that death rates from respiratory diseases, lung cancer, and cardiovascular disease in the mining and smelting area of southwestern Montana are 50–120% higher in that area than in other regions in Montana, Schwinden related.

Now, Montana is gathering information on which to take whatever measures are necessary to ensure that emissions from coal development activities do not exacerbate health problems for Montana's residents. Currently, the Air Quality Bureau of Montana's Department of Health and Environmental Sciences is engaged in a project called the Montana Air Pollution Study.



Montana Lt Gov Schwinden
the local view

MAPS hopes to find a correlation between air pollution and human health in selected areas of the state, areas that experience frequent inversions and those that contain numerous industrial sources. Measurable parameters include sulfur oxides, nitrogen oxides, hydrocarbons, ozone, fluorides, total suspended particulates, and respirable dust.

The state is also concerned about its water quality. Its water quality monitoring program encompasses regular physical, chemical, biological, and sediment sampling at 101 fixed stations distributed over the state's 16 major drainage basins. Last year, the Water Quality Bureau monitored 16 stations for chemical and physical parameters and 46 stations for biological parameters.

Montana is also concerned with effluent monitoring, the objective being compliance with waste discharge permits conditions. This year, Montana will compliance monitor 15 major industrial and 10 major municipal discharges.

Schwinden also noted a reliance on remotely acquired data. He reported that remote sensing will be a key integrative element in the Montana Coal-Fired Power Plant Project. "High resolution camera systems installed in both high-altitude and in low-flying aircraft should provide an excellent permanent control record of the study area" he said.

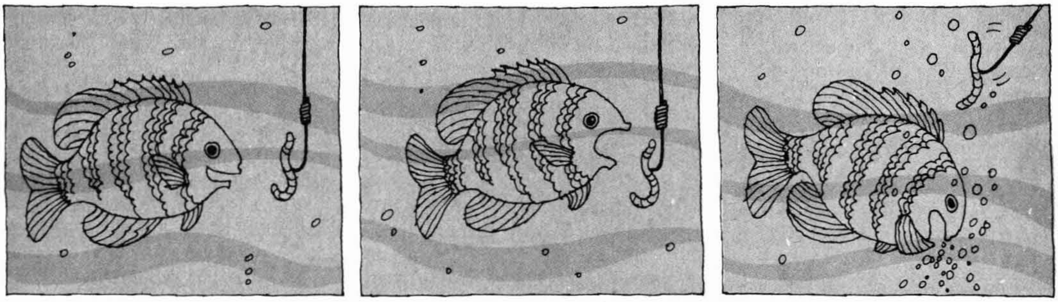
Looking ahead

Hopefully, today's fad of environmental monitoring will not become tomorrow's blab. With our amazing analytical detection capabilities it is important to avoid a total technical excellence in monitoring. The tools for sensing must be simple, reliable and far less costly then they now are.

We continue to need reliably good data obtained at a low, yet affordable, cost. We should never increase that cost at the loss of efficiency. But it is also important to address the evaluation and assessment of the data. The evaluation of data is of grave concern. Certainly, it will vie for discussion at the next conference. SSM

Aquatic toxicology comes of age

ASTM conferees heard the recent developments in this emerging discipline



Did you know that fish can cough? That this coughing reflex can be measured? And that the measure of this reflex is an index of aquatic pollution? If your answers to these questions are no's, read on. If, however, you answered affirmatively, you have some knowledge of aquatic toxicology, the not-so-widely recognized stepchild of mammalian toxicology.

The fish is the thing

To disseminate some of the current thinking in this exotic field, the American Society for Testing and Materials (ASTM) held its second Symposium on Aquatic Toxicology last November. More than 225 people came to hear sessions on applications and principles of physiological toxicology, methodology and data, bioconcentration and the fate of chemicals in the environment.

Two things rapidly became evident. First, mammalian toxicologists extrapolate data back to man, while aquatic toxicologists extrapolate data back to whole ecosystems. And second, the fish is to aquatic toxicology what the guinea pig and rat are to mammalian toxicology. Thus, while other aquatic organisms may be used to monitor for toxicity, it is the fish that is most widely used as the test model.

Among the parameters measured to estimate toxicity are the cardiac, opercular (breathing) and cough rates in fish. These parameters offer two advantages: they are easy to measure and they can be measured on site. In fact, fish monitored for these parameters can be turned into biological monitoring systems for the industrial monitoring of sublethal concentrations of toxicants.

W. S. G. Morgan, a member of the National Institute for Water Research, Republic of South Africa, has reported on an automated fish biomonitoring system that he designed for use by industry and municipalities to test for water quality and to control effluents entering a water system.

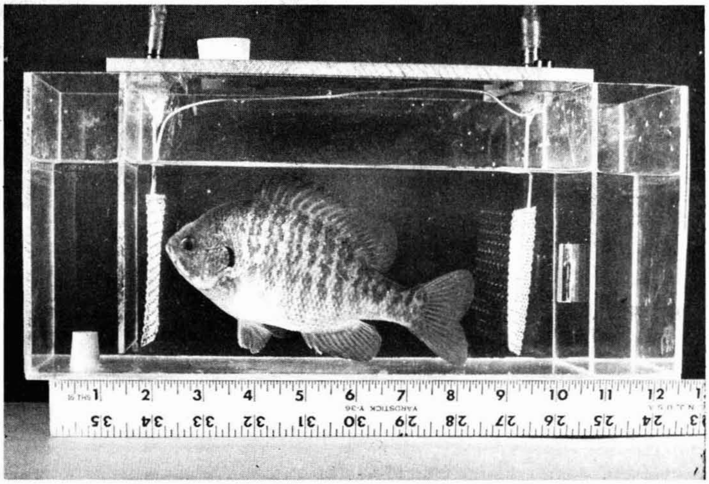
A biomonitoring system

At this conference, John Strange of the National Center for Toxicological Research (Jefferson, Ark.) described Morgan's automated system in some detail. Morgan's system, according to Strange, uses 12 fish "sensors," an alarm system and a mechanism for diverting a toxic effluent.

The fish sensor exposed to an effluent containing a toxic material usually reacts by increasing its breathing rate. If the breathing rate is significantly greater than a predetermined level, and thus indicative of a toxic state, the alarm is triggered, and an electrical voltage is induced at the rear panel output. This output signal can electrically close valves to divert the polluted water to a holding tank for further analysis.

Morgan's system has been monitoring the effluents from a municipal waste treatment plant in Pretoria, South Africa, since 1975. Closer to home, a system, similar to Morgan's but including an on-line computer, will be installed at the Army's Radford (Va.) Ammunitions Plant on the New River this month. This system will monitor for industrial munitions effluents containing TNT, nitroglycerine and rocket propellants.

The Army's system was designed by John Cairns, the father of the bio-



Biomonitoring. *Bluegill in air-lift electrode chamber*

monitoring concept, and Kenneth Dickson, both at Virginia Polytechnic Institute (VPI). This system was designed to be totally automated, including the data analyses, and totally compatible with automated physicochemical monitors. Dickson put the cost of the physical system at $50 000.

Morgan, and Cairns and Dickson, state that their biomonitoring setups can act as early-warning systems. Strange, in some of his original research, has verified these claims. In experiments in which channel catfish were exposed to sulfate concentrations ranging from 0–3200 mg/L, Strange found that the cough rate increased with increasing concentrations of sulfate, and that the increases preceded any other sign of stress. In fact, the fish showed elevated cardiac rates only at the two highest sulfate concentrations.

Robert Drummond, an aquatic research biologist with EPA in Duluth, Minn., also found that cough reflex changes, or what he calls "gill purges," usually occurred before breathing or cardiac changes, and that the frequency of coughing was directly proportional to the concentration of the toxicant (heavy metals).

Drummond told *ES&T* that the cough reflex is probably a "more sensitive indicator" of toxicity than other physiological parameter, and that the reflex not only alerts for immediate acute effects, but is also a good indicator of potential long-term effects.

A mechanism of action?

Bernice Katz of the Florida Institute of Technology postulates that the wide variance in species tolerance and even mortality to toxicants can be related to membrane permeability. For freshwater fish, the fragile gills, the site for water uptake and waste (ammonia) excretion, may be the initial target organ or, at least, the first step in a chain of cellular events that lead to illness or death.

Katz has, in a preliminary fashion, tested her permeability theory using low concentrations of inorganic substances such as chlorine and the heavy metals silver, copper, cadmium and zinc. She postulates that the culprits are not the chlorine or heavy metals themselves, but rather these substances complexed with the excreted metabolic waste product ammonia.

For example, chlorine may react with ammonia to form chloramine, which then re-enters the gill membrane changing its permeability and eventually disrupting its structural integrity. This change in membrane permeability causes sodium to leave the fish and water to be taken up passively by the fish. In short, Katz postulates that a complex of ammonia and toxicant causes membrane permeability changes that result in an efflux of sodium coupled with a passive influx of water, and that these osmotic changes lead to gill damage and fish morbidity or mortality.

Switched-off bacteria

Beckman Instruments (Carlsbad, Calif.) has developed a rapid water toxicity biomonitoring system that uses lyophilized luminescent bacteria as the sensors and the bacteria's light output as the measure of the toxicant.

Beckman's Anthony A. Bulich told the ASTM conference that certain strains of bacteria emit light as a by-product of their metabolism. But, in the presence of a toxicant (pesticides, for example) their light output diminishes in proportion to the concentration of the pollutant.

In trials that tested a chemical plant's effluent, this biomonitoring system was found to compare favorably in sensitivity with a more traditional 96-h acute fish toxicity test. But, Bulich claims, the bacterial test was more reproducible and simpler to run.

According to Bulich, this bacterial toxicity test has "excellent potential as a rapid and reliable indicator of toxicity in aquatic samples."

Decisionmaking

A Pesticide Task Group, coordinated by the American Institute of Biological Sciences (AIBS), was formed in October 1976 to aid the EPA in its decisionmaking procedures. This task group developed criteria for the basic test data; identified conditional test protocols; and identified methods to evaluate the effects of pesticides in the aquatic environment.

The task group has not released its final report, but its chairman, Calvin Ward of Rice University, plans to submit the final version to AIBS this month. AIBS will then transmit it to EPA.

Kenneth Dickson of VPI and State University summarized some of the criteria that would trigger additional testing and listed some of the conditional tests for the ASTM meeting. Dickson said that at a minimum the report would recommend:

- that the basic data required for pesticide registration include an estimate of the maximum acceptable toxicant concentration (MATC)
- that a task group be formed to assess the fate of pesticides in the aquatic environment.

Dickson said that while the criteria for hazard assessment were developed for pesticides, the task group sees no reason why these cannot be used for other toxic substances. In fact, the task group successfully applied the procedure to some heavy metals and organic chemicals such as surfactants.

Growing up

Ann Spacie, an aquatic toxicologist at Purdue University but formerly with Union Carbide, told *ES&T* that her discipline, like the environmental era, began with Rachel Carson and **Silent Spring.** Although the discipline is now in its infancy, Spacie is certain that the principles of mammalian toxicology will be found applicable to aquatic toxicology, thus speeding up its maturation process. LRE

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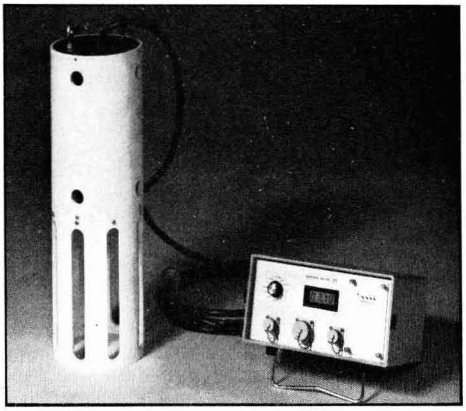

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The design, location, construction and continued safe operation of nuclear power plants, fossil-fuel power generating plants, mining operations and other large-scale energy-related installations depends on pulling together almost unimaginable masses of raw data into coherent, understandable, useful information.

NUS Corp. (Pittsburgh, Pa.) supports this important work by providing consulting and engineering services. Its Ecological Services Division provides scientific expertise, management support and documentation for more than 200 such data collection projects annually.

Then NUS clients utilize the resultant information in a wide variety of planning, construction and environmental monitoring projects including oil-shale operations, coal exploration, deepwater tanker ports, nuclear power plants and many others.

These projects involve the collection and processing of data related to everything from hydrology and seismology to physics and microbiology. The statisticians and data processing personnel at the NUS division handle from 390 000 to 780 000 data records each year.

The voluminous reports that are the result of extensive field sampling, lab analysis, and statistical evaluation are used by client's design and operations engineers, in court records, in public hearings and as resource materials by governmental regulatory agencies such as the Environmental Protection Agency and the Nuclear Regulatory Commission.

These reports, both their content and the procedures used to prepare them, affect the investment of billions of dollars and man-hours. They may be audited at any time; therefore, complete documentation and data accuracy are crucial.

The cost of any given NUS project averages from $1-2 million, for example, or, about 2-3% of the total cost for building a nuclear power plant. Data entry and data preparation account for about 10% of the total budget for an environmental impact study or monitoring program.

The computer system

The NUS division utilizes a Mohawk Data Sciences (MDS) System 2409 key-disk data energy system. NUS manager of data analysis and biostatistical studies Henry Hess says that the company's major reasons for implementing the MDS System 2409 three years ago were its ability:

NUS Corp.'s Hess
200 data collection projects annually

- to achieve the data entry accuracy and productivity rates essential to valid statistical evaluation
- to provide data management and entry system
- to keep researchers abreast of current publications in their fields.

"These areas continue to be our most important areas of usage," Hess says. "At NUS, our job is to apply the skills and discipline of modern technology, at all levels, to maintaining the complex balance between the environment and man's need for energy. We feel that the MDS System 2409 is a small, but important, tool in helping us to accomplish that task."

The MDS configuration was implemented on September 1, 1974 to replace old IBM 129 keypunch equipment. It includes a 65K MDS System 2409 used for data entry, validation, editing and concurrent remote-batch communications with an IBM 370/168 and 370/158 located at an outside services vendor in Pittsburgh and CDC 6400 in McLean, Va. The specifics: the communications links are 4800 baud dialups. The system also includes five keystations; four nine-track, 800 bpi tape drives; a 400 cpm card reader; a teletype console; and a dual disk system with a combined storage capacity of 4 056 000 bytes.

For data management

This application, implemented last May, is the first stage in a project to gather and organize data on which EPA can base effluent guidelines for the iron and steel industry. Working with the Cyrus Wm. Rice Division of NUS, the Ecological Sciences Division created such a data entry and management system to run on the MDS 2409.

Responses to inch-thick questionnaires sent out to management personnel in this industry are being keyed-in on the System 2409, validated, edited and batched for data management on the IBM 370/168 in Pittsburgh. To date, more than 400 questionnaires have been received and entered, and 150 000 records have been produced.

Entering data. *Operator assures the required data accuracy with a keydisk system—a Mohawk Data Sciences 2409 System*

For information retrieval

In 1975, Hess's staff addressed the problem of keeping pace with new developments in the ecological sciences by creating an information retrieval system on the MDS System 2409. The application, written in MDL (Mohawk Data Language), provides an easily accessible and current bibliography of publication for the scientific personnel at Pittsburgh.

More than 8.3 million documents—reprints of journal articles, abstract sheets and technical materials—can be listed on two disks. A researcher who needs to review a specific subject area may reference as many as 20 000 key words that are included in the file and which may be modified by as many as 50 operands. The system automatically examines 2000 documents per second.

For example, one might key in "FISH, 1974, OHIO" and get back a complete list of all publications relative to ecological studies on fish in the state of Ohio either performed or published in 1974. The list includes title, author, publication and publication data. The files are updated periodically in order to keep them current. Hess cites the ease of code generation with MDL as a factor in designing the system to run on the System 2409.

For aquatic information

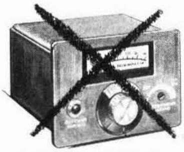
The first use of the System 2409, involving a unique state-of-the-art enhancement of MDS' Key-Disk Operating System (KDOS), was created to handle the highly specialized data entry requirements of the NUS division. Called EDVAL (Ecological Data Validation System), the system allows keystation operators to enter the taxonomic classifications of biological samples with a minimum number of keystrokes and, therefore, a reduced risk of error.

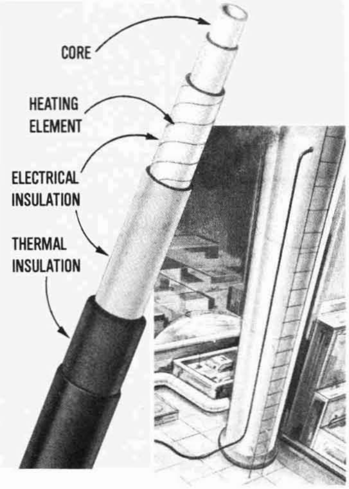
Essentially, the purpose of EDVAL was to reduce the long and complex Latin names to the shortest possible unique form, and to provide operators with no special training in the sciences with a means of looking up correct phylogenetic classifications.

The number of biological entities occurring in a given aquatic sample, for example, are posted on taxonomic lab sheets, which become source documents for data entry. These entities may includes fish, ichthyoplankton (fish eggs, larvae and post-larvae), phytoplankton (microscopic aquatic plants), zooplankton (miscroscopic aquatic animals), and benthic macroinvertebrates (organisms that live in the substrates of lakes, rivers or streams).

A given entry may require as many as two or three fields to uniquely classify it. In order to meet this requirement, Hess' staff replaced a standard MDS table handler with a larger resident disk table handler. Using EDVAL, the operator has only to key-in a minimum number of characters; usually the first four or five are sufficient. At that point, the EDVAL software takes over and displays the entire name and phylogenetic classification. EDVAL also displays the number of fields required to classify the biological entity. If family, genus, species and variety are needed, these too may be accessed quickly from the data stored on disk.

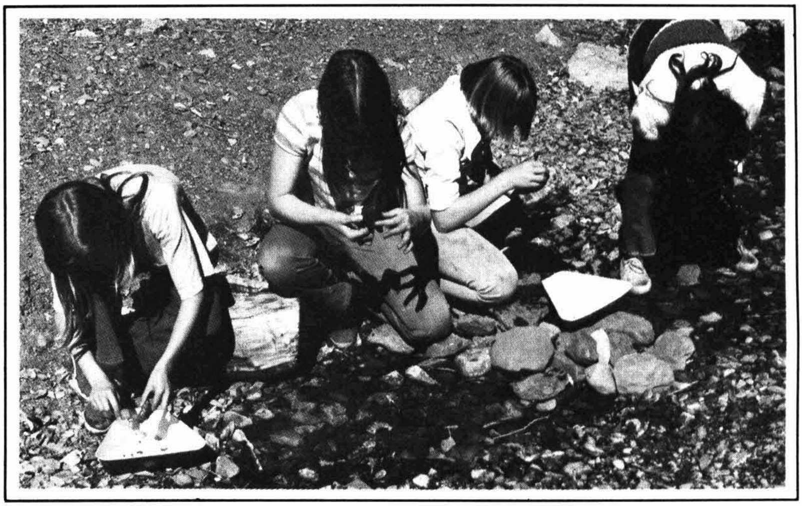
Hess explains, "EDVAL and the editing and validation capabilities of the MDS System 2409 have reduced our data entry error rate from 30% to 1–2%. Further, we have the ability to go back and update, delete or change data stored on the disk. The ability is especially important in light of the fact that new scientific discoveries and sampling methods sometimes create the need for new or modified formats."





ENVIRONMENTAL EDUCATION TODAY

A nascent discipline that "is beginning to work in small yet significant ways"



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It is imperative at the outset to agree on a working definition of "environmental education." There is by no means a consensus. The latest definitive book on the subject offers "no clear, single answer" to "what makes education environmental."

The definition that would probably get as many votes as any among professional environmental educators is that which evolved from a recent Belgrade conference under UNESCO auspices.

There are a number of "loaded" terms in that definition that help account for both the problems and the potentials of environmental education.

Defining the discipline

First, environmental education is "life-long." Some of our environmental problems cannot wait the arrival of a new generation with a surer ecological conscience. Some environmental problems the next generation will face are now not in our ken. So environmental education programs have to encompass all ages continually. Because environmental education is not just what happens in the conventional sixth-grade science unit on conservation, it has not been possible to "package" it as we have been able to do with driver education, for example. Nor has it been possible to work through only one echelon of the country's educational apparatus, or only one set of local, state, or federal bureaus, or only one level of parent-teacher associations.

Second, environmental education is "multidisciplinary." While the biological and physical sciences enable us to discover and understand the basic operations of the biosphere, it is the social sciences and the humanities that enable us to discover and deal with human perceptions of and interactions with natural ecosystems. Even more fundamentally, environmental education is concerned with the *interrelationships* among the fields of knowledge, if only in response to the basic ecological principle that everything is connected to everything else. The multidisciplinary nature of environmental education again has made it difficult to penetrate the established organization of our educational system.

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Environmental education . . .

. . . a life-long, multidisciplinary approach to teaching, mass communication, community participation, or some other activity aimed at the development of a world population that is aware of, and concerned about, the environment and its associated problems and that has the knowledge, skills, attitudes, motivations, and commitment to work individually and collectively toward solutions of current problems and the prevention of new ones.

Third, environmental education is multi-process. What might be called the environmental education system includes all media of communications, government agencies, voluntary associations, business and labor, and a wide range of informal educational organizations, as well as schools and colleges. There can be no single environmental education curriculum, instructional method or learning mode.

Finally, environmental education assumes a certain consensus on "current problems" and on their "solutions." The fact that environmental education has a public problem-solving stance renders it a volatile proposition for both public school teachers and college professors, more comfortable—and safer—in the antiseptic confines of the classroom. Try attacking blatant water pollution in a papermill town, or excessive air conditioning in the Sun Belt!

It is from its complicated nature, however, that environmental education offers the greatest possibilities for progress. Its multidisciplinary nature is exerting significant impact on teaching, research, and public service. Its multi-process characteristic capitalizes on the manifold communication avenues that exist in a democracy. And the focus of environmental education on a search for solutions to public problems stimulates that ever-needed link between learning and life.

Environmental education act

Environmental education was not born with the Environmental Educational Act of 1970. All P.L. 91-516 did was provide token federal institutionalization. As we have defined the term, the roots of environmental education go back to the nineteenth century. Environmental action in modern form may be said to date from 1954 when an unprecedented consortium of conservation groups successfully blocked a major dam that would have flooded Dinosaur National Monument.

What came to be called environmental communication hit full stride in 1962 with the publication of Rachel Carson's **Silent Spring.** This was followed in rapid order by Stewart Udall's **Quiet Crisis,** a paperback edition of Aldo Leopold's **Sand County Almanac,** and Robert and Leona Rienows' **Moment in the Sun,** Barry Commoner's **The Closing Circle,** and Paul Ehrlich's **Population Bomb.**

The term "environmental education" was coined in 1964, and a 1968 issue of *Education Record* carried an article on "The University and Environmental Education." A 1969 issue of the Pennsylvania Education Association's journal was devoted to environmental education, and the same year saw the appearance of *The Journal of Environmental Education.* On the crest of E-Day in the Spring of 1970, every general circulation magazine in the country carried a cover story on environmental issues. Today there are 93 specialized environmental publications with significant readerships.

So the Environmental Education Act of 1970 was the expression of a movement, not its progenitor. The Act called for an investment of $4 million in 1971 and increasing amounts thereafter, but only $2 million a year has ever been appropriated. In 1971, out of 1925 proposals only 71 were funded, and 37 of those were for less than $10 000 each. The next year, the U.S. Office of Education "lost" the annual appropriation in its bookkeeping system. A posture of benign neglect continues to characterize the administration of the Act. It is currently in a "lame duck" year.

But the Act has had symbolic importance exceeding its own substance. As an expression of the will of Congress, it has opened up to environmental education programs other sources of federal funds, such as the Water Resource Research Act of 1964, the Elementary and Secondary Education Act of 1965, the Higher Education Act of 1965, the Vocational Education Amendments of 1968, and

5 basic themes of environmental education

Unity

All components of any system are, in varying degrees, interconnected and interdependent. The integrity of the biosphere, and of humankind as a resident, is dependent upon the intricate balance of many subsystems—biophysical and socioeconomic.

Fragility

No social system is immutable. All natural systems have a limited tolerance for perturbation. The rate and extent at which physical and social degradation is introduced into the environment as well as to the rate and extent at which energy is dissipated, and natural and human resources are exploited or manipulated, must be considered.

Diversity

Long-term biological and sociological evolutionary processes invariably move toward increased complexity and higher levels of organization. By virtue of their diversity, mature natural and built ecosystems are adaptive enough to withstand a variety of traumas without loss of identity. But the cultural intrusions of modern man have reduced ecological variety and have threatened loss of stability to various ecosystems and ultimately to the total biosphere.

Quality

Once seemingly efficient technologies and cultures have proven counter-productive in that they fail to function symbiotically with natural systems and human nature. If an environment capable of fulfilling humankind's higher-order aesthetic and humanistic needs is to be restored and maintained, certain value reorientations, some difficult tradeoffs, and some changes in life-style are in order.

Polity

Environmental protection calls for a public decision-making process equipped for surveillance of the total environment and capable of imposing long-range economic, social, or legal sanctions against those elements presenting a threat to the public interest.

the continuing appropriations to the Cooperative Extension Service, the National Science Foundation, and the Sea Grant Program.

All told, however, the U.S.'s investment in environmental education has not been in keeping with the magnitude of the task. By and large, the cost of environmental education has been assumed by local and state educational systems, and by voluntary associations that have been in the vanguard of environmental action.

One federal act, however, has made a major impact on public environmental education. The National Environmental Policy Act of 1969 pronounced environmental quality an official American goal and, to that end, required that any major expenditures of federal funds be accompanied by an environmental impact statement (EIS). Many states followed suit.

The EIS requirement gave substance to cross-disciplinary instruction in public schools, lent focus to curricular innovations in colleges and universities, gave the news media an important point of entry to environmental coverage, energized the campaigns of voluntary associations, and confronted government agencies and private industries with the realities of the environmental decade.

What's being taught?

In a country where local control of public education is an article of faith and fact, it is very difficult to generalize about the current nature of environmental education, particularly in the absence of any current national survey. The U.S. Office of Education has yet to render a meaningful report on what federal monies have produced under the modest programs funded. In a recently published book, **Environmental Education in Action,** the authors have tried to identify and describe some representative public school activities today.

In essence, environmental education in the elementary and secondary schools is a relatively new approach to teaching about our relationship to our environment, an integrated process dealing with our natural and man-made surroundings, aimed toward developing behavior patterns that will enhance our survival in a world of finite resources. Environmental education is *not* simple nature study or outdoor resource management, although they are properly included; it is not a cumbersome new program requiring big outlays of funds or a self-contained course to be added to an already crowded curriculum.

While environmental education programs may differ greatly in their details, most of them thus share certain common characteristics. First, a recognition of environmental problems on a scale transcending yesterday's concerns. Second, a hard core of ecological content, presented with varying degrees of rigor. Third, a component of conscience, of a value system. Fourth, a commitment to private and public action. And fifth, a focus on a comprehensive rather than compartmentalized approach to change in man-environment relationships.

What is not being taught?

Environmental education has not been accorded a primary place, even a clear place, in the curricula of the schools. Much lip service has been rendered within the educational community to the environmental cause, particularly in the present decade, but concomitant outpouring of coordinated support has been lacking. There has been no environmental equivalent to the educational space race of the 1950's, no NSF-style (and level) of support for environmental education.

Certainly, there has been no lack of recognition of environmental problems in the classroom, but such recognition often surfaces on a simplistic, emotional level. The idea of "punishing" industry for its participation in environmental degradation is easy to espouse, but the question of how to chastise the perpetrator and correct the problem without massive negative societal effects is tougher and not so readily addressed. While it is not difficult to preach the "morality" of life-styles of high environmental integrity, the consequences of maintaining such life-styles are not generally well communicated.

Where do such concerns fit within a departmentalized, compartmentalized curriculum? They are not among the "basics," in the sense of the three R's, nor are they solely the concern of science, or social studies, or the language arts, or the humanities, or vocational education. Are students intellectually equipped to deal with such complex problems on the primary level? If so, they are one-up on their elders. In which of the 45-minute "pigeonholes" does environmental education belong? If it belongs in more than one, how should it be coordinated between/among them? Should it be a separate "subject"? If so, who would teach it? And in all cases, at what expense in terms of time and space for the remainder of the curriculum, including those items that have been there traditionally and those others that press for curricular consideration?

These questions are easier to ask than to answer: no attempts at responses are made here. But a few simple facts are evident. There are, have been, and will continue to be heavy pressures on the schools to expand their roles as social agencies as well as to include more and more specialized subject matters in response to a multiplicity of specialized concerns. There is, has been, and will continue to be strong interest in returning to the basics. Concurrently, there is, has been, and will continue to be massive criticism of a perceived lack of effec-

Freshwater biology. *These students are getting a practical exercise at the National Wildlife Federation's Conservation Summit* tiveness on the part of the schools in performing such functions. Again concurrently, tightening public monies has made it increasingly difficult for the schools to respond to new demands, to cope with multiphased criticisms, even to determine what priorities are appropriate, or at least acceptable. It might be easier if the schools were to tell the public what the schools can and cannot do, but taking a strong stand when the school budget comes up for public approval annually is not easy.

Many of its proponents see environmental education as a process rather than a body of content. The common denominators we have listed above imply a marriage of content and process. They demand a real-world context rather than a set of abstractions and a clean set of academic exercises. At the same time, however, these denominators require solid conceptual bases in both the natural and social sciences plus development of an environmental conscience. Above all, they are predicated on an integrated view of the world, what it really is, how it all fits together, how the resolution of one set of problems may initiate another set.

It seems reasonable to say that schools deal effectively with environmental education to the extent that they are successful in integrating those common denominators. Unfortunately, it is not easy; it is not frequently accomplished. Those somewhat successful environmental educational problems have no rigid commonality of approach, no sacred set of subject matter. At best, such programs can serve as imperfect models that furnish clues for useful, functional approaches.

Oldsters participate. *There is no age barrier to environmental education as this New York state program illustrates*

The role of science and technology

One of the most significant features of the science curriculum reforms of the 1950's and 60's, as evidenced by many NSF-supported preuniversity educational efforts, was the involvement of professional scientists in the orientation, selection, and development of teaching materials for preuniversity science instruction. At least at the outset, scientists insisted that the "what" was less important than the "why."

We will stipulate that primary and secondary school science subjects are better taught today than before the days of PSSC, CHEMS, CBA, BSCS, ESCP, IPS, HPP, ISCS, SAPA, ESS, and their siblings, though some may not accept this viewpoint. One of the costs, however, has been less attention to "practical" concerns, to societal needs, and to real-life problems than is appropriate to environmental education.

Education in the social sciences, both primary and secondary, has historically not been concerned with contemporary problems though we will again stipulate that the "modern" K-12 social studies have made giant strides from the older-style political histories. What attention has been directed toward the contemporary scene has not focused on inherent scientific and technologic realities. Unfortunately, C. P. Snow's delineation of "the two cultures" has not created an impact sufficient to generate action in closing that gap with respect to either organizational patterns or curricular concerns; neither have the admonitions of others who support integrated views or decry the separatism of the natural and social sciences.

Perhaps the greatest contribution that might be made by science and technology in fundamental environmental education is in communicating its content and the social, political, and economic implications of its content, in language intelligible to the oft-targeted but elusive "intelligent layman." If environmental education is essential for everyone, as its proponents would insist, it follows that it must be presented in ways that are readily understandable. Science and technology are not the proper decision-makers here, any more than are politics, economics, or sociology. Educators must make the decisions of what to teach, how, and when, bringing into full play their expertise in how learning is properly and most appropriately facilitated. But they need help, and desperately, in knowing the truths of the complexities of the environment, the tradeoffs, the potential outcomes.

Getting involved, earlier

The "pollution mess" that scientists and engineers are called upon to clean up is often a mess they had a hand in making. As Eric Hirst, an Oak Ridge research engineer, has written, "Technology is one of the basic causes of our current environmental problems; engineers and scientists must share in the blame." The U.S. Department of Agriculture entomologists who refined DDT as an insecticide at Orlando, Florida, in 1942 had no idea, of course, that they were putting at eventual hazard the lives of eagles and humans; they were making Pacific swamps safe for soldiers. The physicists who unleased the power of the atom at Los Alamos in 1945 were likewise bent on winning a war. Yet, as historian Roderick Nash says, "The conclusion cannot be avoided: science, undiluted with ethical and humanitarian influences, can be humankind's greatest problem rather than its greatest blessing."

Clearly, environmental education has a role to play in the education of future scientists and engineers. Environmental science is not a synonym for environmental education. The sciences, of course, play a major role in any program of environmental education, but only one role. To address any environmental problem at its roots is to deal with the fundamental cause—man and his ideas, as Nash emphasizes. The undergraduate education of scientists and engineers that

Some current public school activities

- A New Jersey computer-based resource information font for teachers wishing to confront their students with environmental concepts, problems, issues, and options.
- A Maine network of local programs tied to a central demonstration program to heighten public awareness in maintaining and improving the quality of the total environment.
- An Indiana program built around 5-day visits by fifth graders to a nature center.
- An Ohio applied science learning unit for secondary school students with a community action concern.
- A Montana project featuring cooperation between the Bureau of Land Management and local schools.
- An Iowa program involving active student participation in the political processes necessary to implement solutions to environmental problems.
- A Pennsylvania curriculum aimed at developing attitudes and understandings rather than strictly the exposure to information.
- The outreach work of the TVA with Tennessee Valley schools.
- A computerized urban planning game focused on an air pollution control exercise.
- Florida's state-funded environmental education apparatus.
- An Alabama curriculum that confronts pupils with issues and options.
- A California schoolyard classroom devoted to the discussion of an ecological life-style and "appropriate" technology.
- A well-tested Wisconsin curriculum materials development system.

does not include such a departure is an anachronism today.

At the level of the professional master's degree, environmental education is increasingly represented by a program composed of equal increments of science and technology, public decision-making processes, analytical and design tools, and synthesis and integration.

Research training leading to the Ph.D. likewise is increasingly recognizing the legitimacy of team investigations that break out of the straightjackets of conventional disciplines. Many universities in their extension programs are offering refresher courses for practicing scientists and engineers in the political and ethical dimensions of technology.

In turn, scientists and engineers can and should make significant contributions to environmental education programs. Objective by nature, scientists can replace with ecological data the emotional tenor of many environmental debates. Pragmatic by training, engineers can serve to keep discussions on a real-world level. Both can help identify technological solutions that violate the first or second laws of thermodynamics and both can indicate what technologies are available yet underutilized.

That environmental education is headed in the right direction is confirmed by one very simple test. At one representative state university, we compared the course offerings in the years 1965–66 and 1975–76 in terms of how many course titles included the words *ecology, ecological, environment, environmental,* or *energy*. Discounting the shortcomings of this test, the net figure is still striking: a 443% increase in course offerings in the 10 years. The engineering school alone had a 338% increase. The summer term by itself had a 900% increase. Hopefully, academia's new environmental cast will produce a citizenry with an ecological conscience at last.

What is needed?

What important questions regarding environmental education ought educational researchers be formulating? An answer might include these queries.

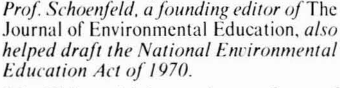
What modes of learning are best adapted to environmental education? What is the role of concept understanding in attitude formation, or vice versa? What is the nature of values as they affect behavior change, if they do? How can environmental education (EE) concepts be integrated into existing curricula? At what grade levels should specific concepts be taught? Does knowledge of EE concepts necessarily affect behavior? Can we accurately measure values with current methods?

At the post-secondary level, should general environmental studies precede, follow, or be taken concurrently with professional environmental regimens? How can we best determine the worth of an agency or method in meeting the over-all goals of EE? How does the determination and dissemination of relevant facts and the classification of values influence environmental attitudes? How can we maintain the distinction between teaching and preaching, between education and indoctrination?

Imposed values are not lasting guides for behavior. Accepting and implementing this simple rule may well be the single most difficult aspect of environmental education at all levels. That some of these issues, and others, are increasingly being addressed is evidenced by representative papers presented by educators at the 1977 convention of the National Association for Environmental Education.

When all is said and done, however, there are no Nielsen ratings for measuring public participation in environmental education or any environmental IQ tests to measure our national level of ecological literacy. It would not make any difference if there were.

The payoff in environmental education is in individual and collective action for an environment capable of sustaining life processes and fit for sanative living. On that score, the record is surely mixed. The authors are inclined to believe, however, that environmental education is beginning to work in small yet significant ways.



Clay Schoenfeld (l) *is joint professor of journalism and wildlife ecology, and chairman of the Center for Environmental Communications and Education Studies at the University of Wisconsin–Madison. Prof. Schoenfeld, a founding editor of* The Journal of Environmental Education, *also helped draft the National Environmental Education Act of 1970.*

John Disinger (r) *is associate professor of environmental education in the School of Natural Resources and associate director of the Educational Resources Information Center for Science, Mathematics, and Environmental Education (ERIC/SMEAC) at The Ohio State University.*

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ACS ADVANCES AND SYMPOSIUM TITLES ON PESTICIDES AND AGRICULTURAL CHEMISTRY

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Pest Management with Insect Sex Attractants
Morton Beroza, Ed.

This latest research explores the use of nontoxic behavior chemicals for pest control. Nine papers discuss: multicomponent pheromones, air-permeation with gossyplure, control of lepidopterous pests, and EPA registration requirements. Included also is a comprehensive listing from insect behavior-controlling chemicals, many of which may be useful in pest management.

192 pages. Cloth. (1976) $17.75

Arsenical Pesticides
E. A. Woolson, Ed.

Ten papers discuss current research on the analysis, soil behavior, biotransformations, accumulations, cycling, and modeling of arsenate and arsenical pesticides in nature. Specific topics include determination of traces of arsenic, behavior and phytotoxicity of arsenicals in soils, bioaccumulation, arsenic cycle, microbiological methylation, and arsenicals in animals.

". . . an excellent, up-to-date, and valuable review of the literature. . . ."

"Highly recommended for libraries serving graduate programs or research scientists involved in pesticide research."
Choice (1975) **July / Aug.,** 363

176 pages. Cloth. (1975) $12.50

Chlorodioxins—Origin and Fate
Etcyl H. Blair, Ed.

Fourteen papers discuss the latest research on radio labeling, crystal isolation, thermal stability, electron spin resonances and visible absorption spectra, photochemistry, and toxicology, perinatal effects, lethality, biological distribution of toxin, environmental significance, incidence, and mechanisms.

140 pages. Cloth. (1973) $10.50

Pesticidal Formulations Research. Physical and Colloidal Chemical Aspects
J. W. Van Valkenburg, Ed.

Fifteen papers survey critical surface tension of fibers, transport of a water-insoluble substance through a membrane, contact angle of surface-active agents, vapor pressure of pesticides, role of surfactants in sprays, biological activity, evaporation, spray formation and drift, and several studies on specific pests and pesticides.

212 pages. Cloth. (1969) $13.95

Pesticides Identification at the Residue Level
Francis J. Biros, Ed.

Is our environment really becoming more toxic, or are pesticides falsely condemned by instruments designed as quantitative rather than qualitative tools? Eleven papers discuss philosophical aspects of ultramicroanalysis, instrumental techniques, microchemical methods, and biological assay.

182 pages. Cloth. (1971) $12.95

Organic Pesticides in the Environment
Aaron A. Rosen and H. F. Kraybill, Eds.

Twenty-three papers give a clear perspective of environmental hazards in soil, water, and air; surveys effects of mammal enzyme systems, residues in human body tissues, effects of chronic poisoning by organophosphorus insecticides. Methods of sampling and analysis are included such as IR identification of chlorinated insecticides and electron capture chromatography to determine organic insecticides in water.

309 pages. Cloth. (1966) $19.50

Natural Pest Control Agents
Donald G. Crosby, Ed.

Plants and animals produce agents which can control life processes in insects or other plants. Twelve papers survey such known agents as repellents in arthropods; insecticides in pyrethrum and cruciferous crops; insect toxicants in bacteria; virus and growth regulators in plants.

146 pages. Cloth. (1966) $10.50

New Approaches to Pest Control and Eradication
Stanley A. Hall, Ed.

Eight chapters survey the "silver bullet" approaches in insect eradication, including male annihilation, chemosterilants, anti-feeding agents, bacterial disease, and sex attractants.

74 pages. Paper. (1963) $6.25

Air Pollution Damage to Vegetation
John A. Naegele, Ed.

Ten papers cover the chemical basis of the air pollution problem; damage from ozone, photochemical smog, PAN, and oxides of nitrogen and sulfur; acute and chronic responses of horticultural and agronomic crops; biochemical effects; plant toxicology; population shifts, and the future of crop production.

"The subject is well-treated, in a short but quite informative manner. The problems are depicted clearly." (Agro-Ecosystems (1975) **2**, *95-97)*

137 pages. Cloth. (1973) $10.75
137 pages. Paper. (1973) $6.25

Removal of Trace Contaminants from the Air
Victor R. Deitz, Ed.

Sixteen chapters provide critical and in-depth coverage of air pollution characterization and removal. The collection stresses interactions among particulates and gas phase contaminants; pesticides; occupational contaminants; cigarette smoke and aerosol filtration; sulfur dioxide; trace gas adsorption; nitrogen oxides; and high ozone concentrations.

207 pages. Cloth. (1975) $17.25

Mechanism of Pesticide Action
G. K. Kohn, Ed.

Fourteen papers take a three-faceted approach in discussing current research on the mechanism and metabolism of broad groups of pesticides, activity relationships of specific pesticides, and analysis of cellular and model systems. Specific aspects include insecticide metabolism, fungicides, acaricides, herbicides, and insect chemosterilants.

180 pages. Cloth. (1974) $12.50

Fate of Organic Pesticides in the Aquatic Environment
Samuel D. Faust, Ed.

Occurrence, recovery by extraction, confirmation by mass spectrometry and NMR, interaction with particulates, sorption by organic clays, herbicidal residues, photodecomposition of picloram, chemical hydrolysis and oxidation of diazinon, parathion and paraoxon, persistence of carbamates, and degradation of chlorinated hydrocarbons.

280 pages. Cloth. (1972) $17.75

Air Pollution Effects on Plant Growth
Mack Dugger, Ed.

Eleven papers present new avenues of research on the interaction of air pollution oxidants with biological systems. Topics include ozone effects on cell permeability; alterations in metabolite pools; pigmentation and physiology of plant injury; plant bioenergetics; and sites of ozone damage.

150 pages. Cloth. (1974) $10.50

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Energy resource development: the monitoring components

At the same time that this nation is developing its coal resources in the western part of the U.S., it is developing air & water instrumentation and monitoring techniques to ensure adequate surveillance and safeguards protective of health and welfare. George Morgan, director of the EPA Environmental Monitoring and Surveillance Laboratory, tells ES&T *readers of the activities of eight different federal agencies to determine the source, the transport, and fate of environmental pollutants.*

George B. Morgan
EPA Environmental Monitoring and
Support Laboratory
Las Vegas, Nev. 89114

It is necessary that adequate control technology be imposed upon energy resource development so that environmental pollutants are kept to an acceptable level. The objective of environmental pollution control is to prevent adverse effects of the pollutants. In order to achieve this objective we must know several types of information. First, we must establish the relationship between the exposure to and effects from the pollutants on the critical receptor. Second, we must know the relationship of the total exposure to which the receptors are subjected and the sources. And, finally once controls are implemented, we must evaluate their effectiveness in maintaining the exposure levels at an acceptable concentration.

Monitoring and measurements systems and techniques are essential in determining the types of information necessary. The information presented in this report covers 18 papers from eight different Federal agencies. This is truly a multimedia, interdisciplinary approach toward evaluating the total effects of energy development upon our environment. Through such an interagency effort, it is possible to develop a compatible data base to determine the source, transport and fate of environmental pollutants. It is only from such a compatible data base that logical decisions can be made as to the types of strategies for energy resource development.

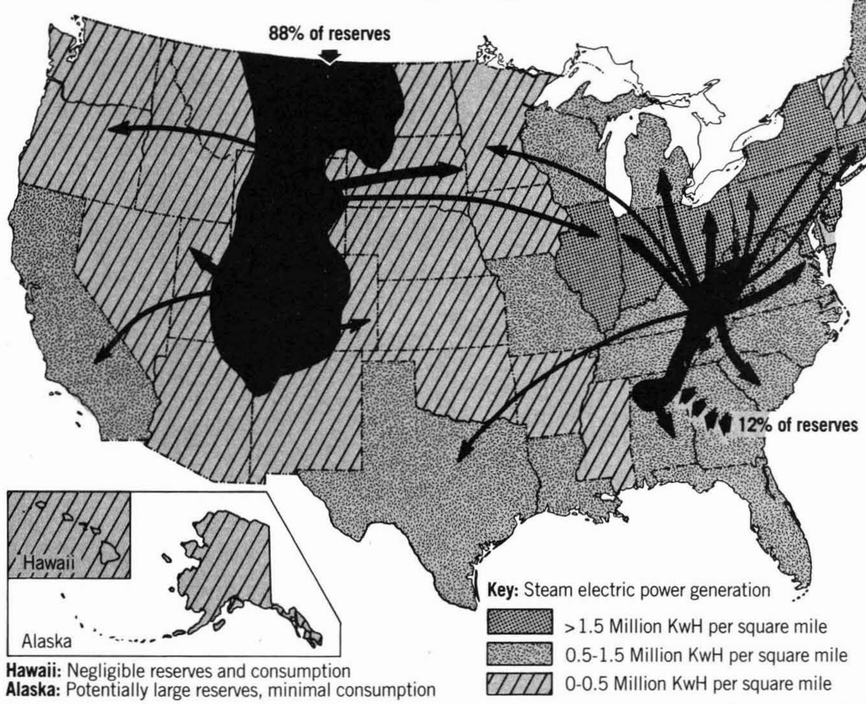
The Western Air Quality Monitoring and Western Water Quality Data Integration Projects conducted by EPA are designed to provide integrated and validated monitoring data (baseline and trend) and assessment reports for the western areas of the U.S. that are or will be the most seriously impacted by present or projected energy related development activities. In the air monitoring area, emphasis is placed on fine particulates, NO_x, SO_x, reactive hydrocarbons, toxic substances and visibility. The geographical coverage of studies to be conducted under this project includes the Northern Great Plains, the Four Corners area, oil shale areas of Colorado and Utah, the Black Mesa area of Arizona and areas of New Mexico. It is quite obvious that the continued and accelerated development of the various energy resources in the West potentially impact the environmental quality of these regions.

The air quality monitoring network in the Western Energy Resource Development Area (WERDA) now consists of 474 stations. Depending on the analysis desired, these stations are stratified according to the surveillance classifications of the sampling site, that is: population, source, or background. Less than half of these stations are located in rural areas and related to latter category of background monitoring sites.

Under the Interagency Energy Program significant progress has been made to identify and expand the air quality monitoring networks; for example, 77 sites have been added throughout the 8 state-region for sulfate and nitrate analyses. The network of the Ute Research Laboratory is also being used to collect samples for trace element analysis, that is: iron, cadmium, chromium, copper, lead, cobalt, manganese, nickel and molybdenum.

Visibility deterioration, probably the first observable impact on air quality from energy development and related activities, is not presently being quantitatively measured.

Low sulfur coal reserves vs. steam electric power generation



Hawaii: Negligible reserves and consumption
Alaska: Potentially large reserves, minimal consumption

We are proposing a network of visibility monitoring stations, and tentative sites have been selected.

A major advancement following the air quality monitoring data to be used for the regional scale assessments has been made through the initiation of a quality assurance program. Seventeen participating laboratories, including Federal, State, private and contractor, are involved in a uniformally applied audited, cross-check program that permits all data to be entered into a SAROAD data base (*ES&T*, November 1970, p 902).

The accelerated energy development in WERDA is in direct competition with other users for the limited available water resources. The extraction of raw materials, fuel refinement, transport and utilization and the accompanying demographic changes will place additional demands on available water. Loss of water through evaporation, adsorption into process waste streams and exportation to other regions is only one area where water resources will potentially be affected by the increased development activities.

In response to the need for baseline data with which the impact of energy development activities can be assessed, the U.S. Environmental Protection Agency has initiated a water quality data integration program. Participating with the EPA are elements of the U.S. Geological Survey. Several other Federal, State, and local agencies are cooperating in the study.

The specific objective of the program is to establish a base of biological, chemical, and physical information which will serve:

- as a baseline upon which alterations to water quality can be assessed
- as a basis for relating pollutants and/or effects to specific activities
- as a basis to provide input to the energy and environmental planning process.

Energy resource development scenario information and data regarding existing facilities together with existing and anticipated pollutant speciation, locations and concentrations data were used to identify a network of water quality monitoring stations in the WERDA. Over 200 currently active, data-rich (25 or more parameters monitored for a period of at least two years) surface water monitoring stations were selected for this network. Other stations and those of special studies are incorporated when and as necessary to fill specific data gaps. Data gathered are coded into STORET, EPA's water quality data base (*ES&T*, February 1971, p 115) and are retrieved for statistical analyses, listings and summarizations.

A quality assurance program has also recently been initiated that includes site visits to participating laboratories and performance audits, using periodic check samples.

There is a problem with the relatively large amount of data to be reviewed and assessed. This problem is compounded by the ephemeral nature of the western water resources. Many tributary streams to the major waterways are seasonally intermittent and flow in others is intermittently surface and subsurface.

USGS: The agency concerned in a big way with water monitoring

The Water Resources Division of the U.S. Geological Survey operates a network of 6200 water quality monitoring stations nationwide. Of these, 590 are in the Rocky Mountains and Northern Great Plains States of Colorado, Montana, North Dakota, New Mexico, Utah, and Wyoming, of which 73 are funded partially from EPA funds. EPA funds provide for the collection and analysis of a broader set of water quality parameters than that normally obtained by the USGS. These data are used to establish baseline water quality, sediment, and flow conditions against which future assessments of impact can be made. The report submitted by USGS gives reports obtained from three of the 22 projects involved in the interagency program.

One of the projects is to determine the quality of water at the Chaco River Basin of New Mexico. Located in this area is the Four Corners power plant (*ES&T*, June 1974, p 516) and its associated Navajo Coal Mines, as well as the San Juan power plant (*ES&T*, June 1976, p 532). Both are considering expansion. The proposed Western Gasification Company's gasification plant and the proposed El Paso Company's gasification plants will also operate in this area.

The major water users will derive their water supplies from the San Juan river system. As much as 500 000 acre feet of the annual average total of the 1.6 million acre feet as measured on the San Juan River at Shiprock may be diverted for these projects. Available data on the quantity and quality of the water resource at the Chaco River Basin are very sparse. The impact of the energy development particularly on water quality in the Chaco Basin and ultimately downstream in the San Juan River and Colorado River must be assessed. Data collected to date represent baseline and present water quality conditions of both surface and groundwater resources that will help to determine the effects of proposed energy development in the area. Both sources of water are extremely hard; the hardness is derived from calcium sulfate.

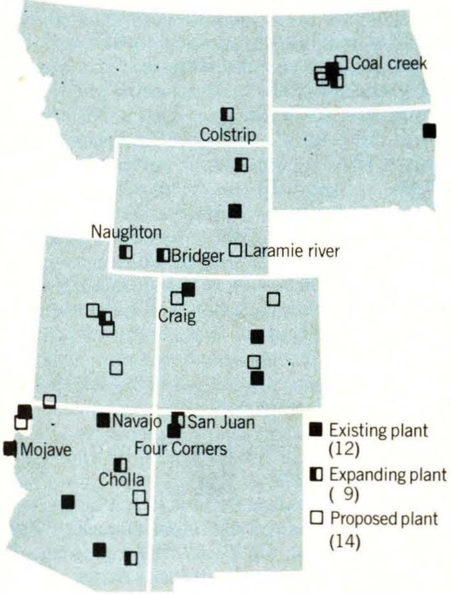
Another USGS project is studying the effects of acid mine drainage in southeastern Ohio. The first phase of this study was a reconnaissance of water quality at 162 sites to document the severity of the acid mine drainage problem and to pinpoint affected streams. The second phase involves a more comprehensive water quality sampling program. Phase II objectives include determination of source and chemical quality of water in each tributary, evaluation of influence of tributary conditions on mainstream water quality, and determination of material loading of streams and tributaries. Data to date indicate that the contrast in the data for an area of abandoned mines, and an area where reclamation had been practiced, is noticeable. The absence of acid drainage from reclaimed and working strip mines emphasizes the importance of rapid reclamation in the prevention of acid drainage.

A third USGS project is to determine water quality in the oil shale areas of western Colorado. The latest developments in oil shale industry indicate increased interest in the modified *in situ* approach. The objective of the basic data collection program is to obtain water quality data needed to define predevelopment conditions and to monitor the effects of construction and operation of oil shale mines, retorts and spent shale disposal areas. Data have been collected and summarized from 22 wells penetrating the three geological units likely to be involved in any *in situ* development.

An important concern of the EPA is impact of western coal and oil shale developments on groundwater, and the manner in which these impacts should be monitored. An EPA project to provide these answers is currently underway. The areas for study were selected where extensive development was being projected, that is: Campbell County Wyoming and the oil shale tract UA and UB in northeastern Utah.

Fossil fueled power plants greater than 300MW

(Named plants—capacity greater than 1000 MW)

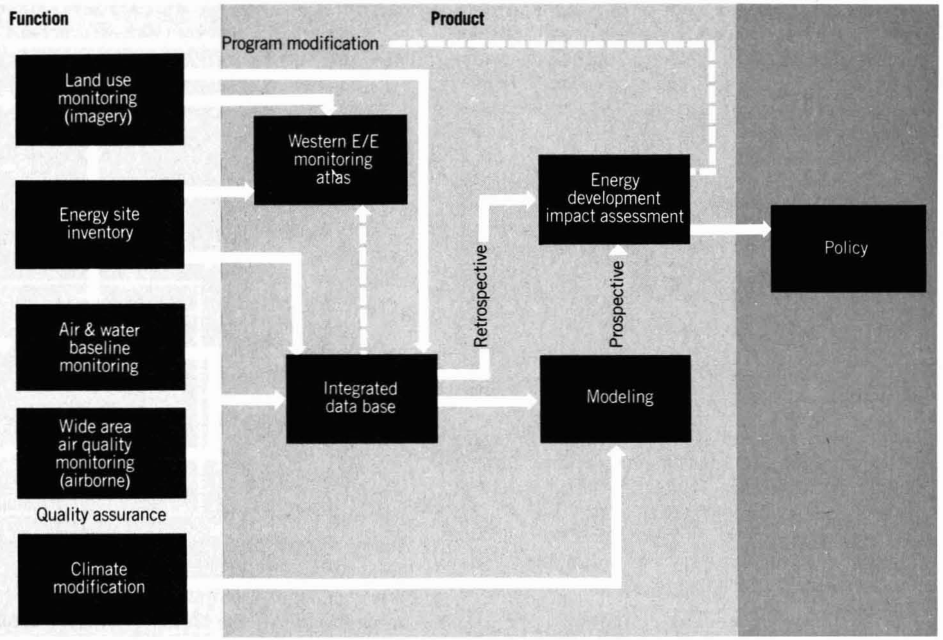


Groundwater: EPA has developed a predictive methodology for monitoring its quality

Groundwater availability and usage can usually be determined without much difficulty. Impacts on groundwater quality from mining, however, are much more difficult to assess. A typical misconception is that the baseline or background monitoring systems can also be used to assess the impact of man's various activities on groundwater quality. This is not true in most cases of subsurface pollution. Many years and even decades may pass before change in groundwater quality is observed. Once degradation of the subsurface regime has taken place, it is extremely difficult and costly to remedy. The EPA approach to this problem is to systematically monitor potential sources of pollutants before they enter the subsurface or the less accessible water itself. Over the next year, EPA plans to collect, organize, and interpret the background data for each potential pollution source.

At the end of the first year, a pollutant source prioritization report will be completed for each project area to identify the pollution sources needing the most detailed monitoring. Also at the end of the first year, another report will be completed that details oil shale mining approaches: Keregen recovery processes and hydro-generation processes. Following this report by three to six months will be a monitoring program designed for the coal mining aspects. A similar monitoring program design for the oil shale mining and processing operations is expected in 18 to 24 months. We expect to have operational monitoring networks established for oil and coal within 24 to 30 months.

Western energy environmental monitoring studies



An additional research need that concerns the oil shale aspect of the project has been identified. The oil companies, operating in tract CA, which is near tract CB in Colorado, have announced plans for oil shale development. Also, oil companies in tract CB have announced that they have developed an *in situ* process for the processing of oil shale. Monitoring for potential groundwater quality impact associated with *in situ* oil shale development will be difficult. A proposal for expanding the EPA monitoring program has been prepared.

Remote sensing: NASA and EPA are processing digital data acquired by Landsat and aircraft over coal strip mines while TVA is looking at SO_2 vegetation damage

In the summer of 1975, NASA and EPA entered into a 5-y program entitled Western Energy Overhead Monitoring Project for the purpose of transferring hardware and software techniques for processing remotely sensed digital data. The project has been divided into three phases. Phase I was an 18-month period during which time NASA capabilities were applied to processing digital data acquired by both Landsat and aircraft over coal strip mines in the Western United States. Following the evaluations of the hardware and software for this capability, a data processing system was developed, assembled, and transferred to EPA/EMSL-LV in January 1977. The system has been installed and key EPA personnel have been trained in the use of the data processing system during November/December 1976.

Recommended analysis procedures and multispectral data applications were documented in the NASA/ERL Report entitled: "Western Energy Related Overhead Monitoring Project Phase I Summary of Activities July 1, 1975 through December 31, 1976." The report is presently being reviewed by EPA to determine the application and effectiveness of the suggested procedures. During Phase II of the project, recommended procedures will be applied, verified, and evaluated using current data sets as well as future data sets made available through an intensive field program now underway. Research and development activities continue in parallel with objectives to evaluate new procedures for solving complexities associated with strip-mining activities data processing. These procedures, which are now being tested by pilot studies, will result in the state-of-the-art procedures converging into a final set of recommendations and future requirements.

A project underway in the Air Quality Branch of the TVA is entitled: "Remote Sensing of Sulfur Dioxide Effects on Vegetation." The objective of this project is to test, refine, and develop remote-sensing instrumentation and techniques for surveillance of SO_2 effects on vegetation in the vicinity of power plants. The work involves gathering and analyzing spectral reflectance data using imaging and non-imaging sensors and an array of instrument platforms including cherry pickers, helicopters, and airplanes. Progress to date has been primarily in the area of establishing procedures based upon past experimentation and determining plant damage following SO_2 exposure.

During 1977, selected crops and trees were subjected to fumigation of SO_2 under controlled conditions. These plants were examined by photographic recording and image analysis, spectroradiometry, and image acquisition from airborne sensors and cherry pickers with subsequent image analysis. The laboratory fumigation and photography of the affected plants have been completed. The field spectroradiometer operations and over-flights occurred in mid-summer 1977 when crops and trees were most susceptible to the effects of SO_2. Future work during the post-1977 period will concentrate upon remote sensing using satellite data. Currently available satellite imagery does not show promise for detecting subtle SO_2 effects on vegetation because of the limitation in image resolution. It is too soon to draw conclusions on the value of ongoing laboratory fumigation, chamber photographic experiments, color image enhancements and spectroradiometric measurements. By late 1977, these experiments should be completed and several remote-sensing overflights should have been conducted.

Air instrumentation developments

A prime emphasis is concerned with pollutants associated with the burning of coal

EPA is conducting a project for pollutant measurement methods development. These pollutants from coal burning include sulfur oxides, or acid. The organic products of coal combustion that may be described as carcinogens or more broadly materials of high physiologic impact are included. Existing methods for the measurement of sulfates in airborne particulates has long been known to be subject to interference.

Because sulfuric acid is known to be extremely reactive, its successful measurement must be accompanied in something approaching real time. Collection on a highly inert filter followed by rapid analysis has been sėlected as the potentially feasible approach. The separation, identification and eventual quantification of desired individual compounds from the incredibly complex mixture of organic materials generated by the combustion of coal is being attempted by combining in a synergistic fashion the separative resolution of gas chromatography, the analytic capability of mass spectrometry, and the recognitive skills of the computer. This appears the only feasible technique in today's state-of-the-art measurement.

One aspect of the ongoing research is leading toward developing a hypersensitive SO_2 instrument that has the sensitivity of approximately 0.1 ppb. This flame photometric analyzer, capable of operating aboard a small aircraft, is expected to be available this month.

A method developed for the microdetermination of sulfate and of strong acid has been modified and further improved. A technique has also been developed for collecting small particles on a fluorocarbon membrane filter followed by subsequent analysis by x-ray fluorescence spectrometry. This method has the advantage that it maintains separation of sulfuric acid from other particulate matter, therefore permitting selective analysis.

Tenax GC, a thermostable porous polymer, has been demonstrated to be capable of retaining the vapors of nonpolar substances very efficiently and of releasing them upon heating. This has become the favored method of sampling for organic vapors in the atmosphere. Samples collected by this method are thermally transferred to a gas chromatography column and the column effluent passed into a mass spectrometer for resolution.

Because of the importance of particulates relative to chronic health effects, several projects are underway in particulate methodology. Prototype standard reference materials for x-ray fluorescence analysis of particulates has been developed. The standards are being developed by thermally evaporating thin metallic films onto polycarbonate filters and by sputtering glasses containing known quantities of trace elements with an argon ion beam onto polycarbonate filters. Another approach is the use of fully characterized glass microbeads to simulate real particles.

Two measurement methods have been developed for particulate monitoring. The first is an instrument for measuring the size distribution of particles of known density. This instrument will be used to characterize aerosol generators. The second instrument is for the measurement of sulfur in particulate matter. The principle of operation is the combination of an electrostatic precipitator with a flame photometric detector.

Another method is being developed to distinguish the sulfur compounds in particulates by thermally evaporating the compounds. This procedure takes advantage of the fact that different compounds vaporize at different temperatures.

Work is underway to provide standard reference materials for elemental analysis of fuels and raw materials, for example, western and eastern coal.

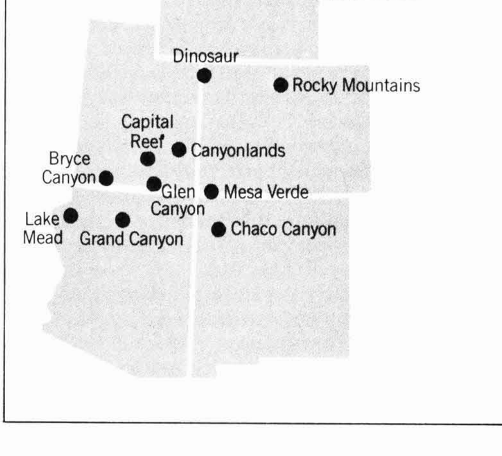
Occupational: NIOSH is involved in half-dozen projects including personal monitors

The Measurement Systems Section of NIOSH is presently conducting a project entitled: "Energy Related Research Program in the Measurements Research Branch." The six areas in this energy project are described.

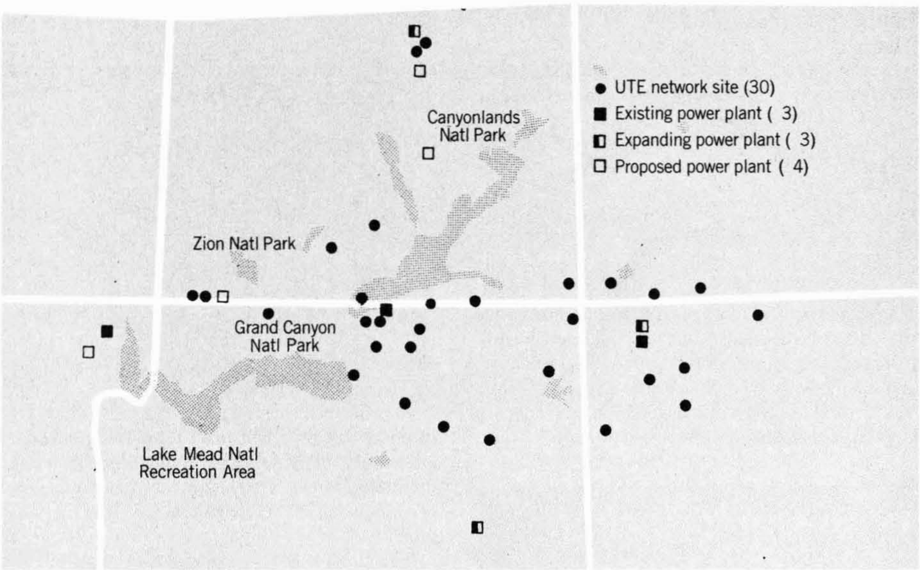
A portable, battery-operated fibrous aerosol monitor has been successfully developed. The instrument counts individual fibers of asbestos or fibrous glass in real time and gives the concentration of fibers per cubic centimeter in less

Proposed visibility monitoring sites

(At national parks, national monuments and national recreation areas)



UTE research lab HI-VOL network



than three minutes. The instrument is presently undergoing laboratory and field testing.

A miniature gas chromatograph has been greatly improved where column gas-handling valves and detector are etched onto the surface of a silicon wafer. The size of the entire gas chromatograph assembly makes it compatible to the data handling integrated circuitry so that the entire gas chromatographic instrument can be packaged in a volume not much larger than a pocket calculator. Some of the improvements that have been made on this system include:

- chemical bonding of the polyethylene glycol and Apiezon L lining material to the capillary column surface
- development of a thermistor detector compatible with the column size and volume
- development of miniature solenoid valves with nickel parylene membranes for carrier gas and sample gas handling. Sensitivity of previous versions of this GC at room temperature with a one microliter per second carrier gas flow rate and a sample volume of about 25 nanoliters have been on the order of 50 parts per million with good separation of peaks.

Initial work has begun on developing a portable microwave spectrometric analyzer. No significant progress has been made as yet.

Design criteria for an automated, personal sample fiber counter has been received and evaluated. This instrument will be based on light-scattering principles and is intended to complement the fibrous aerosol monitor mentioned above. It will be capable of counting fibers of asbestos and fibrous glass that have been collected on filters. This obviates the need for tedious human counting as presently required by the regulations.

Commercially available personal sampling devices for cold environments have been evaluated for their performance at temperature down to −50 °C. Various aspects of low temperature use have been considered, such as battery type, lubricant properties and physical damage. The results thus far indicate the primary limitation in all the pumps is the battery.

Work is currently underway to develop a specific personal sampling and analytical methods for hydrogen sulfide, H_2S, using a solid sorbent.

Nuclear and radiological: TVA intends to evaluate and refine the models used to predict the radiological impact of releases to the atmosphere from nuclear power

A study being conducted by TVA entitled: "Development and Evaluation of Improved Radiological Assessment Capabilities," is designed to improve radiological surveillance procedures regarding both sampling and radiochemical analyses of samples. The primary objective of this project is the development of an optimum radiological monitoring program. Studies leading to the attainment of this objective have been divided into three major subareas:

- development of a model intraorganization quality assurance program for radiological surveillance that will include all TVA environmental and nuclear plant laboratories
- improvement of radiological monitoring techniques with emphasis on gamma spectroscopy methodologies, which are among the most frequently employed analytical tools
- evaluation of presently used environmental radiological surveillance programs. The end product will be a surveillance program capable of meeting required analytical sensitivities and of providing adequate assessment information in a cost-effective manner.

A quality assurance program is being developed that will assist in demonstrating the accuracy and reliability of output empirical data and could serve as a model for the nuclear industry. During this fiscal year, it is envisioned that a manual entitled: "Handbook for Analytical Quality Control in Radiological Laboratories for TVA Laboratories" will be prepared and distributed nationwide.

Another report that will be forthcoming from this project will result from the studies of gamma spectroscopy methodologies. Interested organizations will have documented information regarding the resolution of complex gamma spectra and the assignment of lower levels of detection.

To supplement the ongoing work, additional studies should be performed in the following areas:

- Environmental radiological surveillance programs. Field testing of surveillance programs proposed in the ongoing study and the evaluation of exposure pathways not considered in detail in the present study should be conducted to ensure proper measurement of environmental impact.
- Analytical model refinement. Additional work will be necessary regarding the collection of radionuclides specific data around large nuclear facilities.

Water monitoring developments

A main concern is to find the composition of effluents from coal and oil shale gasification projects

The **EPA** supervises a contract to determine the composition of effluents from coal and oil shale gasification projects. More specifically, the objective of this project is to identify and measure chemical constituents in liquid and solid waste from several energy-related industries, with coal conversion and oil shale processes being studied first. To avoid or minimize unnecessary duplication in this area, all pertinent scientific and governmental literature has been reviewed in this area. The investigators have identified information gaps, sampled effluents at appropriate energy projects presently in operation and performed chemical analyses for chemical elements and volatile organic compounds. This report covers the six types of energy activities and produces tables of all elements and all organic compounds identified in the reports reviewed; for example, 41 chemical elements and 61 organic compounds were found in effluents from coal conversion and oil shale processing. This report also covers the methods for elemental and organic analyses.

Forty-five samples have been analyzed from *in situ* coal gasification at Hannah and Gillette, Wyoming, from a low Btu coal gasification plant at Morgantown, West Virginia, and from an *in situ* oil shale gasification project at DeBeque, Colorado and Laramie, Wyoming.

Examples of reported data illustrate the complexity of some of the analyzed samples. In some of the samples more than 74 elements and 200 organic compounds were reported. These analyses provide specific information that was not previously available for these energy processes.

Another EPA contract that was recently awarded will provide analogous information about effluents from several energy activities including coal gasification and liquefaction, oil shale processing, coal mining copper and coal-fired power plant operations.

A U.S. **Geological Survey** project is primarily in the area of development, testing and application of methods, techniques and instruments for measuring water and water-related constituents and characteristics. More specifically, the four areas of this project are:

- development of methods for characterizing and monitoring levels of chronic toxicity
- development of instrumentation of high volume analysis of petrochemicals and associated compounds
- development of bedload samplers for measuring stream sediments
- development of flumes and weirs and other devices and techniques for measuring sediment-laden stream flows. A major contribution of this study has been the development of methods permitting elucidation of the role of physicochemical factors on bio-availability of sediment-bound trace metals.

In order to meet the requirement for the large amount of data, this project is also developing criteria by which laboratory managers can determine the most effective methods and best instruments for analyzing large volumes of samples from petrochemicals and associated compounds.

This project is developing one or more samplers for accurately measuring the discharge of bedload in natural streams. This will be done by testing and calibrating existing samplers to define the operating characteristics and efficiencies in sampling different sizes of sediment under various hydraulic conditions. Based upon this information, sampler designs will be modified and new bedload samplers will be designed.

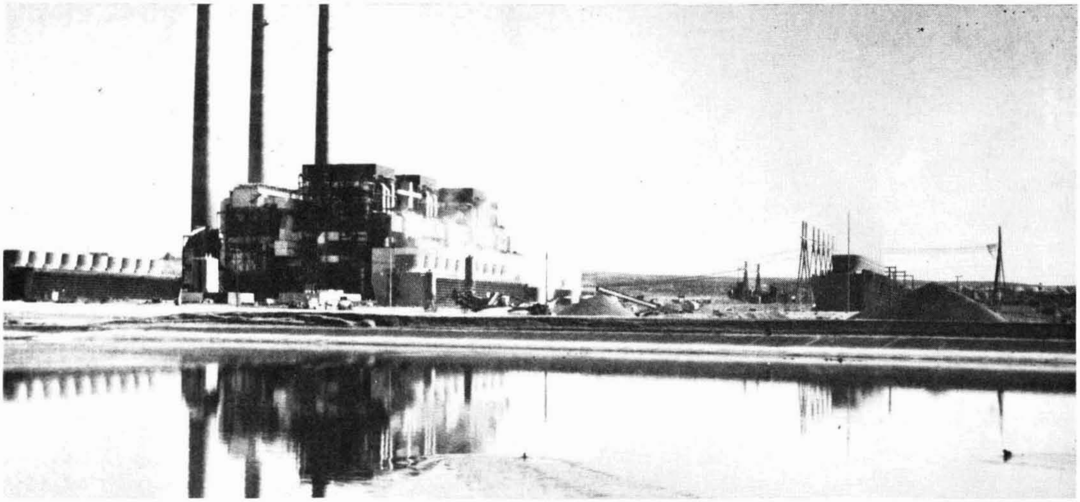
Investigations are underway into alternative techniques of measuring stream flow in open channels. Presently, three methods of measuring discharge or velocity are being considered, all of which require little or no contact with the water: fluorometric; photometric or video; and microwave.

The **Office of Marine Technology of NOAA** has a program which is directed at developing appropriate mechanisms whereby the measurement uncertainties associated with environmental data can be defined and controlled within prescribed limits. These data quality provisions when applied to environmental monitoring programs result in qualified data; that is, data with known error bands a defined relation to accepted standards.

Development of a laboratory dissolved oxygen standard is currently in progress. This standard will serve as a substitute for the Winkler method, which is currently used as a reference method for calibration of dissolved oxygen measurements systems. This standard will operate in a test bath over a range of −2 to 35 °C and from 0 to 40 parts per thousand in salinity. The dissolved oxygen range will span 0 to 15 parts per million.

The development of a dynamic test apparatus for laboratory testing of flow sensors is nearing completion. This apparatus will generate controlled dynamics superimposed on steady flows to determine measurements capabilities of flow sensors in a nonsteady flow environment. This test apparatus is being designed and fabricated by the Naval Ship Research and Development Center. The capability to stimulate field conditions will provide more realistic definition of sensor characteristics and limitation.

Transfer standards are utilized to assess the compara-



Navaho plant. *Arizona's largest power plant (2250 MW), Navaho, burns 24 000 tons of coal each day. Water, used for cooling and taken from Lake Powell, is placed after use in holding ponds seen here*

bility of results obtained between different laboratories performing similar calibrations. A conductivity/temperature/depth system has been selected as one of the transfer standards development areas. This system is presently undergoing a laboratory evaluation over a 6-month time interval to verify its measurement capability. Subsequently the system will be shipped to another laboratory for calibration. The uncertainity goal for this calibration technique is ±0.01% of the reading.

Control technology, standards, and remote sensing

Using data from Landsat and aircraft, EPA and NASA will be characterizing power plant and other emissions

A joint **EPA/NASA** project is being conducted to develop and apply an advanced electro-optical technique to the measurement and characterization of power plants and other source effluents. There are five tasks in this project.

A first task is to evaluate Raman lidar for remote measurement of the concentration of SO_2 at power plant stack plumes. An existing system at NASA Langely has been modified and improved and is now in the stage of being calibrated. Preliminary results show that at a range of 500 meters and night background light levels, the Raman lidar system can measure SO_2 concentrations of 1000 parts per million with 10%.

A second task is to apply aerosol scattering lidar techniques to the study of plume dispersion under various atmospheric conditions. This project involves modifying an existing lidar technique developed by NASA for dispersion studies of plumes from rocket launches. This task was originally scheduled for completion in 1976; however, no funds were allocated to this task during the second year because of severe budget constraints. Funds have been allocated for this task during the third year and work will be resumed subject to approval by the EPA Project Officer.

A third task is to develop and apply the tunable infrared differential absorption lidar technique to the remote measurements of molecular plume effluents. It employs the principle of differential absorption technique where sequential measurements are made first on an absorption line and then at a nearby wavelength off the absorption line, thereby providing information on range-resolved data for particular gases. The contract has been let for the tunable IR laser, which was delivered last year. This task is scheduled for completion in late calendar year 1978.

A fourth task is to develop the use of a laser hetrodyne detector as a means to increase the sensitivity of long path continuous wave absorption measurements using diffuse deflectors. The infrared heterodyne radiometer is scheduled for completion in December 1977, at which time a technical report on evaluation of this system will be furnished to EPA.

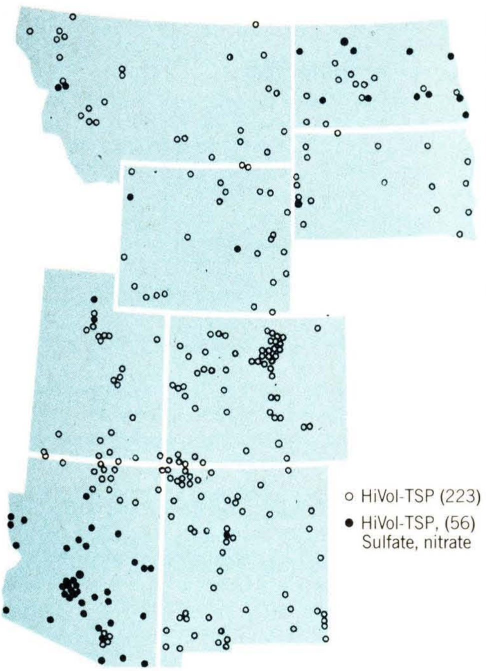
The objective of task 5 is to develop and deliver to EPA an improved *in situ* HCl chemiluminescent monitor evaluated at concentrations as low as 5 ppb of HCl in ambient and polluted air. The instrument has been evaluated in the laboratory to determine the operational characteristics.

NOAA is tracking particulate pollutants and measuring their transport by Doppler LIDAR

The Wave Propagation Laboratory, NOAA, is investigating lidar techniques for analyzing and tracing particulate pollutants from energy production. Improvement of lidar techniques is required to increase accuracy of identification and measurement of size distribution, shape factors and concentration. Two steps have been taken to improve remote detection and measuring methods for particular pollutants.

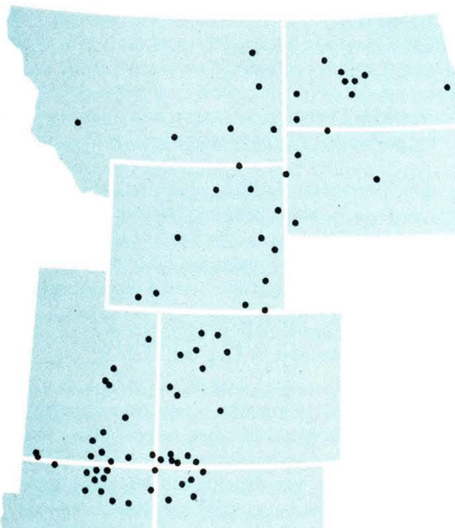
The depolarization technique has proven useful in studying plume dispersion in impact assessment programs and in distinguishing plumes from natural background aerosols. Preliminary results on two wavelength techniques have indicated potential for improved identification of

Particulate sampling in WERDA (1976)



New sulfate-nitrate monitoring sites

Sulfate-nitrate monitoring stations added during 1977 (79)



particles. Therorectical studies have resulted in improved identification of particles, and also in improved application of mathematical inversion algorithms to deduce the properties of particles from their electromagnetic signatures.

The depolarization technique in impact assessment studies has been successfully used at Colstrip, Montana. Initial tests of the dual wavelength system are encouraging for estimating mean particles sizes. In the immediate future, field tests will be conducted on the depolarization technique and the two wavelength techniques. Plans are being formulated for the study of differential absorption and inelastic scatter techniques.

The Wave Propagation Laboratory (NOAA) is also carrying out a project entitled Doppler lidar for measurements of pollutant transport. Doppler lidar measures the small-scale boundary layer wind field by frequency analyzing the signal backscattered from aerosols. The purpose of this research program is to develop and test operational techniques for the high-resolution measurement of atmospheric wind, turbulence, and aerosol backscatter aspects of pollutant transport.

Results include both technique refinement and field measurements such as wind profiles to a range of 1 kilometer and a height of 200 meters, velocity spectra of vortices, FM-CW lidar ranging, three-component velocity measurements, and plume backscatter. Planned research includes aerosol profiling, range extension and more efficient data processing. The research task is two years into a five year program. Milestones are on schedule.

An **EPA** study is evaluating airborne active remote sensing of pollutants associated with energy production. All of these systems utilize lasers to produce the interrogating signal and all of the systems operate in a downward mode from airborne platforms.

The first system is a downward-looking lidar that ranges aerosol scattering in the atmosphere below the plane. An operational system has been tested that features a real-time display of lidar return signals.

Ground and flight testing of a prototype earht-reflected differential absorption system for ozone monitoring has been completed and suggests great utility in studying long-range oxidant transport problems. A system for monitoring sulfur dioxide is being designed and a computer simulation model has been created to optimize component selection system response and display options.

Laser fluorescence techniques are presently being evaluated for use in monitoring the presence or effects of environmental pollutants in water. The concentration of surface water chlorphyll *a* in algae is presently being monitored using the helicopter-borne laser fluorosensor. A similar system is also being designed which will map and quantify surface water total organic carbons.

Dept. of Energy seeks information on air emissions and water effluents useful in guiding control technology

The objective of DOE's Division of Biomedical and Environmental Research program is to provide information on potentially troublesome effluents or emissions that would be useful in guiding control technology considerations and that is needed in order to develop a comprehensive assessment of environmental and health effects. The specific projects within this program are as follows:

The **Argonne National Laboratory** is developing methods for the chemical characterization and analysis of airborne particulate material as a function of the particulate size and time. This technique is based on the infrared spectroscopic analysis of particulate samples. Samples are collected with a Lundgren impactor. The extract of these samples is then analyzed using infrared spectroscopy. During August and September of 1975 a field comparison study was conducted in the St. Louis Region, comparing the Lundgren impactors and the EPA sampling method. Sulfates were found in the fine fraction as expected. Overall good agreement was found between the two methods.

A project being conducted at the **Brookhaven National Laboratory** is to determine the primary emissions of sulfate species from various types of fossil-fueled combustion sources and relate the magnitude of these emissions to variables affecting the combustion and emission control processes. This study also includes the collection and analysis of sulfuric acid.

A **Lawrence Berkeley Laboratory** project is to develop an elemental sulfur monitor. The first prototype of this sulfur monitor is in the final stages of construction and should be available for field testing by the time of the New Orleans Symposium. Another Lawrence Berkeley project is to develop a beta particle attenuation method for the large-scale measurement of total particulate mass of samples collected on membrane filter.

A **Lawrence Livermore Laboratory** project is to determine a satisfactory method for extending the sensitivity of the microwave ammonia monitor by preconcentration. The objective here is to select a preconcentration method so that ammonia can be measured quantitatively down to one part per billion by a field-usable instrument.

The **Los Alamos Scientific Laboratory** is evaluating the present EPA particulate sampling method (Method 5) and developing improved methods for extracting particulate samples from stacks. Over the last 18 months, this project has been directed at evaluation of glass fiber sampling filters operated at 120 °C and 10.3 cm/s air velocity. Efficiency for filters tested at 120 °C and 10.3 cm/s so far has exceeded 99.9% for particle sizes above 1 μm and approximately 99.6% efficiency for smaller particles.

A project at the **Oak Ridge National Laboratory** is to develop instrumentation and methods for characterizing aqueous effluents from oil shale, oil refining and geothermal sources. One feature of this research is to limit the application of analytical techniques that are presently available for routine analysis. These researchers are not only using instrumentation methods but also are developing and incorporating bioassay techniques into the characterization scheme.

The **Lovelace Biomedical and Environmental Research Institute** is improving the methods available for chemical and physical characterization of aerosols from process-utilizing fossil fuels, particularly coal. Methods for identification and quantitation of potential toxic organic emissions are being developed as are *in vitro* methods to predict the solubility of particles in the lung following inhalation. Reliable aerosol impactors have been developed for laboratory use.

The objectives of an **Ames Laboratory** project is to develop the basic sciences, the investigative methods and the hardware so that the demanding analytical requirements associated with the characterization and quantification of heavy weight organic pollutants and effluents from oil shale and oil-refining operations can be met in a viable practicable manner. In addition, this project is developing methods in hardware so that trace-element impurities occurring in geothermal effluents in brines can be determined quantitatively, simultaneously and with adequate sensitivity.

NBS is developing standard methods and standard reference materials for air and water pollutants

The National Bureau of Standards project entitled, "Standard Reference Materials, Instrumentation and Methods for Energy Related Air Pollution Monitoring," is directed toward providing standard reference materials for gaseous pollutants and airborne particulates arising from fossil fuel combustion and from the chemical extraction of fuels and raw materials. In addition, a project has been initiated for the development of a method to distinguish specific sulfur compounds in particulates derived from gaseous sulfur compounds.

Four standard reference materials for source monitoring have been issued that consist of gas blends of SO_2 in nitrogen concentrations ranging from 500 ppm to 2500 ppm. Other standard reference materials currently under development are NO_2 in air at concentrations ranging from 250 ppm to 2500 ppm, oxygen in nitrogen, and hydrogen sulfide in a hydrocarbon gas blend.

Other standards being developed for ambient air monitoring are carbon monoxide in air and gas blends of SO_2 and NO_2 in nitrogen. These standards are being investigated as alternatives to the NBS permeation tubes.

The National Bureau of Standards is also developing measurement methods and standard reference materials for monitoring water pollution associated with energy production and use. There are three areas covered in this program. The first is the energy-related water polluted analysis instrumentation, which is coordinated with the EPA Environmental Research Laboratory at Athens, Georgia. Projects currently underway in this area primarily deal with the measurement of organic species and of toxic elements. This method involves the coupling of electrochemical detection to liquid chromatography.

The second area in this program is the development of standard reference materials for monitoring water pollution resulting from energy production and use. During the first year of this program, workshops were held to determine the standard reference material needs for the analysis of the various effluents associated with offshore petroleum, oil shale, coal gasification, power plant operation, mine drainage, etc. A method has also been developed that may be used to generate known concentrations of organic compounds. Known concentrations of the compounds are coated on glass beads packed in a column for subsequent aqueous elution.

The third area encompasses a provision of standards for radiological pollutant measurement quality assurance. This effort is aimed at providing a series of standards for the measurement of radionuclides with an emphasis on alpha emitters. To date, SRM's for Po^{210}, mixed gamma solution, and mancos shale (Ra^{226} and Ra^{228}) have been delivered to EPA.

George B. Morgan *is the director of EPA's Environmental Monitoring and Surveillance Laboratory. Mr. Morgan is a member of the U.S. delegation to the U.N. Environmental Program Working Group, and to the U.S./U.S.S.R. Joint Working Group on Cooperation in the Field of Air Pollution Modeling, Instrumentation and Measurement Technology.*

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HACH Model 2100A Laboratory Turbidimeter

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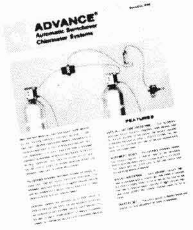
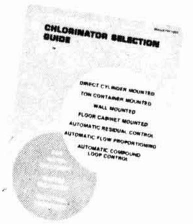
CIRCLE 11 ON READER SERVICE CARD

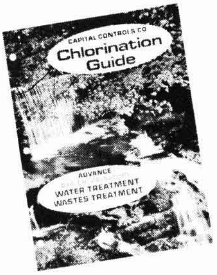
INFORMATION ON CHLORINATION

FOR WATER AND WASTEWATER TREATMENT



BULLETIN 1770, AUTOMATIC SWITCHOVER CHLORINATION SYSTEMS. Provides description of the ADVANCE chlorinator switchover system that assures continuous chlorination. Includes features, operation description and sizing table, as well as layouts and dimensions.





BULLETIN 4004, CHLORINATION GUIDE. Helpful background information various types of drinking water treatment, industrial process and washdown water treatment. Also covers aspects of municipal and industrial wastes treatment.

BULLETIN 1001, CHLORINATOR SELECTION GUIDE; a digest of information on the ADVANCE® line of gas chlorinators. Includes illustrations, descriptions, capacities and definitions of terms.

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CIRCLE 2 ON READER SERVICE CARD

Editorial Policy

Environmental Science & Technology reports on aspects of the environment and its control by scientific, engineering, and political means. Contributions by authors outside the full-time staff of writers appear either as feature articles or current research papers. The purposes of features and research papers are different, however, and are outlined for the convenience of authors.

Feature articles. Manuscripts submitted for possible use as features need contain no new or original information, but should attempt to explain some aspect of the environment, pollution, or pollution control so that a heterogeneous readership, composed of technically trained people and others with responsibility for or interest in environmental control, can quickly grasp the essentials.

Feature articles receive some editing attention from the full-time staff, and many of the guidelines detailed below for research manuscripts do not apply. Potential authors are encouraged to consult recent issues for the approach used in features and to contact the Managing Editor before writing.

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All research articles emphasizing analytical methodology for air or water analysis must include substantial application to environmental samples. *ES&T* faces some overlap with other journals in this area, and articles that do not contain, in the editors' judgment, a significant emphasis on environmental analysis will be returned to the authors for submission elsewhere.

Manuscripts should be prepared with strict attention to brevity. The vast majority of articles are expected to be fewer than four published pages. Processing time will be shortened if the editors do not have to return manuscripts to be condensed.

Contributed research papers will, in general, describe complete and fully interpreted results of original research. Review papers will be considered only when they serve to stimulate new research ideas or lead to new and significant generalizations.

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Send manuscripts to *Environmental Science & Technology,* 1155 Sixteenth St., N.W., Washington, D.C. 20036. Address feature manuscripts to Managing Editor; research manuscripts to Manager, Manuscript Reviewing Office.

Current Research Author's Guide

This manuscript preparation guide is published to aid authors in writing, and editors and reviewers in expediting the review and publication of research manuscripts in *Environmental Science & Technology.* For a detailed discussion with examples of the major aspects of manuscript preparation, please refer to "Handbook for Authors of Papers in the Journals of the American Chemical Society".

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Use specific and informative titles. They should be as brief as possible, consistent with the need for defining the subject of the paper. If trade names are used, give generic names in parentheses. Key words in title assist in effective literature retrieval.

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List the first name, middle initial, and last name of each author. Omit professional and official titles. Give the complete mailing address where work was performed. If present address of author is different, include the new information in a footnote. In each paper with more than one author, the name of the author to whom inquiries should be addressed carries an asterisk. The explanation appears on the Contents page.

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Consult a current issue for general style. Assume your readers to be capable professionals not necessarily expert in your particular field. Historical summaries are seldom warranted. However, documentation and summary material should be sufficient to establish an adequate background. Divide the article into sections, each with an appropriate heading, but do not oversectionalize. The text should have only enough divisions to make organization effective and comprehensible without destroying the continuity of the text. Keep all information pertinent to a particular section within that section. Avoid repetition. Do not use footnotes; include the information in the text.

Introduction. Discuss relationship of your work to previously published work, but do not repeat. If a recent article has summarized work on the subject, cite the summarizing article without repeating its individual citations.

Experimental. Apparatus: List devices only if of specialized nature. Reagents: List and describe preparation of special reagents only. Procedure: Omit details of procedures which are common knowledge to those in the field. Brief highlights of published procedures may be included, but details must be left to literature cited. Describe pertinent and critical factors involved in reactions so the method can be reproduced, but avoid excessive description. Results and discussion: Be complete but concise. Avoid nonpertinent comparisons or contrasts.

Manuscript requirements

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If pertinent references are unpublished, furnish copies of the work or sufficient information to enable reviewers to evaluate the manuscript.

In general, graphs are preferable to tables if precise data are not required. When tables are submitted, however, they should be furnished with appropriate titles and should be numbered consecutively in Roman numeral style in order of reference in the text. Double space with wide margins, and prepare tables in a consistent form, each on a separate 22 × 28 cm sized sheet.

Submit original drawings (or sharp glossy prints) of graphs, charts, and diagrams prepared on high-quality inking paper. All lines, lettering, and numbering should be sharp and unbroken. If coordinate paper is used, use blue cross-hatch lines since no other color will "screen out".

Typed lettering does not reproduce well: use black India ink and a lettering set for all letters, numbers, and symbols. On 20 × 25 cm copy, lettering should be at least 0.32 cm high—for example, with a Leroy lettering set, use template 120C and pen No. 0. Lettering on copy of other sizes should be in proportion. Label ordinates and abscissas of graphs along the axes and outside the graph proper. Do not use pressed wax for numbering or lettering; it rubs off in all the mailings and handlings necessary before receipt by printer.

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Number all illustrations consecutively using Arabic numerals in the order of reference in the text. Include a typed list of captions and legends for all illustrations on a separate sheet.

If drawings are mailed under separate cover, identify by name of author and title of manuscript. Advise editor if drawings or photographs should be returned to the author.

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The nomenclature should correspond, as closely as possible, to that used by the ACS primary publications.

Use consistent units of measure (preferably metric).

If nomenclature is specialized, include a "Nomenclature" section at the end of the paper, giving definitions and dimensions for all terms. Write out names of Greek letters and special symbols in margin of manuscript at point of first use. If subscripts and superscripts are necessary, place them accurately. Avoid trivial names. Trade names should be capitalized and defined at point of first use. Identify typed letters and numbers which could be misinterpreted, for example, one and the letter "l", zero and the letter "O".

Formulas and equations

Chemical formulas should correspond to the style of *Chemical Abstracts*. Chemical equations should be balanced and numbered consecutively along with mathematical equations. The mathematical portions of the paper should be as brief as possible, particularly where standard derivations and techniques are commonly available in standard works.

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Authors are requested to call special attention—both in their manuscripts and in their correspondence with the editors—to safety considerations such as explosive tendencies, precautionary handling procedures, and toxicity.

Acknowledgment

Include essential credits in an "Acknowledgment" section at the end of the text, but hold to an absolute minimum. Give meeting presentation data or other information regarding the work reported (for example, financial support) in a note following Literature Cited.

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ES&T RESEARCH

Accumulation of Saturated Hydrocarbons in Tissues of Petroleum-Exposed Mallard Ducks (*Anas platyrhynchos*)

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Center for Bio-Organic Studies, University of New Orleans, New Orleans, La. 70122

■ Mallard drakes were dosed with 5 mL a day of South Louisiana crude oil for 14 days. Tissues from control and experimental ducks were then examined for petroleum hydrocarbons by combined high-resolution gas chromatography and mass spectrometry. Three characteristics of the saturated hydrocarbon fraction were used to assess the presence of crude oil: the *n*-alkane distribution pattern, the presence of homologous series of petroleum-derived hydrocarbons, and the *n*-C_{17}/pristane ratio. Oil was found in every experimental tissue examined but the brain. The skin (and underlying adipose tissue) contained the highest level of saturated petroleum hydrocarbons. The other tissues were ranked relative to the skin as follows: skin > uropygial gland > breast muscle, heart muscle > liver > brain. The blood contained low levels of petroleum-derived hydrocarbons 3–4 h after the final dose of crude oil. That saturated petroleum hydrocarbons did not accumulate in the duck tissues in the same relative amounts observed in South Louisiana crude oil suggested selective uptake and/or metabolism.

In 1975 an estimated 6.113 million metric tons of petroleum hydrocarbons were dumped or seeped into the oceans (*1*). Much of this oil eventually made its way into the salt marshes and estuaries that function as nursery grounds for many marine organisms. The sensitivity of marine organisms to petroleum hydrocarbons is species specific and dependent upon the developmental and biological states of the organisms (*2–6*).

Seabirds are also sensitive to petroleum pollution, especially petroleum introduced by oil spills. The smothering effect of oil on waterfowl is well documented (*7*), but oil toxicity due to chronic exposure to low levels of petroleum is less well understood (*8*). Accumulated petroleum hydrocarbons have been found in various seabirds following oil spills (*9, 10*) and in oil-dosed adult (*11*) and baby chicks (*10*).

Mallard ducks that frequent or inhabit salt marshes and estuaries (*12*) are undoubtedly exposed to low levels of petroleum. These readily obtainable ducks would be excellent waterfowl with which to study the effects of chronic low-level oil exposure. Mallards exhibited sublethal toxic responses to single doses of petroleum hydrocarbons (*13, 14*), but Snyder et al. (*10*) were unable to detect petroleum hydrocarbons in the tissues of an oil-dosed mallard drake. In an attempt to reconcile this apparent contradiction, this study was undertaken to determine if mallard ducks do indeed accumulate petroleum hydrocarbons and, if so, in which tissues.

The information obtained will be of value in petroleum toxicity studies and perhaps in monitoring the level of petroleum contamination in waterfowl. This investigation represents a continuing effort by this laboratory to utilize combined high-resolution gas-liquid chromatography and mass spectrometry techniques to study the effects of petroleum pollution on the environment.

Experimental

Reagents. Spectroquality *n*-hexane and benzene (Matheson Coleman & Bell) were glass distilled prior to use.

Organism. Mallard ducks (*Anas platyrhynchos*) approximately one year old were obtained from Whistling Wings in Hanover, Ill. Four ducks were dosed by intubation with 5 mL a day of API reference South Louisiana crude oil for 14 days, and four undosed drakes served as controls. Purina Layena feed and tap water were provided ad libitum.

Extraction and Fractionation. The ducks were decapitated, and the following tissues saved for analysis: liver, breast muscle, skin (with underlying adipose tissue), heart muscle, brain, uropygial gland, and blood. Tissues were pooled prior to extraction. The wet weights of the control and experimental pools are given in Table I.

Total lipids were extracted by refluxing diced tissue at approximately 100 °C for 24 h in 60 mL of *n*-hexane and then 48 h in 60 mL of benzene. The *n*-hexane and benzene extracts were brought to 2–3 mL in a Buchi Rotavapor-R (Brinkman Instruments) set at 35 and 45 °C, respectively. The extracts were then combined, and the benzene was replaced with *n*-hexane by adding 50 mL of hexane and reducing the volume of the total lipid extract to 2 mL in a Buchi Rotavapor-R (Brinkman Instruments) set at 35 °C.

The total lipid extracts of the skin and liver were saponified prior to fractionation by refluxing overnight in 7% KOH methanol:water (9:1). The nonsaponifiable lipids were extracted with *n*-hexane and brought to a 2-mL volume on a Buchi Rotavapor-R before being subjected to column chromatography.

The total lipids, nonsaponifiable lipids, and API reference South Louisiana crude oil, obtained from the API reserve at

Table I. Wet Weights of Pooled Duck Tissues

Tissue	Control (g)	Exptl (g)
Liver	50.4	50.0
Breast muscle	53.4	51.0
Skin	48.7	48.8
Heart muscle	28.0	35.8
Brain	14.6	18.6
Uropygial gland	8.1	9.9
Blood	50.1	50.3

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Table II. Mass Spectral Identification of Saturated Hydrocarbons in South Louisiana Crude Oil

Peak	Compound
1	4-Methyloctane
2	*n*-Nonane
3	Branched $C_{10}H_{22}$
4	*n*-Propylcyclohexane
5, 6	Branched $C_{10}H_{22}$
7	Alkylated cyclohexane $C_{10}H_{20}$
8	*n*-Decane
9	Branched $C_{11}H_{24}$
10	*n*-Butylcyclohexane
11, 12	Branched $C_{11}H_{24}$
13	*n*-Undecane
14	*n*-Pentylcyclohexane
15–17	Branched $C_{12}H_{26}$
18	Alkylated decalin $C_{12}H_{22}$
19	*n*-Dodecane
20	C_{13}–isoprenoid
21	*n*-Hexylcyclohexane
22	Branched $C_{13}H_{28}$
23	C_{14}–isoprenoid
24	*n*-Tridecane
25	Branched $C_{14}H_{30}$
26	*n*-Heptylcyclohexane
27–30	Branched $C_{14}H_{30}$
31	C_{15}–isoprenoid
32	*n*-Tetradecane
33	*n*-Octylcyclohexane
34	C_{16}–isoprenoid
35	Branched $C_{15}H_{32}$
36	*n*-Pentadecane
37	*n*-Nonylcyclohexane
38	Branched $C_{16}H_{34}$
39	*n*-Hexadecane
40	*n*-Decylcyclohexane
41	C_{18}–isoprenoid
42	*n*-Heptadecane
43	C_{19}–isoprenoid (pristane)
44	*n*-Undecylcyclohexane
45	*n*-Octadecane
46	C_{20}–isoprenoid (phytane)
47	*n*-Dodecylcyclohexane
48–56	*n*-Nonadecane–*n*-heptacosane

Texas A & M, were fractionated on 30 × 1.0 cm i.d. glass columns. The columns were packed with 20 cm of activated silica gel (grade 923, 100–200 mesh) topped with 1 cm of activated alumina (F-20, 80–200 mesh). Each column was washed with 50 mL of hexane before a 2-mL sample was layered onto the surface of the alumina. Fifty milligrams of South Louisiana crude oil in 2 mL of *n*-hexane was added to a single column. The saturated hydrocarbons were eluted with 60 mL of *n*-hexane and the aromatic hydrocarbons, which were stored for later analysis, with 60 mL of benzene. Both fractions were brought to a volume of approximately 1 mL and transferred to separate 1-mL cone-bottomed minireaction vials. The volume of each sample was reduced to 10–500 μL prior to gas chromatographic analysis.

Analytical. Gas chromatography (GC) was carried out on a Hewlett-Packard Model 5840 gas chromatograph equipped with a flame ionization detector. The column was a 30 m × 0.3 mm i.d. glass capillary prepared in the manner described by Grob and Grob (*15*). The wettability and bonding strength of the glass column were increased by the formation of $BaCO_3$ crystals on its internal surface. This was followed by deactivation of active adsorption sites with Carbowax 20M (Applied Science, Inc.) and Emulphor (Applied Science, Inc.). The column was then coated with SE-52 (Applied Science, Inc.) by use of a static coating technique.

Combined gas chromatography and mass spectrometry (GC/MS) was done on a Hewlett-Packard Model 5931A GC/MS system equipped with a 5933A data system. The column for GC/MS was 166.7 m × 0.51 mm i.d. of stainless steel coated with OV-101 (Applied Science, Inc.). The column was cleaned with a series of acids, bases, and organic solvents and dynamically coated with a 30% solution of OV-101 (*16*).

Results and Discussion

The data obtained from gas chromatograms of saturated hydrocarbon extracts of tissues can be used to determine the presence of petroleum contamination. A gaussian distribution of *n*-akanes as opposed to a pattern of odd carbon dominance and the presence of certain homologous series of hydrocarbons are usually indicative of the presence of petroleum (*17*). The *n*-C_{17}/pristane ratio, which has been used as an indicator of oil degradation by marine organisms (*18*), may also in some instances serve to denote the presence of petroleum hydrocarbons. In this experiment gas chromatograms of tissues from oil-dosed ducks were compared, using the three criteria stated above, to equivalent gas chromatograms of tissues from control ducks to determine the presence or absence of oil.

Mass spectral identification of the saturated hydrocarbons of South Louisiana crude oil (Table II) indicated the presence of three readily identifiable homologous series of hydrocarbons: the *n*-alkane series (C_9–C_{27}), the isoprenoid series (C_{13}–C_{20}), and the *n*-alkylcyclohexane series (C_9–C_{18}). Since the *n*-alkane series is present in all biological systems (*19*), only the isoprenoid and *n*-alkylcyclohexane series were used as petroleum markers.

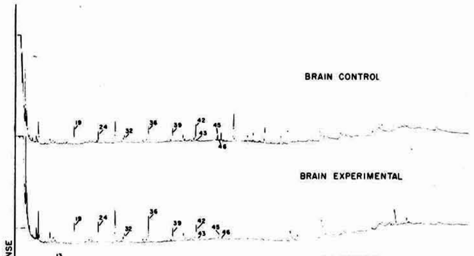

Figure 1. Comparison of gas chromatograms of saturated hydrocarbons in brain and skin of control and oil-dosed ducks with those found in South Louisiana crude oil

Numbers refer to compounds identified in Table II. Samples run on glass capillary column 30 m × 0.3 mm i.d. coated with SE-52. Helium flow rate, 2 mL/min; temperature programmed from 50 to 240 °C at 2 °C/min

The gas chromatogram of saturated hydrocarbons in South Louisiana crude oil illustrated in Figure 1 indicates that n-C_{13} was the major n-alkane, and that there was a somewhat gaussian distribution of the other n-alkanes. The isoprenoid series, peaks 20, 23, 31, 34, 41, 43, 46, and the n-alkylcyclohexane series, peaks 4, 10, 14, 21, 26, 33, 37, 40, 44, and 47, were also prominent. Numerous branched alkanes and at least one other cycloalkane were detected, but the mass spectral data did not allow precise identification of these compounds.

Also in Figure 1, the gas chromatogram of the crude oil saturated fraction is compared to the same fractions from skin and brain tissues of experimental and control ducks. The experimental skin showed the most pronounced indications of petroleum of all the tissues examined. In the experimental skin fraction there was a distinct gaussian distribution of n-alkanes about the most prominent n-alkane, n-C_{17}. Further indication of the presence of petroleum hydrocarbons was provided by the n-alkylcyclohexane series, which was observed from C_{15}–C_{18}, and the isoprenoid series, detected, with the exception of the C_{17} homolog, from C_{15}–C_{20}. In the control skin the major n-alkane was n-C_{11}. A slight odd carbon dominance pattern was observed from C_{21} to C_{27}, but not in the series of lower molecular weight n-alkanes. Pristane and phytane were present, but the remainder of the isoprenoid series and all of the n-alkylcyclohexane series were not detected. The brain did not accumulate a detectable level of saturated petroleum hydrocarbons. The gas chromatograms of hydrocarbons from the experimental and control brain tissues were almost identical. In both, there was a slight odd carbon dominance pattern from C_{12} to C_{18}, and except for pristane and phytane, no members of the isoprenoid series or n-alkylcyclohexane series were observed.

Gas chromatograms of saturated hydrocarbons of skeletal and cardiac muscle tissues from experimental and control ducks are presented in Figure 2. Petroleum hydrocarbons were detected in both the heart and breast muscles of the oil-dosed ducks. In the experimental breast muscle the n-alkane in highest concentration was n-C_{17}, and the C_{12}–C_{25} n-alkanes showed an odd-even ratio approaching unity. The isoprenoid series C_{16}–C_{20} was also clearly present. Normal C_{15} was the major n-alkane in the control breast muscle, and there was a distinct odd carbon dominance pattern from C_{12} to C_{20}. Except for pristane and phytane, none of the isoprenoid series or n-alkylcyclohexane series was detected in the control.

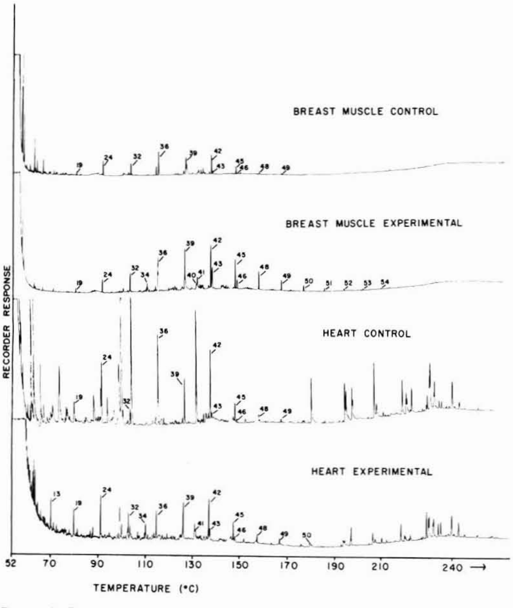

Figure 2. Comparison of gas chromatograms of saturated hydrocarbons in breast muscle and heart muscle of control and oil-dosed ducks
Numbers refer to compounds identified in Table II. Gas chromatographic conditions same as in Figure 1

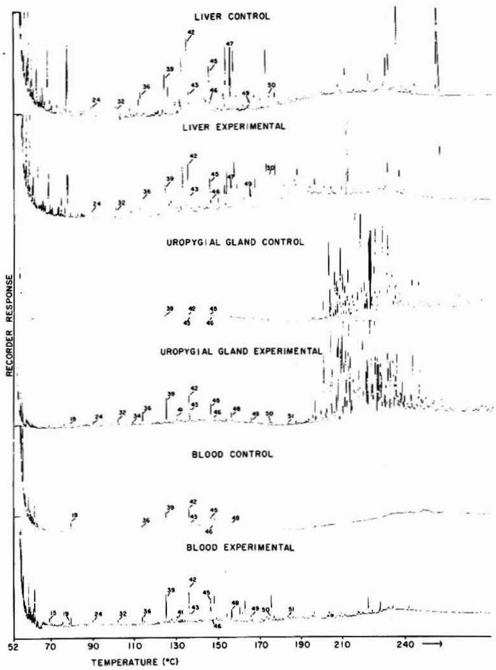

Figure 3. Comparison of gas chromatograms of saturated hydrocarbons in liver, uropygial gland, and blood of control and oil-dosed ducks
Numbers refer to compounds identified in Table II. Gas chromatographic conditions same as in Figure 1

In the heart muscle from oil-dosed ducks the petroleum hydrocarbons were less well defined. A petroleum n-alkane pattern appeared superimposed over a strong odd carbon dominance pattern similar to the one observed in the control heart muscle. In the cardiac tissue from oil-dosed ducks, the major n-alkane peak was n-C_{13}. The second largest peak, however, was n-C_{17}, and there was an almost gaussian distribution of n-alkanes from C_{14} to C_{21}. No n-alkylcyclohexanes were detected, but the complete isoprenoid series from C_{16} to C_{20} was observed. The n-C_{17}/pristane ratio was also significantly lower in tissues from oil-treated (4.21) compared to the control (11.52) group. The major n-alkane peak in the control heart muscle was n-C_{17} with C_{13} as the second most abundant. There was a pronounced odd carbon dominance pattern from C_{13} to C_{20}. Pristane and phytane were both observed. However, no other members of the isoprenoid series or any of the n-alkylcyclohexane series were detected.

Figure 3 illustrates gas chromatograms of saturated hydrocarbons of liver, uropygial gland, and blood from control and experimental ducks. Petroleum hydrocarbons are clearly evident in the uropygial gland, but only a low level of petroleum is indicated in the liver and blood of oil-dosed ducks. In the experimental and control livers, n-C_{17} was the major n-alkane and their distributions from C_{13} to C_{21} were essentially the same. Also, no members of the isoprenoid or n-alkylcyclohexane series were detected in livers from oil-dosed and control ducks. The n-C_{17}/pristane ratios gave the only indication of the presence of petroleum hydrocarbons in livers from the oil-treated group. The n-C_{17}/pristane ratio for this liver tissue pool was 2.89 compared to 3.68 for the control. This indication of the presence of petroleum in livers of oil-dosed ducks was confirmed by GC/MS identification of naphthalene, methylnaphthalene, and dimethylnaphthalene in the aromatic fractions from the liver tissue pool and also from South Louisiana crude oil but not in that of the control liver.

Saturated hydrocarbons from the uropygial gland exhibited a bimodal distribution. The major low molecular weight compounds in the experimental tissue was n-C_{17}, and there was a gaussian distribution of the other n-alkanes from C_{12} to C_{22}. The isoprenoid series from C_{16} to C_{20} was observed, but no n-alkycyclohexanes were detected. The low n-C_{17}/pristane ratio of the glands from oil-dosed ducks (2.23) compared to that of the control tissue (3.89) also indicated the presence of oil in uropygial glands of the treated ducks. As in the oil-treated group, n-C_{17} was the major low molecular weight n-alkane in the control gland, but no odd carbon dominance pattern was evident. Also, except for pristane and phytane, the isoprenoid and n-alkylcyclohexane series were absent.

In blood from oil-dosed ducks the major n-alkane was n-C_{17} with the other n-alkanes (C_{13}–C_{22}) present in a gaussian distribution. The isoprenoid series from C_{18} to C_{20} was also evident, but no n-alkylcyclohexanes were observed. The low n-C_{17}/pristane ratio for blood from dosed ducks (3.85) compared to the undosed control (6.36) further suggests the presence of petroleum after oil treatment. The dominant n-alkane in blood from treated and control ducks was n-C_{17}, but there was no odd carbon dominance pattern. Also, except for pristane and phytane, none of the isoprenoid or n-alkylcyclohexane series was detected in control blood.

In Table III the n-C_{17}/pristane ratios of the different tissues are compared. The large variance of the ratio among tissues of both control and experimental ducks indicates that use of the C_{17}/pristane ratio alone as indication of the presence of petroleum contamination in specific tissues could lead to erroneous conclusions, especially if adequate controls are not available. With regard to the conclusions drawn in this experiment, however, it is significant that the n-C_{17}/pristane ratios of all the tissues from oil-dosed ducks are lower than the corresponding control tissues except for the brain which, according to the other data, did not accumulate saturated petroleum hydrocarbons.

In the tissues of oil-treated ducks that contained petroleum-derived hydrocarbons, n-C_{17} was the most prominent peak in a more or less gaussian distribution of n-alkanes. On the other hand, South Louisiana crude oil had a different n-alkane distribution pattern, with n-C_{13} being most abundant. Such observations suggest that there was differential uptake and/or metabolism of the saturated petroleum hydrocarbons by the ducks. Pancirov (20) previously reported that the most prominent n-alkane in API reference South Louisiana crude oil was n-C_{17}. The discrepancy between Pancirov's results and the data reported here is possibly due to differences in the handling of the oil during fractionation and analysis. Great care must be taken to guard against loss of the more volatile compounds of petroleum.

Table III. Normal Heptadecane-to-Pristane Ratios in Tissues of Undosed Ducks and Those Given South Louisiana Crude Oil

Tissue	Undosed	Dosed[a]
Liver	3.68	2.89
Breast muscle	6.02	2.04
Skin	2.84	1.51
Heart muscle	11.52	4.21
Brain	10.00	10.50
Uropygial gland	3.89	2.23
Blood	6.36	3.85
Mean ± SD	6.33 ± 3.31	2.79 ± 1.06[b]

[a] South Louisiana crude oil n-C_{17}/pristane = 1.89. [b] Brain value not included in calculation.

Saturated petroleum hydrocarbons were detected in every oil-dosed duck tissue examined but the brain. Petroleum hydrocarbons have been observed in the tissues of several other marine birds. Snyder et al. (*10*) reported the presence of petroleum-derived hydrocarbons in the liver of an oil-exposed western grebe and in the liver and brain of a similarly exposed surf scoter. That no petroleum hydrocarbons were detected in the duck brain was unexpected since increases in brain and muscle hydrocarbons of immature herring gulls from the site of the West Falmouth oil spill have been reported (*9*). The lack of detectable petroleum hydrocarbons in the brains of oil-exposed ducks suggests that saturated hydrocarbons do not readily cross the blood brain barrier. Landan et al. (*11*) fed ^{14}C-octadecane to adult chickens and found that the brain had one of the lowest specific activities; the fat and liver had the highest.

No attempt was made to precisely measure the concentration of saturated petroleum hydrocarbons in the tissues of oil-dosed ducks. However, from the data collected thus far, it was possible to rank the tissues in terms of their ability to accumulate petroleum alkanes as follows: skin (with underlying adipose tissue) > uropygial gland > breast muscle, heart muscle > liver > brain. It appears that under these experimental conditions, petroleum hydrocarbons were stored primarily in the skin and adipose tissue.

Ducks in the experimental group received the final 5-mL dose of petroleum only 3–4 h before they were sacrificed. Since their blood showed only trace amounts of oil, it appears that most of the petroleum hydrocarbons were removed from the blood in 3–4 h.

Accumulations of hydrocarbons in the tissues of other animals have been shown to depend on dosage and length of exposure (*21, 22*). Landan et al. (*11*), however, found that there was a maximum effective dosage above which there was no increase in hydrocarbon absorption by adult chickens. These observations suggest that Snyder et al. (*10*) did not detect oil in the liver, kidney, brain, and fat of an oil-dosed mallard drake because the duration of the experiment (48 h) was too short. The two 10-mL doses of Bunker C fuel oil that Snyder applied were massive, but they probably exceeded the maximum effective dosage which made length of exposure the limiting factor.

Summary

Using gas chromatographic and mass spectrometric techniques, every tissue from the oil-dosed ducks showed evidence of petroleum-derived hydrocarbons but the brain. This suggests that saturated petroleum hydrocarbons do not readily cross the blood–brain barrier. On the basis of rough approximations of the amounts of saturated petroleum hydrocarbons accumulated, the tissues could be ranked as follows: skin (with underlying adipose tissue) > uropygial gland > breast muscle, heart muscle > liver > brain. Few saturated petroleum hydrocarbons were detected in the blood 3–4 h after the final oil dose, suggesting that the blood was rapidly cleared of the absorbed hydrocarbons. Note that saturated petroleum hydrocarbons did not accumulate in the duck tissues in the same relative amounts observed in the South Louisiana crude oil. This may result from differential uptake and/or metabolism of such compounds.

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Accumulation of Aromatic Hydrocarbons in Tissues of Petroleum-Exposed Mallard Ducks (*Anas platyrhynchos*)

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■ Mallard drakes were dosed with 5 mL a day of South Louisiana crude oil for 14 days. Tissues from control and oil-dosed ducks were examined for aromatic petroleum hydrocarbons by combined high-resolution gas chromatography and mass spectrometry. Petroleum aromatics were found in every experimental tissue analyzed. The skin and underlying adipose tissue had far more accumulated aromatic hydrocarbons than the other tissues, which included: liver, breast muscle, heart muscle, brain, uropygial gland, and blood. Aromatic hydrocarbons did not accumulate in the same relative concentrations as found in the crude oil. The more toxic 2 and 3 condensed ring aromatics were accumulated to a greater extent than the alkylbenzenes. Squalene was detected in the feed and in every tissue examined, including the blood. Biphenyl was also present in the feed and accumulated in every control and experimental tissue but the blood.

Aromatic hydrocarbons are of particular interest to those studying the effects of petroleum on waterfowl. Aromatic hydrocarbons are generally more toxic than paraffins, and the toxicities of various oils have been linked to their aromatic contents (*1, 2*). Aromatic hydrocarbons are also more water soluble than paraffins (*3*). Consequently, the water soluble fractions of crude and refined oils are made up predominantly of aromatic hydrocarbons (*1, 4*). Fortunately, high levels of aromatic hydrocarbons do not persist in the water column (*5*). That certain estuarine organisms concentrate petroleum aromatic hydrocarbons (*6–8*), however, evidences the potential hazard to estuary inhabitants chronically exposed to these compounds.

Knowledge of the tissue distribution of petroleum hydrocarbons accumulated by mallard ducks will be of value in elucidating sublethal physiological responses of these organisms to low-level oil exposure. In a previous paper (*9*) we reported the tissue distribution of saturated petroleum hydrocarbons in oil-dosed mallard drakes. In this paper we present complementary data on the distribution of aromatic petroleum hydrocarbons in the same mallard drakes.

Methods and Materials

Details of the experimental procedures were described elsewhere (*9*). Mallard drakes (*Anas platyrhynchos*) were dosed with 5.0 mL a day of API reference South Louisiana crude oil for 14 days. The ducks were sacrificed, and the liver, breast muscle, skin, heart muscle, brain, uropygial gland, and blood removed for analysis. Total lipids were extracted with hexane and then benzene. The liver and skin total lipid extracts were saponified prior to fractionation on a silica gel column. Saturates were eluted with hexane, and the aromatic hydrocarbons were eluted with benzene in the second fraction. Gas chromatographic analyses of the aromatic fractions were carried out on a glass capillary column coated with SE-52. A 0.02 in. × 500 ft stainless steel capillary column coated with SE-52 was used in the combined gas chromatography and mass spectrometry analyses.

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Table I. Mass Spectral Identification of Aromatic Hydrocarbons in South Louisiana Crude Oil

Peak	Compound
1	Isopropylbenzene
2	*n*-Propylbenzene
3, 4	Methylethylbenzene
5	Isobutylbenzene
6	1,2,3-Trimethylbenzene
7	Methylpropylbenzene
8	Diethylbenzene
9, 10	Dimethylethylbenzene
11	Tetramethylbenzene
12	Naphthalene
13	2-Methylnaphthalene
14	1-Methylnaphthalene
15	Biphenyl
16	Ethylnaphthalene
17	2,6-Dimethylnaphthalene
18	1,3-Dimethylnaphthalene
19–20	Dimethylnaphthalene
21	Methylbiphenyl
22	Methylethylnaphthalene
23–26	Trimethylnaphthalene
27–30	Dimethylbiphenyl
31	Diethylnaphthalene
32	Tetramethylnaphthalene
33	Trimethylbiphenyl[a]
34	Methylfluorene[a]
35	Tetramethylnaphthalene
36	Phenanthrene
37–39	Methylphenanthrene
40	Dimethyldibenzothiophene[a]
41	Dimethylphenanthrene

[a] Tentative identification.

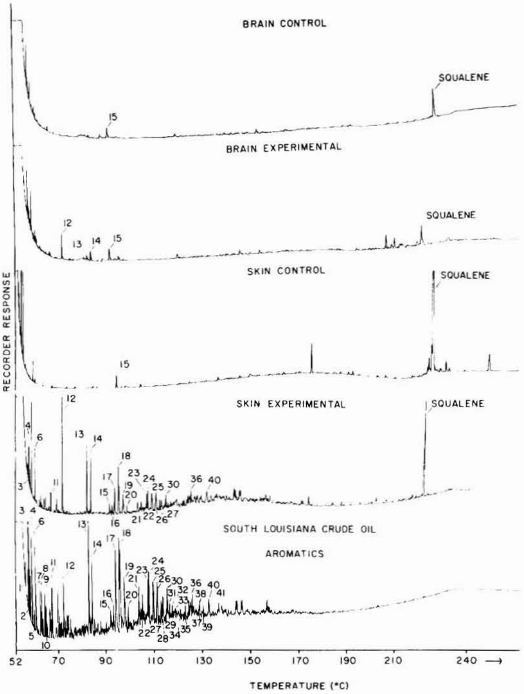

Figure 1. Comparison of gas chromatograms of aromatic hydrocarbons in brain and skin of control and oil-dosed ducks with those found in South Louisiana crude oil

Numbers refer to compounds identified in Table I. Samples run on glass capillary column 30 m × 0.3 mm i.d. coated with SE-52. Helium flow rate, 2 mL/min; temperature programmed from 50 to 240 °C at 2 °C/min

Results and Discussion

Aromatic hydrocarbons are synthesized by certain terrestrial plants (*10*) and microorganisms (*11*), but the alkyl-substituted aromatic hydrocarbons in petroleum have not been reported in biological systems (*12*). Evidence of such compounds in the tissue of oil-dosed ducks, therefore, was used as an indication of accumulated aromatic petroleum hydrocarbons. When alkylated aromatic petroleum hydrocarbons were not present in detectable amounts, the presence of an aromatic hydrocarbon in the tissue and oil samples, but not in the control, was used to identify it as an accumulated petroleum aromatic. The aromatic hydrocarbons identified in South Louisiana crude oil are listed by gas chromatographic peak number in Table I.

In Figure 1 the aromatic fractions from the skin and brain of oil-dosed and control ducks are compared to the benzene fraction of South Louisiana crude oil. In South Louisiana crude oil, C_9H_{12} and $C_{10}H_{14}$ alkylbenzenes (peaks 1–10) were readily detectable, as were several other alkylated aromatic series. The naphthalene series from $C_{10}H_8$ to $C_{14}H_{16}$ (peaks 12–14, 16–20, 22–26, 31, and 32) represented the major class of aromatics present. The biphenyl series from $C_{12}H_{10}$ to $C_{14}H_{14}$ (peaks 15, 21, and 27–30) and the phenanthrene series from $C_{14}H_{10}$ to $C_{16}H_{14}$ (peaks 36, 37–39, and 41) were minor constituents of the fraction.

Numerous aromatics of petroleum origin were present in the skin of the oil-dosed ducks. Several alkylbenzenes (peaks 3, 4, 6, and 11) were identifiable, and the complete naphthalene series (peaks 12–14, 16–20, 22–26, 31, and 32) was present. Representatives of the biphenyl series (peaks 15, 21, 27, and 30) and phenanthrene (peak 36) were also detected. In the control skin the only compound of possible petroleum origin was biphenyl (peak 15).

Naphthalene (peak 12), both dimethylnaphthalenes (peaks 13 and 14), and biphenyl (peak 15) were detected in the brain tissue of the oil-dosed ducks. Biphenyl was the only aromatic present in the brain tissue of the nondosed ducks. Detection of aromatic petroleum hydrocarbons in the brain was unexpected since our previous work (*9*) indicated that saturated petroleum hydrocarbons did not accumulate in the brain. This suggests that aromatic hydrocarbons may be selectively transported across the blood brain barrier.

A comparison of oil-dosed and control heart and breast muscle is presented in Figure 2. Naphthalene (peak 12) and biphenyl (peak 15) were detected in both the oil-exposed heart and breast muscles. Biphenyl was also present in both control tissues.

In Figure 3 the liver, uropygial gland, and blood of oil-dosed and nondosed ducks are compared. Blood from the experimental ducks contained naphthalene (peak 12) and both methylnaphthalenes (peaks 13 and 14). Naphthalene was detected in the control blood, but was also present in equivalent concentration in the sample blank for blood. Biphenyl was neither detected in the control nor the experimental blood samples.

Naphthalene (peak 12), both methylnaphthalenes (peaks 13 and 14), biphenyl (peak 15), and a single dimethylnaphthalene (peak 18) were detected in the oil-dosed uropygial gland, but only biphenyl was found in the control uropygial gland. In the experimental liver, naphthalene and biphenyl were detected. Biphenyl was the only petroleum-type aromatic found in the control liver.

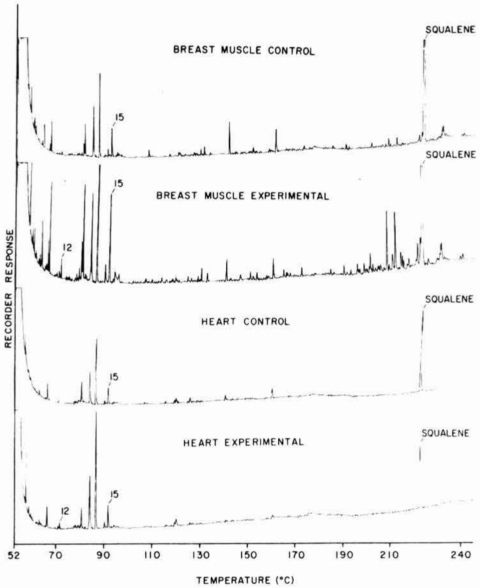

Figure 2. Comparison of gas chromatograms of aromatic hydrocarbons in breast muscle and heart muscle of control and oil-dosed ducks
Numbers refer to compounds identified in Table I. Gas chromatographic conditions same as in Figure 1

Biphenyl, therefore, was detected in every tissue sample but the experimental and control bloods. That biphenyl was also detected in South Louisiana crude oil suggested that the control tissue biphenyl might be of petroleum origin. It seemed unlikely, however, that biphenyl would accumulate to the exclusion of all other aromatic petroleum hydrocarbons in the control tissues when it did not do so in the oil-dosed tissues. Since a biological origin of biphenyl was also doubtful, the aromatic hydrocarbons in the duck's feed were analyzed. Twenty grams of Purina-Layena feed were extracted and fractionated, and the benzene fraction was analyzed by GC/MS. Biphenyl and squalene were detected in the feed. Although these data do not rule out the possibility of a biological origin of biphenyl, it suggests that the biphenyl in the control tissues was introduced via the feed. Biphenyl in the experimental tissues probably accumulated from both the ingested feed and oil. Lack of detectable biphenyl in the blood suggests that the blood had been cleared of detectable levels of biphenyl since the ducks had last eaten.

Squalene, a precursor of cholesterol (*13*), was found in every duck tissue but was in highest concentration in the liver. Liu et al. (*14*) reported that duck white meat (breast muscle) contained more squalene than either the dark meat or skin. The detection of squalene in the feed in this study suggests that at least some of the squalene present in the duck tissues may be of dietary origin.

Although precise quantitative data were not gathered in this experiment, it was obvious from the gas-chromatographic analyses that the skin accumulated aromatic petroleum hydrocarbons to a greater extent than any of the other tissues examined. Our previous work (*9*) indicated that the skin also accumulated saturated petroleum hydrocarbons in larger amounts than the other tissues. This is consistent with Tatem's (*7*) observation that excess hydrocarbons are stored in tissues that contain large amount of lipids, and suggestive of compartmentalization of accumulated hydrocarbons of the type proposed by Stegman and Teal (*8*) for the oyster.

Also, as was true for the saturated hydrocarbons (*9*), aromatic petroleum hydrocarbons did not accumulate in oil-dosed duck tissues in the same relative concentrations as those found in South Louisiana crude oil. This suggests differential uptake and/or metabolism of aromatic hydrocarbons. As illustrated by the experimental skin (Figure 1), the more toxic 2 and 3 condensed ring aromatics (*1*) were accumulated to a greater extent than the alkylbenzenes. The increase in concentration of naphthalene over that found in crude oil was particularly striking in the skin and was observed in each experimental tissue as well. Anderson et al. (*6*) reported that all of the estuarine animals that they exposed to water solubilized aromatic petroleum hydrocarbons accumulated alkylnaphthalenes to a greater extent, relative to exposure concentration, than naphthalene. This difference in accumulation of aromatics between ducks and other estuarine organisms may be due to a combination of several factors such as: species differences in aromatic hydrocarbon accumulation, differences in the methods of exposure, and differences in the hydrocarbon content of the oil fractions used. Anderson's group worked with aquatic estuarine organisms that were exposed to the predominately aromatic water soluble fractions of various oils or to water solutions of aromatic hydrocarbons (*1, 6*). The ducks in this experiment were administered 5 mL per day of whole crude oil by intubation.

Naphthalenes are acutely toxic petroleum aromatics (*4*) and are preferentially concentrated and retained in the tissues of certain estuarine organisms (*6*). Although some organisms are capable of metabolizing and excreting naphthalenes (*15–17*), these compounds are still considered by many to be the major contributors to petroleum toxicity (*1, 7*). Since naphthalenes are major components of the aromatic fraction of South

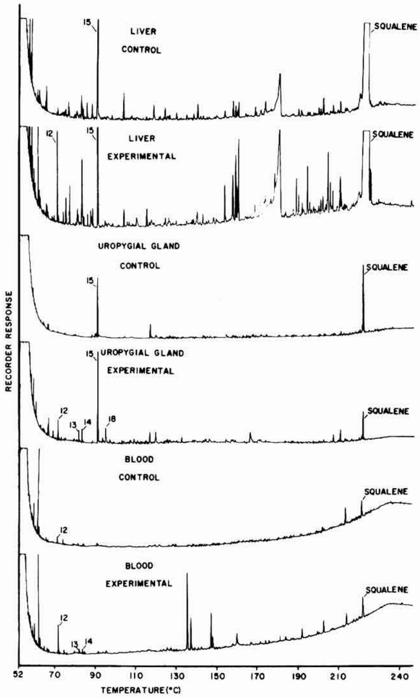

Figure 3. Comparison of gas chromatograms of aromatic hydrocarbons in liver, uropygial gland, and blood of control and oil-dosed ducks
Numbers refer to compounds identified in Table I. Gas chromatographic conditions same as in Figure 1

Louisiana crude oil, it was not unexpected that they were the dominant class of aromatics accumulated in each tissue.

The widespread accumulation of naphthalenes in oil-dosed duck tissues may account for certain of the sublethal toxic responses exhibited by mallards exposed to oil (*18, 19*). Hartung and Hunt (*19*) observed that mallards fed high doses of cutting oil and diesel oil exhibited symptoms of nervous disorders. They reported that organic phosphates present in these two oils reduced blood acetylcholinesterase activity, thereby interferring with portions of the nervous system. In a separate study, Roubal (*20*) found that naphthalene perturbed the membrane surfaces of fish nervous tissue and postulated that aromatics alter the capacity of membranes for ion exchange. The detection of naphthalenes in brain tissue of oil-exposed ducks in this experiment suggests that accumulated aromatic petroleum hydrocarbons may have directly contributed to the nervous disorders observed by Hartung and Hunt (*19*) in oil-dosed mallards.

To obtain a more complete picture of the effects of chronic low-level oil exposure on mallard ducks, it is now necessary to link quantitative tissue distribution of accumulated petroleum hydrocarbons to specific sublethal physiological responses. Efforts toward this end are presently underway at this and other laboratories.

Summary

Aromatic petroleum hydrocarbons were detected in every tissue from oil-dosed mallards analyzed by combined gas chromatography and mass spectrometry. The aromatics did not accumulate in the same relative concentrations observed in the South Louisiana crude oil, suggesting differential uptake and/or metabolism. Two and three condensed ring aromatics were accumulated to a greater extent than the alkylbenzenes in tissues of oil-dosed ducks. Of these, the complete naphthalene series, naphthalene, methylnaphthalenes, and dimethylnaphthalenes, was found in the highest concentration. The skin and underlying adipose tissue accumulated the largest amount of aromatic petroleum hydrocarbons. The detection of aromatic hydrocarbons in the brain suggests that they may contribute to observed sublethal effects of petroleum on the mallard's nervous system. Squalene, which is a biosynthetic precursor of cholesterol, was detected in every tissue analyzed including the blood. Biphenyl was found in every control and experimental tissue investigated but the blood. A nonbiological origin for the tissue biphenyl and at least some tissue squalene was suggested by the detection of biphenyl and squalene in the feed.

Acknowledgment

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Technetium-99 in the Atmosphere

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■ The technetium-99 and strontium-90 concentrations were measured from a composite rain sample (1015 L) collected in the spring of 1975. The concentrations were $(4.5 \pm 1.5) \times 10^{-3}$ and 0.11 ± 0.02 dpm/L, respectively. The results indicated that ^{99}Tc concentration decreased from those samples measured in 1961, 1962, and 1967, whereas the ^{99}Tc/^{90}Sr ratio showed a steady increase during this time period. All observed ^{99}Tc/^{90}Sr values were larger than the anticipated values from the neutron-induced fission of ^{235}U or ^{239}Pu, indicating sources of ^{99}Tc other than fission.

Element number 43, technetium, was only a theoretical possibility until 1946 when Perrier and Segrè (*1*) first synthesized and isolated it. Jensen (*2*) had previously established that technetium should have no stable isotopes. Hence, technetium is considered to be an "extinct" element—no longer found on earth. However, in 1951, Merrill (*3*) reported technetium in type S stars, demonstrating the fact that technetium existed outside the earth.

Natural terrestrially occurring technetium, as ^{99}Tc ($t_{1/2}$ = 0.21 million years), was established by Kenna and Kuroda (*4, 5*) when this fissiogenic isotope was isolated from African pitchblende. The origin of this trace quantity of technetium was attributed primarily to the spontaneous fission of ^{238}U. This represented the first isolation and identification of terrestrial technetium.

Immediately following this discovery, two rainwater samples were analyzed for ^{99}Tc (*6*). In 1971, Attrep and coworkers (*7*) reported the concentration of ^{99}Tc in 13 rainwater samples. Also in that year, Foti et al. (*8*) reported a neutron activation method for the determination of ^{99}Tc in air samples. Water samples of undisclosed origins were analyzed for ^{99}Tc by Golchert and Sedlet (*9*). More recently, Thomas (*10*) reported on the concentration of atmospheric ^{99}Tc in which the ^{99}Tc/^{137}Cs ratio was measured.

There is an interest in the presence of long-lived radioisotopes in the environment such as ^{99}Tc and ^{129}I. These nuclides are produced during nuclear testing and during reactor operation. Due to their entry into the environment, the knowledge of the amounts of these isotopes is important as a baseline inventory as well as a monitor of their behavior in nature.

Therefore, the purpose of this investigation was to determine the ^{99}Tc and ^{90}Sr concentrations in rainwater at a later period than those reported, in order to observe the trends for these radionuclides in the atmosphere and speculate on the environmental origins of technetium.

Experimental

Rainwater was collected in a 3 × 3 m rain collector located on the roof of the Science Building at East Texas State University, Commerce, Tex. (altitude, 170 m; 33° 15′ north latitude; 95° 53′ west longitude). The samples were acidified with nitric acid upon collection and transferred to containers in the laboratory for evaporation. The collection period was from April 1974 to June 1974, representing eight rains. A total of 1015 L was collected and evaporated.

All reagents used for the radiochemical analyses were the highest purity obtainable. All glassware, new or whose history was known, was washed thoroughly with soap and water, soaked with chromic acid, soaked in dilute hydrofluoric acid, and finally rinsed with distilled water.

Table I. ^{99}Tc and ^{90}Sr Concentrations in Rainwater

Year	^{99}Tc (dpm/L)	^{90}Sr (dpm/L)	^{99}Tc/^{90}Sr (activity/activity)	Ref
1961	$(4.0 \pm 2.0) \times 10^{-3}$	2.2 ± 0.6[a]	$(1.8 \pm 1.1) \times 10^{-3}$	(*6*)
1962	$(8.0 \pm 1.1) \times 10^{-2}$	34 ± 9[a]	$(2.4 \pm 0.7) \times 10^{-3}$	(*6*)
1967	$(1.4 \pm 0.3) \times 10^{-2}$	2.4 ± 0.6[a]	$(6.0 \pm 2.0) \times 10^{-3}$	(*7*)
1974	$(4.5 \pm 1.5) \times 10^{-3}$	0.11 ± 0.02	$(4.0 \pm 1.5) \times 10^{-2}$	This work

[a] Estimated errors of 25%.

The Tracerlab Omniguard low level gas flow proportional counter used for counting the samples had a background of 0.7 counts/min.

Evaporation of the rainwater was accomplished in 4-L glass beakers. Prior to evaporation, the following carriers were added: Re(VII), Mo(VI), Cu(II), Sr(II), and Ba(II). The rainwater was then made basic to minimize the loss of technetium as Tc_2O_7 during evaporation.

The analysis procedure used for the isolation of technetium from rain was essentially that described by Attrep and coworkers (*7*). A detailed description will not be given here since it has been previously reported. The analysis included a series of hydrogen sulfide precipitations, α-benzoinoxine precipitations for the removal of copper and molybdenum, a methyl ethyl ketone extraction cycle, and ion exchange separations. The chemical yield for this sample (7.17%) was based on the recovery of rhenium as was done by previous investigations (*4, 5, 7*).

Prior to the analysis of the actual sample, a reagent blank was analyzed using the technetium procedure. This reagent blank did not indicate any activity. It was then assumed that there was no contribution of activity from the reagents used.

Strontium-90 was isolated from the composite portions of the initial separation steps of the technetium analysis. This analysis included the precipitation of carbonates, repeated removal of barium as barium chromate, precipitation of strontium with fuming nitric acid, and repeated ferric hydroxide scavenges. The strontium was finally precipitated as strontium carbonate. The chemical yield for the complete analysis was 11.8%. Time was allowed for radioequilibrium to be established for ^{90}Y which was milked using a ferric hydroxide precipitation, mounted, and counted. The characteristic 64-h half-life was observed. The concentration of ^{90}Sr was determined from the ^{90}Y counting data.

Counting efficiencies for both the ^{99}Tc and ^{90}Y systems were estimated according to the method described by Bayhurst and Prestwood (*11*) and were 44 and 49%, respectively.

Results and Discussion

The purified technetium sample was counted for over a year, and the activity average of these counts is 0.144 ± 0.047 cpm. The counting error is one sigma. The average counting time per count was 38 h. No decay was observed during the counting period. This activity, corrected for chemical yield

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and counter efficiency, is equivalent to $(4.5 \pm 1.5) \times 10^{-3}$ dpm/L rainwater. The ^{90}Sr activity for the rain sample is 0.11 ± 0.02 dpm/L rainwater.

These data and the other ^{99}Tc and ^{90}Sr data from rain samples collected in 1961, 1962, and 1967 are given in Table I. The 1961 and 1962 samples were collected at Fayetteville, Ark. (*6*). The 1967 ^{99}Tc value is the average of 13 samples collected during that year. The ^{90}Sr value is an average as reported at Fayetteville, Ark. (*12*), for the same time period of collection of our sample. Although our laboratory had attempted the ^{90}Sr analysis for those samples, there was some question as to the reliability of those values. Therefore, we chose to use the Fayetteville data. These data are shown graphically in Figures 1 and 2.

In Figure 1 the concentrations of each ^{99}Tc and ^{90}Sr in dpm/L of rainwater are plotted vs. time. The striking feature of this plot is the apparent similarities of concentration patterns of two nuclides.

In Figure 2 the ratio of ^{99}Tc/^{90}Sr is given for the four samples. Also, the production ratios (activity) for ^{99}Tc/^{90}Sr from three fissionable materials are indicated. The first observation is that the ^{99}Tc/^{90}Sr ratio from 1961 to 1974 increases steadily. Secondly, the observed ratios are considerably higher than what would be anticipated from a nuclear device employing either uranium or plutonium. A ^{99}Tc value of less than 0.012 dpm/10^3 SCM surface air in 1970 was observed by Thomas (*10*). He estimated in that report a possible sevenfold enrichment of ^{99}Tc to ^{137}Cs relative to the anticipated value from fission yields. This is consistent with our observations for ^{99}Tc relative to ^{90}Sr.

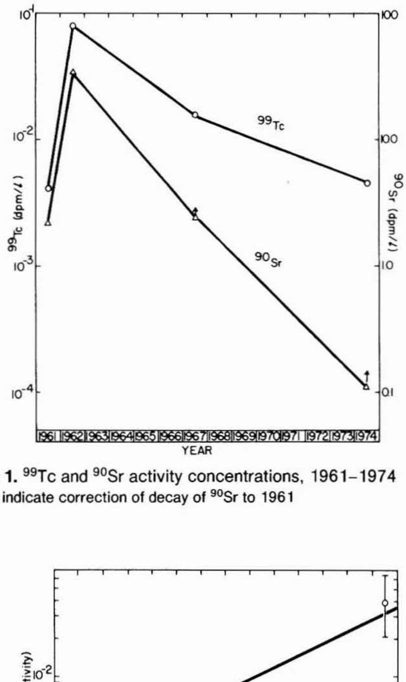

Figure 1. ^{99}Tc and ^{90}Sr activity concentrations, 1961–1974
Arrows indicate correction of decay of ^{90}Sr to 1961

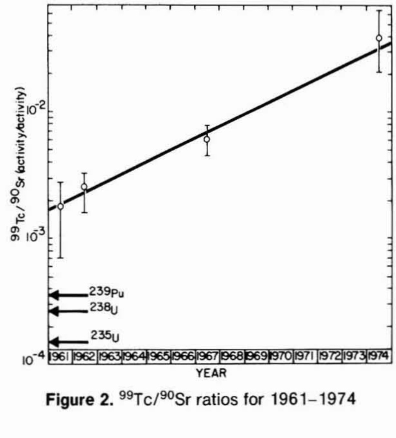

Figure 2. ^{99}Tc/^{90}Sr ratios for 1961–1974

The nuclear industry, which includes reactors and nuclear fuel reprocessing, can be considered as a source of ^{99}Tc to the environment. Recently, Carr et al. (*13*) discussed an experimental reprocessing procedure for recovering uranium. This report indicated a release of fission products to the atmosphere during a molten-salt fluoride process from spent uranium–aluminum fuel elements. In a particular run, 120 mCi of technetium was lost. This would be expected since the vapor pressure of Tc_2O_7 at 100° is 0.1 torr (*14*). It is conceivable that given the proper conditions of temperature and oxidative conditions, technetium may be lost to the environment from such reprocessing procedures. Losses from reactors are not expected.

It is also interesting to note the release of the long-lived fission products, ^{129}I, ($t_{1/2} = 17$ million years) into the environment. Recent reports by Ballard et al. (*15*) and Daly et al. (*16*) have indicated the presence of iodine-129 in the thyroid glands of grazing animals and in milk and water near nuclear fuel reprocessing plants. Technetium (as TcO_4^-), like iodine, will concentrate in the thyroid gland of mammals. These investigations suggest strongly that reprocessing plants are a source of environmental technetium-99.

The steady increase in the ratio of ^{99}Tc/^{90}Sr observed probably may be due in part to the increase of nuclear fuel reprocessing operations. Evidence to support this has been presented by the presence of such long-lived nuclides as ^{129}I and ^{99}Tc in the environment.

Many anomalous observed ratios of fission products in the atmosphere have been explained by the phenomenon of fractionation in the detonation process. In this case, the observed ^{99}Tc/^{90}Sr ratio does not fit the anticipated effect of fractionation. The mass 99 and 90 decay chains (*17*) which lead to ^{99}Tc and ^{90}Sr are given below:

$$\begin{tikzcd}[column sep=small]
\text{33-s }{}^{99}\text{Zr} \arrow[r] & \text{2.4-min }{}^{99}\text{Nb} & & \\
& & 0.87\ \text{6.0-h }{}^{99m}\text{Tc} \arrow[dd] & \\
{} \arrow[r] & \text{67-h }{}^{99}\text{Mo} \arrow[ur] \arrow[dr] & & \text{Stable }{}^{99}\text{Ru} \\
& & 0.13\ \ 2.1 \times 10^{5}\text{-yr }{}^{99}\text{Tc} \arrow[ur] &
\end{tikzcd}$$

and

$$\text{33-s }{}^{90}\text{Kr} \rightarrow \text{2.7-min }{}^{90}\text{Rb} \rightarrow \text{28-yr }{}^{90}\text{Sr} \rightarrow$$

The precursors to ^{99}Tc are zirconium and niobium which have low volatility properties. Thus, immediately following an atmospheric detonation, these fission product precursors would be removed during the formation of larger particles as the surrounding area cools. Clark et al. (*18*) have shown that this particle formation occurs in a relatively short time period following detonation. However, the precursor to ^{90}Sr is a gas and would escape condensation during the initial large particle formation. Eventually, the members of the mass 90 chain would concentrate on/in smaller particles. The net result of this fractionation would be a high ^{99}Tc/^{90}Sr ratio in large particles which are deposited preferentially as local fallout and a low ^{99}Tc/^{90}Sr ratio in smaller longer airborne particles.

Therefore, it is anticipated that the ^{99}Tc/^{90}Sr value should be lower than that estimated from the fissionable nuclides (^{235}U or ^{239}Pu). The opposite is observed, indicating more strongly that other significant sources of ^{99}Tc are contributing to the total ^{99}Tc atmospheric inventory.

Nuclear explosive devices are probably constructed with small amounts of transition metals like ruthenium and, in particular, molybdenum in their steel casings. If this is correct, then the reaction and decay process

$$^{98}\mathrm{Mo}\ (n, \gamma)\ ^{90}\mathrm{Mo} \rightarrow {}^{99}\mathrm{Tc}$$

can occur because of the intense neutron flux at detonation.

Molybdenum-98 has an isotopic abundance of 24.4%; the thermal neutron capture cross section is 0.5 barns. With molybdenum in the vicinity of the nuclear explosion, there would be activation of this isotope to provide the excess amounts of ^{99}Mo and eventually ^{99}Tc. In two reports, Clark et al. (*18*) and Kuroda and coworkers (*19*) studied two separate Chinese detonations and did not observe anomalous amounts of ^{99}Mo. In these two tests the Chinese may not have used the transition metals in these devices.

We would suggest that atmospheric technetium-99 has three origins: fission technetium from the fissionable materials in nuclear devices; activation of molybdenum in the nuclear device itself; and influx into the atmosphere from nuclear fuel processing plants. It is impossible to ascertain the contributions of these sources from the data available to date.

It is desirable to sample in the vicinity of reactor sites and fuel processing facilities for the environmental impact of technetium. It is just as important to observe the overall mixing and atmospheric behavior of this nuclide in areas or regions unaffected by local contamination. The latter demonstrates the importance of global effects.

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Nonferrous Smelter Studies: Theoretical Investigation of Role of Multihearth Roaster Operations in Copper Smelter Gas Blending Schemes for Control of SO_2

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■ A possible technology for meeting the Environmental Protection Agency's (EPA) proposed New Source Performance Standards for copper smelting is to blend lean SO_2 gas streams from reverberatory furnaces with stronger gases to obtain a SO_2 concentration sufficient to produce sulfuric acid without use of supplementary fuel. In such an approach, a high concentration of SO_2 in the roaster gases is necessary to counterbalance low concentrations in the reverberatory furnace gases. An analysis is made of the calcining of copper concentrates in multihearth roasters. The oxygen concentration of the exit gas is identified as the primary process control variable for maintaining a high level of SO_2 in the exit gas stream. The SO_2 concentrations in the exit gas that can be attained by controlling the exit gas oxygen concentration at 12 vol %, a value that has been achieved in practice, are estimated for removal of from 0.1 to 0.65 of the charged sulfur, to cover the extent of roasting that might be elected. The effect of arsenic as an impurity in the concentrate on the attainable SO_2 concentration is also shown. The results indicate that with proper control of the oxygen level therein, exit gases from U.S. multihearth roasters could be held at an SO_2 concentration of 5 vol %, dry basis, or higher. The analysis involves four assumptions that appear to be reasonable based on available information: iron present in the charge can be regarded as iron pyrites; the proportion of FeS_2 converted to Fe_3O_4 is constant relative to that converted to Fe_2O_3 at given roasting conditions; the portion of the arsenic that is volatilized and burned is constant for given roasting conditions; and the fraction of copper oxidized is proportional to the fraction of dissociable sulfur removed.

Concentrate Roasting. Figure 1 shows the general characteristics of a multihearth roaster. Charge is fed onto the uppermost hearth. The solids are moved by rakes inward or outward on alternate hearths until they reach openings and drop through the next lower hearth. Hot gases move upward and contact the solids, bringing them to ignition temperature. On the lower hearths the charge may burn with a dull or bright glow as controlled by the operations. According to generally accepted opinion, about 40% of the total sulfur removed is burned while the charge drops from one hearth to another, and about 60% is burned as the charge moves along the hearths (*1*). The calcined solids are removed from the furnace into conveyers for transfer to smelting furnaces.

The roasting conditions are adjusted to produce a calcine that will yield the desired grade of matte in subsequent processing. The desired grade of matte is in turn determined by considering the need for removal of impurities in the converter to which the matte is fed. The multihearth roaster has been

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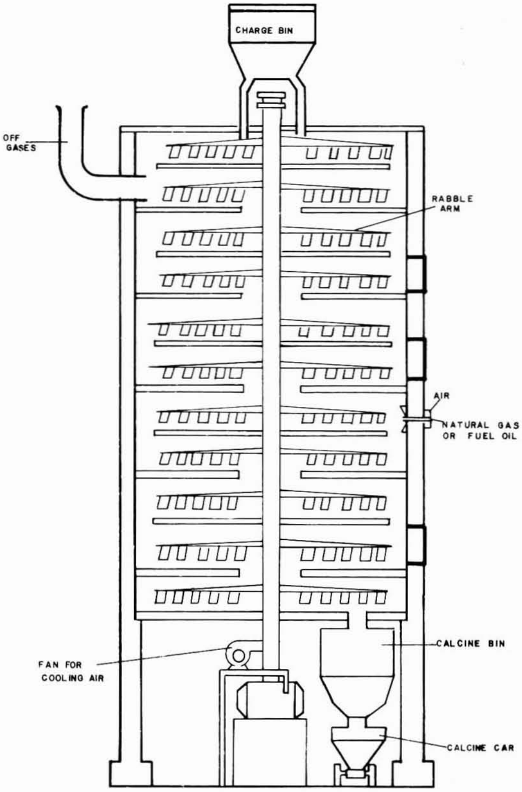

Figure 1. Multihearth roaster

effective in removing arsenic and other impurities; hence, it is preferred over the fluid bed roaster in the United States and elsewhere for roasting copper concentrates that contain high concentrations of such impurities.

The different roaster techniques employed affect the sulfur dioxide (SO_2) concentration of the offgases. One or more furnaces may be used only for drying the charge, in which case fuel is burned to provide needed heat. The exit gases leave at low temperatures (125–150 °C) and with practically no SO_2 (*2, 3*). Material thus dried is usually blended with roasted material to provide a suitable feed for the smelter.

The charge is often fed wet so that the roasting operation begins with removal of water in the upper hearths, then volatizes and burns free sulfur and impurities (especially arsenic sulfide), and finally burns bound sulfur by chemical oxidation (*1–3*). In this case, the offgases can be rich in SO_2 and can contain arsenic oxides and other impurities. The percent of the total sulfur removed from the charged material can be held low or high (low roast or high roast) by adjusting the air and solids throughput rates. As little as 25% of the arsenic in "dirty" concentrates may be removed in the roaster under a low roast (2). Regardless of how high the roast may be or how high the arsenic in the charge, the arsenic content of the calcines seems to fall no lower than 0.3% (*1, 2*).

A possible technology for meeting the Environmental Protection Agency's (EPA) proposed New Source Performance Standards for copper smelting is to blend lean SO_2 gas streams from reverberatory furnaces with stronger gases to obtain SO_2 concentrations sufficient to produce sulfuric acid without use of supplementary fuel. In such an approach, a high concentration of SO_2 in the roaster gases is necessary to counterbalance low concentrations in the reverberatory furnace gases. The purpose of this study is to evaluate the capability of multihearth roasters to produce exit gases with an SO_2 concentration high enough for such blending while still providing acceptable calcines.

Theory

Sulfide copper minerals usually consist of combinations of sulfides in normal valency compounds (e.g., Cu_2S and FeS) and of compounds in which part of the sulfur is particularly reactive and may be removed by volatilization upon heating (e.g., CuS and FeS_2). This sulfur is termed pyritic sulfur. The proportion of pyritic sulfur in common copper minerals is shown in Table I (*4*).

Theoretically, the amount of oxygen consumed in the roasting process in removing a given fraction of the sulfur from the charge is equal to that needed to oxidize the sulfur to sulfur dioxide (SO_2) and that needed to remove the sulfur from the metallic sulfides. Thus, for iron pyrites, sulfur is dissociated according to the reaction:

$$FeS_2 \rightarrow FeS + S$$

and the dissociated sulfur reacts to form SO_2:

$$S + O_2 \rightarrow SO_2$$

The sulfur remaining in the metallic sulfide, FeS, is removed by chemical reaction with oxygen. Under the roasting conditions, two reactions occur:

$$2FeS + 3.5O_2 = Fe_2O_3 + 2SO_2$$

$$3FeS + 5O_2 = Fe_3O_4 + 3SO_2$$

(Small amounts of FeO have also been found in calcines from multihearth roasters.)

An accurate calculation of the oxygen consumed in any specific case requires knowledge of the mineralogical character and degree of transformation of the particular charge. Lacking this information, it is considered reasonable to develop a general formula for estimation of the oxygen consumption using the predominant chemical, metallurgical, and thermodynamic aspects of the process. The development extends prior efforts at modeling the operation mathematically (*5*) to account for the removal of arsenic and for the conversion of a portion of the copper in the charge to copper oxide.

The rate of oxygen consumption (F_{O_2}) is:

$$F_{O_2} = F_c[ax_1 + (b + c)(ax_1 - 0.574\,dx_2 - 0.642\,ex_3 - 0.505\,fx_4) + 0.320\,ex_3 + 0.252\,fx_4],\ \text{kkg/h} \quad (1)$$

where F_c = charge feed rate, kkg/h; a = fraction sulfur removed; $b + c$ = factors converting sulfur to the equivalent amount of oxygen contained in Fe_2O_3 and Fe_3O_4. $b + c = 1/x + 1 + 2/3\,[1 - 1/(x + 1)]$; 0.574 = MW S/MW Fe = 32.06/55.847; d = ratio: S removed by dissociation/dissociable S in charge; 0.642 = 3 (MW S)/2 MW As; e = fraction As removed; 0.505 = MW S/MW Cu; f = fraction of Cu oxidized; x = the ratio (FeS_2 to Fe_3O_4)/(FeS_2 to Fe_2O_3) = $\%Fe_3O_4/\%Fe_2O_3 \times 1.0345$; x_1 = fraction sulfur in the charge; x_2 = fraction iron in the charge; x_3 = fraction arsenic in the charge; and x_4 = fraction copper in the charge.

Table I. Pyritic Sulfur in Common Copper Minerals

Mineral	Compn	Pyritic S × 100 / Total S
Chalcopyrite	$CuFeS_2$	25
Chalcocite	Cu_2S	0
Bornite	Cu_5FeS_4	12.5
Covellite	CuS	50
Pyrites	FeS_2	50

Table II. Mineral Composition of Roaster Charge and Calcine, Clean Concentrate

Mineral components clean charge	kkg per 100 kkg of charge[a]	
	In charge	In calcine
FeS_2	25.18	1.05
$CuFeS_2$	49.01	
ZnS	1.52	
Inerts	24.29	24.29
FeS		6.78
FeO		0.21
Fe_3O_4		2.31
$CuFeS_2$		32.28
$CuOFe_2O_3$		21.83
ZnO		1.27
Total	100.0	90.02

[a] Test 3, Project Study Report PL-480 No. 2-513-1.

Table III. Theoretical Maximum Exit Gas SO_2 Concentration vs. Sulfur Removed in Roasting

Fraction of sulfur removed	Max SO_2 in exit gas, vol %	
	Clean charge	High arsenic charge
0.063		14.9
0.10	20.9	16.7
0.20	20.9	20.9
0.30	20.9	19.3
0.35	17.7	
0.40	16.9	17.1
0.50		16.1
0.54	15.7	
0.65	15.3	

This formula represents the oxygen consumed assuming that the iron is present in the charge as iron pyrites and that the ratio (FeS_2 to Fe_3O_4/FeS_2 to Fe_2O_3) is constant for given roasting conditions. It is also assumed that the portion of arsenic which is volatilized and turned to arsenic oxide (As_2O_3) is constant for given roasting conditions.

The corresponding fraction SO_2 in the roaster gases, x_5 (weight fraction), is:

$$x_5 = \frac{2\,ax_1}{5.32\,ax_1 + 3.32[(b+c)(ax_1 - 0.574\,dx_2 - 0.642\,ex_3 - 0.505\,fx_4) + 0.320\,ex_3 + 0.252\,fx_4]} \quad (2)$$

Air infiltration is disregarded. The corresponding volume fraction SO_2, dry basis, is obtained by:

$$x_{5,\ \mathrm{vol\%}} = 7\,x_5(16 - 9\,x_5) \quad (3)$$

Calculations by Formulas 1–3 agree well if

$$ax_1 \geq 0.574\,dx_2 + 0.642\,ex_3 + 0.505\,fx_4 \quad (4)$$

this is the case when the amount of sulfur removed by roasting exceeds that separated by dissociation of pyrite, or chalcopyrite or covellite, in the concentrate plus the amount removed in the oxidized arsenic and copper. If this condition is not fulfilled, then all the oxygen may be assumed to be consumed in the oxidation of dissociable sulfur. In this case, the fraction of SO_2 in the roaster gases is:

$$x_5 = 2\,F_c ax_1/5.319\,F_c ax_1 = 0.376 \text{ by weight, or } 20.9 \text{ vol \%} \quad (5)$$

Thus, in "light" roasting with removal of dissociable sulfur only, the theoretical maximum SO_2 level in the exit gases is 20.9%. To use these formulas, values must be obtained for *d*, *e*, and *f*. These were estimated by data from roasting of Bor and Majdanpek ore concentrates in Yugoslavia (*1*). Table II shows the mineral content of 100 kkg of charge fed and the quantities of minerals in the calcine produced therefrom. Very low concentrations of arsenic and other impurities in the charge are omitted from the tabulation. These data provided values for *x*, *d*, and *f* (0.164, 0.43, and 0.34, respectively); the fraction of sulfur removed was 0.54. It was assumed that *x* would remain constant over a range of sulfur removal, and that terms in the formulas involving the factor *e* could be neglected in calculating the maximum theoretical SO_2 content of exit gases. The fraction of copper oxidized was assumed to be proportional to the fraction of dissociable sulfur removed, so that $f = 0.8\,d$.

Table III shows the calculated theoretical maximum SO_2 concentrations attainable in the roaster exit gases for selected fractions of sulfur removed. The values are highest for low fractions of sulfur removal; they drop from 20.9 to 17.7 vol % (dry basis) as the sulfur removal increases from 0.30 to 0.35. Beyond this level, a further decrease to 15.3 reflects the increased consumption of oxygen in the chemical removal of sulfur.

Table III also shows the calculated maximum SO_2 concentration vs. the fraction of sulfur removed for exit gases from roasting of a high arsenic-containing charge. For these calculations the charge was assumed to be the same as that processed in Yugoslavia except that 5 kkg of As_2S_3 were present, replacing 5 kkg of the $CuFeS_2$ (Table IV). Arsenic is reported to be easily removable from most charges; the arsenic sulfide can vaporize and then reacts to form As_2O_3 (*1–3, 6, 7*). It was therefore assumed in the calculations that the arsenic was removed preferentially. The results show that the maximum SO_2 concentration in the exit gas is only 14.9–16.7 for sulfur removals up to 0.1, reflecting the consumption of oxygen to form As_2O_3. At 0.2 fraction sulfur removed, the calculated concentration of SO_2 is 20.9. Then, as the sulfur removal increases, the SO_2 concentrations fall again to levels that closely match those of the clean charge.

Principles of Operation

The design and operation of multihearth roasters have focused upon the processing requirements of the smelter plant. If this roaster is to continue to meet these requirements while also supplying exit gases with maximum SO_2 content, a new mode of operation must be developed. This requires an investigation of those factors inherent in the process and the charge that dictate the results obtained.

The literature on roasting of copper-containing ores is extensive (*10*). Townend et al. (*11*) investigated the roasting of lumpy chalcopyrite in an air stream at temperatures between 550 and 750 °C and followed the transformations with a microscope and a microprobe. The roasted particles had an extremely porous zone of hematite covering a compact layer of magnetite. The thickness of the layers was independent of the

Table IV. Mineral Composition of Roaster Charge, High Arsenic Concentrate

Mineral component high arsenic charge	kkg per 100 kkg of charge
FeS_2	25.18
As_2S_3	5.00
$CuFeS_2$	44.01
ZnS	1.52
Inerts	24.29
Total	100.00

roasting temperature. Traces of copper ferrite ($CuFe_2O_4$) were found in a hematite and were presumed to have been formed as the result of establishment of a local equilibrium. Details of the transport of oxygen and sulfur through the impervious magnetite layer could not be explained. Winterharger et al. (*10*) found that during the roasting of copper-containing pyrrhotite, various copper–iron sulfides occurred as sequential phases in the receding sulfide kernel, and copper sulfides were converted to cuprite (Cu_2O). As roasting continued (in air or in SO_2-rich gas), there was a zonal progression of these sequential phases, as would occur if the reaction rate-determining step were the gas-phase diffusion processes occurring in the pores of the roasting product. This rate-determining step has also been shown by other investigations to approximate closely the burning of iron sulfides in air (*12*). The rate of oxidation appears to be determined by the rate of diffusion of gaseous reactants through the solid crust that covers the core of the sulfide particles. Chemical reaction occurs at the boundary of solid metal sulfides and metal oxides. Oxygen diffuses in; SO_2 diffuses out. Unconsumed oxygen in the gases provides the driving force. As oxidation proceeds, diffusion becomes more difficult, and the reaction slows down.

Observations of the operation of existing roasters show that an active oxidation of the charge requires about 13% oxygen in the gases next to the solid particles and a temperature range of 640–760 °C (*7*). At lower oxygen concentrations the fire goes out. Temperatures above the required limits can decrease the rate of oxidation because of the induced agglomerization of particles.

The oxygen contents of exit gases from multihearth roasters monitored at Bor, Yugoslavia, ranged from 11.4 to 19 vol %, dry basis (*1*). It therefore seems that an operation that controls the oxygen concentration at 12 vol % would be quite feasible and, in addition, would assure the necessary oxygen concentration for driving the diffusion-controlled roasting reactions. To allow this concentration of oxygen in the exit gas will limit the maximum attainable SO_2 concentration to 8.9 vol % (dry basis). Of all the operating conditions that must be selected, the choice of exit gas oxygen concentration has the greatest effect on the exit gas SO_2 concentration.

The need to remove arsenic from some concentrates calls for consideration of the temperature to which the solids should be heated during the roast. Among the arsenic sulfides that may be present in copper ores are $FeSAs_2S_3$, As_2S_3, and As_2S_5. The As_2S_3 boils at 707 °C, and As_2S_5 sublimes at 500 °C with decomposition. Arsenic trioxide melts at 310 °C and boils at 457 °C. Thus, if the solids are heated to above 700 °C, the desired arsenic removal would seem to be assured. (Thermodynamic data were not found for arsenides.)

Investigations using a concentrate with 8% arsenic indicate that temperatures somewhat higher than 700 °C may be needed to remove arsenic impurities completely (*3*). The combustion of sulfur can be self-sustained at 2440 °C (*8*). Iron pyrite (FeS_2) will exert an S_2 vapor pressure of one atm at 690 °C; covellite (CuS), one atm at 550 °C (*4*). CuS begins to break down to digenite ($Cu_{1.8}S$) and sulfur at 235 °C in an inert atmosphere (9). Digenite is stable up to 550 °C and then breaks down to chalcocite (Cu_2S) and sulfur. Considering these findings, a temperature of 740 °C was selected for the calcine at the point of discharge.

The exit gas temperature should be kept high enough to avoid condensation of water with attendant corrosion problems. If kept above 460 °C, no As_2O_3 will solidify; but this is not an objective of current practice. The exit gas temperature was set at 200 °C; 100 °C may be an adequate lower limit in some cases, since it provides for 2.29 kg water per kg dry air at saturation.

With these prescribed conditions, a heat balance was formulated using the following reactions judged to be most significant (*1–3, 6, 7*):

	ΔH°_{298} **kcal/kg mol product**
$FeS_2 + O_2 = FeS + SO_2$	−49 790
$2FeS + 3.5O_2 = Fe_2O_3 + 2SO_2$	−297 720
$3FeS + 5O_2 = Fe_3O_4 + 3SO_2$	−416 630
$FeS_2 = FeS + S$	+21 170
$As_2S_3 + 4.5O_2 = As_2O_3 + 3SO_2$	−346 980
$CuS = CuO + SO_2$	−97 860

Additional reactions would of course be included if other reactants, such as ZnS, were present in the charge in sufficient quantity to affect the heat balance significantly. Heat balances were claculated using as a basis 1 kkg of dry charge and a reference temperature of 25 °C (298 K). The accuracy of the calculated results depends upon the accuracy of the required input data: the weight fractions of moisture, associable sulfur, total sulfur, iron, arsenic, and copper in the charge; the weight fraction of hematite, magnetite, dissociable and total sulfur, copper, copper oxides, and other metal oxides in the calcine; the fraction of dissociable sulfur and arsenic actually removed; and the fraction of copper oxidized. Since these data were not

Table V. Thermal Calculations, Clean Charge Basis: 1 kkg Dry Charge; 25 °C; Exit Gas ≥200 °C; Exit Calcine 740 °C. Water Content of Charge: 9 wt %; Radiation + Cooling Losses, 15%

Fraction sulfur removed	0.1	0.2	0.3	0.35	0.4	0.539	0.65
Sulfur removed, kg/kkg	31.05	62.1	93.15	108.7	124.2	167.4	201.8
Ht in calcine, kcal/kkg	152452	147567	142602	144064	143522	141620	140281
Ht in water, kcal/kkg	63445	63445	63445	63445	63445	63445	63445
Wt of exit gas, kg/kkg	342	684	1026	1368	1618	2312	2866
Ht in exit gas, kcal/kkg	11633	23265	34897	57471	67957	97108	120388
Total ht absorbed, kcal/kkg[a]	261659	269418	277087	304728	316164	347500	372732
Ht of reaction, kcal/kkg	−51037	−101872	−163032	−255767	−327306	−526183	−684997
Ht deficiency, kcal/kkg[b]	210621	167546	114055	48959	−11142	−178682	−312266
Required inlet gas temp at balance, °C	785	527	162	66	. . .	. . .	. . .
Oil required, kg/kkg	20.5	16.3	11.1	4.8	. . .	. . .	. . .
Excess exit gas, kg/kkg	400	317.9	216.5	93.6	. . .	. . .	. . .
Total exit gas, kg/kkg	742	1001.9	1242.5	1461.6	1618	2312	2866
Total SO_2 in exit gas, kg/kkg[c]	62.5	124.5	186.5	217.5	248.4	334.8	403.6
Exit gas % SO_2: wt (vol)	8.4 (3.9)	12.4 (5.8)	15.0 (7.2)	14.9 (7.1)	15.4 (7.4)	14.5 (6.9)	14.1 (6.7)
Exit gas % SO_2: wt (vol) in absence of fuel burning	18.2 (8.9)	18.2 (8.9)	18.2 (8.9)	15.9 (7.6)	15.4 (7.4)	14.5 (6.9)	14.1 (6.7)

[a] Includes 15% heat loss. [b] Total heat absorbed + heat of reaction. [c] 2 × sulfur removed + 0.02 × kg oil/kkg.

Table VI. Thermal Calculations, High Arsenic Charge Basis: 1 kkg Dry Charge; 25 °C; Exit Gas ≥200 °C; Exit Calcine 740 °C. Water Content of Charge: 9 wt %; Radiation + Cooling Losses, 15%

Fraction sulfur removed	0.063	0.1	0.2	0.3	0.4	0.5
Sulfur removed, kg/kkg	19.4	30.75	61.5	92.25	123.0	153.8
Ht in calcine, kcal/kkg	149459	142597	138261	133564	133120	128279
Ht in water, kcal/kkg	63445	63445	63445	63445	63445	63445
Wt of exit gas, kg/kkg	590	601	785	1597	1789	2283
Ht in exit gas, kcal/kkg	20072	20442	26697	54363	75133	95902
Total heat absorbed, kcal/kkg[a]	267923	260872	262663	289079	312452	330770
Ht of reaction, kcal/kkg	−163372	−103489	−122627	−270187	−411881	−553575
Ht deficiency, kcal/kkg[b]	104551	157383	140036	18891	−99429	−222804
Required inlet gas temp at balance, °C	227	362	245	41	. . .	. . .
Oil required, kg/kkg	10.2	15.2	13.6	1.9	. . .	. . .
Excess exit gas, kg/kkg	198.9	296.4	265.2	37.1	. . .	. . .
Total exit gas, kg/kkg	788.9	897.4	1050.2	1634.1	1789	2283
Total SO_2 in exit gas, kg/kkg[c]	39.0	61.8	123.3	184.54	246	307.6
Exit gas % SO_2: wt (vol)	4.9 (2.2)	6.9 (3.1)	11.7 (5.5)	11.3 (5.3)	13.8 (6.5)	13.5 (6.4)
Exit gas % SO_2: wt (vol) in absence of fuel burning	6.6 (3.0)	10.2 (4.8)	15.7 (7.5)	11.6 (5.4)	13.8 (6.5)	13.5 (6.4)

[a] Includes 15% heat loss. [b] Total heat absorbed + heat of reaction. [c] 2 × sulfur removed + 0.02 × kg oil/kkg.

available for U.S. smelting operations, calculations were made based upon the data of Table II, for which the fraction sulfur removed was 0.539. It was assumed that the ratio "x" is constant over a broad range of sulfur removed, that all the arsenic was burned as As_2O_3 and removed overhead ($e = 1$), and that the fraction of copper oxidized was 0.8 d.

Thermal calculations and SO_2 concentrations in the exit gases are shown in Tables V and VI for selected fractions of sulfur removed. In the absence of fuel burning, the clean charge (Table V) yielded an 8.9 vol % SO_2 for up to 0.3% sulfur removal. The lower SO_2 concentrations beginning at 0.35 fraction sulfur removal reflect the consumption of oxygen in removing nonvolatilizable sulfur. Heat deficiencies (positive values) occur up to a sulfur removal of 0.35. Some of these could apparently be made up by increasing the inlet gas temperature.

The fuel oil required to supply the needed extra heat is shown, along with the excess exit gas generated thereby and the SO_2 concentration in the total exit gases. The fuel oil was assumed to contain 1% sulfur and to provide 9978 kcal/L when burned with 15% excess air.

Table VI shows the heat balances for the high-arsenic charge of Table IV. When only the arsenic was removed (fr S removed = 0.063), the exit gas SO_2 concentration is 2.2% if fuel oil is burned and 3.0% if not. It is not certain, of course, whether only arsenic could be removed; some volatilizable sulfur would likely also be removed under the operating conditions projected. However, the exit gas SO_2 concentrations shown in Table VI are consistently lower than those shown in Table V, primarily because the elimination of arsenic requires oxygen to form As_2O_3 as well as SO_2.

Discussion

The results in Tables V and VI indicate the effects of a broad range of sulfur removal on the exit gas SO_2 concentration. Smelter operations will not necessarily cover this range of sulfur removal. Thus, if matte from the reverberatory furnace to which this roaster calcine is fed is required to have 38–45% copper, then the fraction sulfur to be removed in roasting will be about 0.4. (The fraction removed will depend, of course, on the concentration of sulfur in the charge.) At this level of sulfur removal, the SO_2 concentration in the exit gases is 7.4% for the clean concentrate and 6.5% for the high arsenic charge.

The projected roaster operation includes both drying and roasting the charge. The removal of water required 17–24% of the heat absorbed, and heat losses another 15%. The charge could be dried in a separate operation (some firms employ one of their multihearth roasters for this purpose).

Better insulation of the roaster and recovery of the cooling air losses could further reduce the heat absorbed. The inlet air could be preheated. In a few cases (e.g., 0.35 fr S removal from the clean concentrate), heat exchange with the exit gases would seem to be sufficient. Any such reduction in heat absorbed would decrease the fuel oil required, and thus effect an increase in the SO_2 level in the exit gases.

As projected, the operation must remove between 110 and 120 kg sulfur per kkg of charge if it is to provide its own heat. Part of the heat load is imposed by requiring enough excess air to provide 12 vol % oxygen in the exit gases. While such an excess may be necessary at the hearths where active burning occurs, it may not be needed in the upper hearths to burn the volatilized sulfur and arsenic. For these reactions, gas-solid mass transfer limitations would not exist.

It is possible that the calcine temperature could be kept considerably lower than 740 °C if only a small fraction of the sulfur is to be removed (2). Not all the arsenic would be removed in such case, but other opportunities to remove arsenic arise in the subsequent processing steps. A calcine discharged at 600 °C would carry out about 30 000 kcal less heat per kkg of charge. If, in addition, the water were removed in a separate operation and the calcine introduced at 100 °C, the total reduction in heat absorbed would be about 45 000 kcal.

Conclusions

This investigation indicates that the SO_2 concentration in exit gases from multihearth roasters can be held above 5% provided at least 60 kg of sulfur are removed per kkg of charge. Maintaining this concentration level requires monitoring the exit gas O_2 concentration and controlling it at 12% and controlling heat losses and calcine exit temperatures. When less sulfur is removed, especially from charges of high arsenic content, the SO_2 concentration is much lower if the same roasting procedure is employed.

Heat losses have been estimated at 15%. Their reduction, by better insulation and by preheating gases to the roaster, could reduce fuel oil requirements at low levels of sulfur elimination and thus avoid some of the attendant dilution of the exit gases. The evaporation of water requires 17–24% of the heat absorbed.

The SO_2 concentrations estimated herein are limited primarily by the requirement of 12% oxygen in the exit gas. This requirement is based on state-of-the-art practice. The feasibility of maintaining roaster operation at lower oxygen concentrations in the exit gas needs to be investigated.

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Nonferrous Smelter Studies: Investigation of Importance of 12 Operating Factors on SO_2 Concentration of Exit Gases from Multihearth Roasting of Copper Concentrates

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■ Multihearth roaster exit gases must be kept at 5% or more SO_2 if gases from all three smelting processes—roasting, smelting, and converting—are to be processed autogenously in a sulfuric acid plant. This study of the practical effects of multihearth roaster operating parameters confirms the findings of a previous theoretical study concerning the importance of control of exit gas oxygen concentration to maintaining the desired SO_2 level, and further clarifies the concept of a new mode of multihearth furnace operation that provides the desired copper calcine while maintaining the necessary SO_2 concentration of the exit gases. Twelve practical operating factors that could affect the exit gas SO_2 concentration are examined by ridge regression analysis of data from 128 tests of a multihearth roaster system. One of these factors, the percent oxygen in the exit gases, accounts for 84% of the variance in their SO_2 content. Several of the tests attain SO_2 levels of 5–7% whenever the exit gas oxygen level is limited to 12% or less.

A possible technology for meeting the Environmental Protection Agency's (EPA) proposed New Source Performance Standards for copper smelters is the blending of lean SO_2 gas streams from reverberatory furnaces with stronger gases to produce a gas with sufficiently high SO_2 concentration to be used as a feed to a sulfuric acid plant. In such an approach, a high concentration of SO_2 in the multihearth roaster gases is necessary to strengthen the blended gases fed to the acid plant so that it may operate with little or no supplementary fuel.

Limited data from U.S. multihearth roasters show from 0.8 to 2.6 vol % SO_2; important details of the measurements (sampling points and test methods) are sparse (*1*). The roasting operation has been carried out elsewhere to yield exit gases with 1.0–7.6 SO_2, dry basis (*2*). A theoretical analysis indicates that an SO_2 concentration of 5% or more can be attained whenever the exit gas oxygen concentration is maintained at or below 12 vol % (*3*).

In addition to the oxygen level in the exit gases, the presence of impurities in the charge fed to the roaster and the fraction of sulfur removed during roasting were shown by theoretical analysis to affect SO_2 concentration. Arsenic and other readily volatilized impurities, if present in the charge, decrease the SO_2 concentration at very low levels of sulfur removal.

Several practical operating factors that could affect the exit gas SO_2 concentration were not investigated theoretically: the effect of the temperature attained by the furnace gases, the dust loading of the exit gases, the fire position (hearth where charge ignition occurs), the charge rate and composition (% copper, % iron, % sulfur), the air feed rate, the underpressure within the roaster, and the furnace availability (percent of time all roasters in a set were operating). This study was made to obtain confirmation of the theoretical findings concerning

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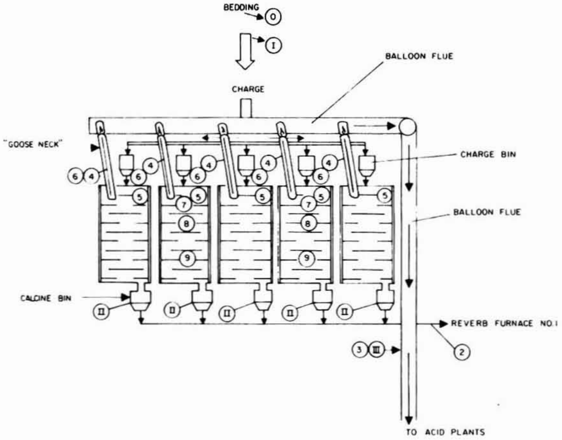

Figure 1. Roasting process sampling and measuring points

exit gas oxygen level and fraction of sulfur removed and to investigate the practical effects of other factors.

Experimental

Tests were conducted at the Bor Copper Smelter, Bor, Yugoslavia, under an international cooperative research effort. There were five multihearth roasters of Maguin (France) design. Blended charge from the bedding area was conveyed to 30-kkg charge bins mounted above each furnace. An air-cooled vertical shaft with two fire-resistant steel rakes at each hearth rotated at 1–2 rpm to transport the charge through the furnace. Ports at the furnace sides regulated air input and allowed visual inspection of the roasting operation. A 10-kkg hopper below each roaster collected discharging calcine for transport to a reverberatory furnace. Roaster exit gases were drawn off below the first hearth into a common balloon flue.

The roasters were tested as a group for 32 days (6 a.m. to 2 p.m.) during which six slightly different charges were processed. Some 33 parameters were measured repeatedly each day. Figure 1 shows the sampling and measuring points. Charge rate and composition were measured at Point I, and calcine output was measured at Point II. Gases were sampled at Point III and tested by Orsat for percent SO_2, CO_2, O_2, CO, and N_2; flow rate was also measured. These were reported on a dry basis. The gas moisture content was also measured. Dust samples were collected at Point III four times a day. Each dust sample required some 45 min, during which time one or more other tests was made. The time period for dust collection was identified as a single test, and all other measurements made while a dust sample was being collected were averaged to provide a single value for the tests. In all, 128 tests were made (four dust samplings per day × 32 days = 128 tests).

The position of the flame in each of the roasters, i.e., the hearth on which ignition first occurred, was visually checked and recorded each hour. Gas temperature was measured in the exit gas duct just outside the roaster and recorded using thermocouples; pressures were also measured by using inclined manometers.

The roasters and the reverberatory furnace together were an interrelated system under which any changes in operation of the latter directly affected the operation of the roasters. As a result, there were periods of individual roaster shutdown, and these were identified by determining the overall percentage of availability of the five multihearth roaster system.

Table I lists selected test results for each of the six experiments. The iron, copper, and sulfur content of the charge was constant for each experiment which employed a single homogeneous blend of material. The variation in composition resulted from the blending of different proportions of the three concentrates supplied to the smelter: Majdanpek concentrate, Bor concentrate, and Import concentrate.

Data Analysis

The data were analyzed to identify the important relationships between the SO_2 concentration of the exit gases and the other 12 variables given in Table I, and to develop therefrom a mathematical model of the roasting process suitable for use in control of the SO_2 concentration of the exit gases over a broad range of calcine quality. For this purpose, the quality of the calcine was expressed by percent sulfur removed.

Approach. Basic statistics (means, standard deviations, and coefficients of variation) were calculated and reviewed, as were simple correlation coefficients. Linear regression coefficients were then used to measure the change in SO_2 concentration relative to the change in the 12 process variables. The regression coefficients were screened by ridge regression techniques to eliminate unimportant process variables. The remaining variables were then used to develop roasting process models. For the entire set of data (128 tests), Table II shows the means, standard deviations, and coefficients of variation (CV) by variable. The relatively high CV's for SO_2 concentration, dust rate, percent S removed, furnace availability, underpressure, and charge rate provide some indication that these variables may have changed sufficiently from test to test to reveal their effects.

Correlation Coefficients. Table III shows the correlation coefficients for the 13 variables under analysis. The SO_2 concentration is identified as **Y** in anticipation of its role as a dependent variable. The O_2 concentration in the exit gas (X_{13}) has the largest pairwise correlation with the dependent

Table I. Selected Multihearth Roaster Data

		Exit gas						Charge						
Exp. no.	Test	SO_2,[a] vol %	O_2,[a] vol %	Flow rate, nm^3/h	Dust rate, kg/h	Temp, °C	Under pressure, mm/H_2O	Rate, t/h	Wt % S	Wt % Fe	Wt % Cu	% S removed	Flame position hearth no.	Furnace avail, %
1	1	3.4	16.5	57000	717	170	2.5	13.6	28.74	25.02	18.50	74.1	6.3	50.0
	15	6.6	12.5	61800	1353	267	3.0	34.9	28.74	25.02	18.50	58.7	5.8	74.2
2	9	2.2	16.2	52100	773	266	4.0	36.8	29.40	23.46	18.19	37.2	6.6	57.3
	16	5.2	13.2	61000	684	288	4.0	34.0	29.40	23.46	18.19	45.9	6.6	73.3
3	8	6.2	13.0	47600	1221	266	3.5	48.6	28.84	25.06	18.31	44.3	6.4	99.9
4	7	5.5	13.0	63800	2155	332	3.0	26.7	30.00	25.38	18.07	57.5	5.2	96.0
5	7	4.1	14.2	68600	1821	358	3.5	30.3	29.00	24.30	18.24	77.5	5.0	87.1
6	3	2.6	18.0	63000	871	187	5.5	27.8	28.33	22.89	19.63	98.8	7.1	26.6

[a] Dry basis.

Table II. Basic Statistics (128 Observations)

Variable		Mean	SD	CV, %
SO_2 in exit gas	X_1 (or Y)	3.95	1.73	43.8
Dust rate	X_2	1 143.21	656.28	57.4
% S removed	X_3	61.89	16.41	26.5
Gas flow rate	X_4	62 665.94	11 787.34	18.8
Furance availability	X_5	58.18	27.80	47.8
Temp, gooseneck	X_6	281.75	47.50	16.9
Underpressure, gooseneck	X_7	3.33	1.13	33.9
Fire position	X_8	6.02	0.69	11.5
Charge rate	X_9	28.92	10.64	36.8
% Cu, charge	X_{10}	18.62	0.60	3.2
% Fe, charge	X_{11}	24.31	1.00	4.1
% S, charge	X_{12}	28.96	0.55	1.9
% O_2, exit gas	X_{13}	14.94	1.85	12.4

variable, −0.92. Several of the predictor independent variables, X, have large pairwise correlations (e.g., X_2 with X_5, X_3 with X_{10}, X_{10} with X_{11}, and X_{11} with X_{12}). This suggests the need for ridge regression analysis (*4–6*) in addition to standard least-squares regression analysis, in further evaluation of the data. The use of these techniques is explained as follows.

Ridge Regression Analysis. The standard multiple linear regression model given in Equation 1 in matrix form was applied as follows:

$$\mathbf{Y} = X\mathbf{B} + \mathbf{e} \tag{1}$$

where $\mathbf{Y}$ = the vector of exit gas SO_2 concentrations; X = the matrix of predictor variables (e.g., % O_2); $\mathbf{B}$ = the vector of regression coefficients to be estimated; and $\mathbf{e}$ = the vector of experimental errors.

Unfortunately, with the predictor variables highly correlated (Table III), the usual least-squares estimates of the regression coefficients, $\mathbf{B}$, tend to become too large in absolute value, and in some cases (e.g., a high negative correlation) these coefficients can have the wrong sign (*4*). Thus, to obtain a better understanding of which predictor variables are important in predicting $\mathbf{Y}$ and to indicate if ordinary least squares is overestimating the $\mathbf{B}$'s, ridge regression estimates of the regression coefficients were obtained by:

$$\hat{\mathbf{B}}^* \equiv \hat{\mathbf{B}}^*(k) = [X'X + kI]^{-1}X'\mathbf{Y}, k > 0 \tag{2}$$

where kI is a diagonal matrix employed to add the value k (which ranges in value from 0 to 1 in increments of 0.1) to each diagonal element of $X'X$. As k is increased, it makes the system behave more as a system where the predictor variables are uncorrelated and therefore gives a better idea of which variables are the important predictors.

Equation 2 was used to generate a ridge trace [$\hat{\mathbf{B}}^*(k)$ vs. k] shown in Figure 2. This trace was used to eliminate ineffective predictor variables. The trace also served to identify the effect of interrelationships among the predictor variables on the regression coefficients and to indicate how sensitive the regression coefficients were to this particular set of data (*4, 6*).

Figure 2 indicates that the ordinary regression coefficients ($k = 0$) are overestimated. Some (e.g., exit gas temperature) decrease rapidly as k increases. For such predictor variables, it is unlikely that another set of data would give the same values of $\hat{\mathbf{B}}^*$. Another indication of the probable overestimation is given in Figure 3, which shows the decrease in the sum of squares of the $\hat{\mathbf{B}}^*(k)$'s vs. k, along with the corresponding decrease in the sum of squares assuming an orthogonal set of data. [If the predictor variables are orthogonal, $X'X$ would be a diagonal matrix and $\hat{\mathbf{B}}^*(k) = X'\mathbf{Y}/(1 + k) = \hat{\mathbf{B}}^*(0)/(1 + k)$.]

Because of the correlations among the predictor variables, the sum of squares of the $\hat{\mathbf{B}}^*(k)$'s is only 57% of its original value at $k = 0.1$. Had the coefficients come from an orthogonal data set, this sum of squares would be 83% of its original value.

Figure 2 also indicates, as expected, that the coefficient of variable 13 (% O_2) is by far the largest. Also, the coefficients of some of the variables (e.g., variable 5) are underestimated at $k = 0$.

After examining Figure 2 in detail, four predictor variables were eliminated; namely, 6 (exit gas temperature), 7 (exit gas underpressure), 8 (fire position), and 10 (% copper in charge). The reasons for these eliminations were as follows: variable 6 because its coefficient was unstable and could not hold its predicting power; variables 7 and 8 because their coefficients were driven toward zero as k increased, and variable 10 because its coefficient was unstable and because of its high correlation with variables 11 and 12 (= −0.79, see Table III).

Having eliminated four variables by the above procedure, another ridge regression was run with the remaining eight predictor variables. The results of this ridge regression were then examined, and an additional four predictor variables were eliminated (variables 2, 4, 9, and 12, which are, respectively, the dust rate, the exit gas flow rate, the charge rate, and the percent sulfur in the charge). A ridge regression was then computed for the remaining four predictor variables, and the resulting ridge trace indicated that the coefficients of the remaining predictor variables were fairly stable as k increased. In addition, a plot similar to Figure 3 indicated that the decrease in the sum of squares of the $\hat{\mathbf{B}}^*(k)$'s as k increases was

Table III. Correlation Coefficients Among Variables Considered (128 Observations)

		Y	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	X_{10}	X_{11}	X_{12}	X_{13}
SO_2 in exit gas	Y	1												
Dust rate	X_2	0.42	1											
% S removed	X_3	−0.05	−0.07	1										
Flow rate	X_4	−0.03	0.36	0.27	1									
Furnace avail	X_5	0.72	0.52	−0.3	−0.1	1								
Temp, °C	X_6	0.12	0.21	0.23	−0.06	0.17	1							
Underpressure	X_7	−0.12	0.00	−0.03	0.37	−0.14	−0.41	1						
Fire position	X_8	−0.27	−0.21	0.12	0.26	−0.46	−0.31	0.3	1					
Charge rate	X_9	0.57	0.35	−0.51	−0.026	0.56	−0.02	0.1	−0.22	1				
% Cu/charge	X_{10}	−0.59	−0.04	0.64	0.34	−0.44	−0.09	0.01	0.3	−0.52	1			
% Fe/charge	X_{11}	0.49	−0.04	−0.57	−0.3	0.32	0.06	−0.08	−0.23	0.37	−0.79	1		
% S/charge	X_{12}	0.44	0.14	−0.44	−0.16	0.31	0.2	−0.04	−0.27	0.33	−0.79	0.55	1	
% O_2, exit gas	X_{13}	−0.92	−0.45	0.28	0.28	−0.7	−0.38	0.26	0.34	−0.47	0.47	−0.34	−0.32	1

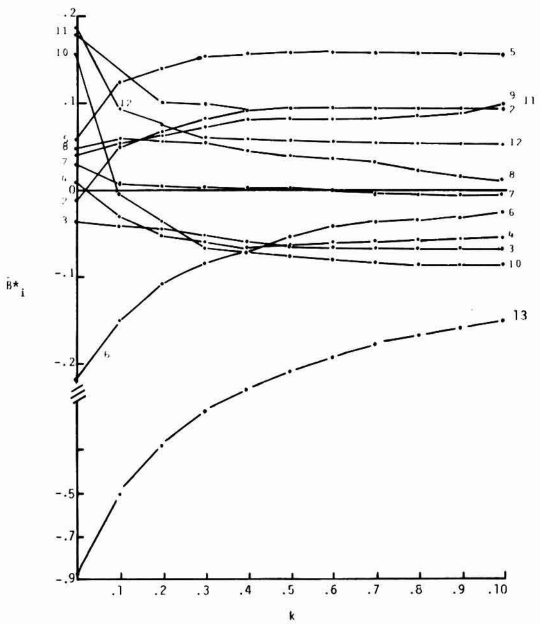

Figure 2. Ridge trace for predictor variables 2–13

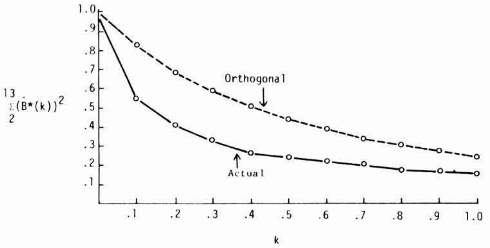

Figure 3. Sum of squares of $\hat{\mathbf{B}}^*(k)$ vs. k, 12 predictor variables

Table IV. Percent of Total Variation in Exit Gas SO_2 Concentration Accounted for by Various Linear Regression Models at $k = 0$

No. of predictor variables in model	Identity of variables	% Variance in exit gas SO_2 concn accounted for
12	Entire set	94.7
8	$X_2, X_3, X_4, X_5, X_9, X_{11}, X_{12}, X_{13}$	90.1
4	X_3, X_5, X_{11}, X_{13}	89.6
2	X_3, X_{13}	88.2
1	X_{13}	83.8

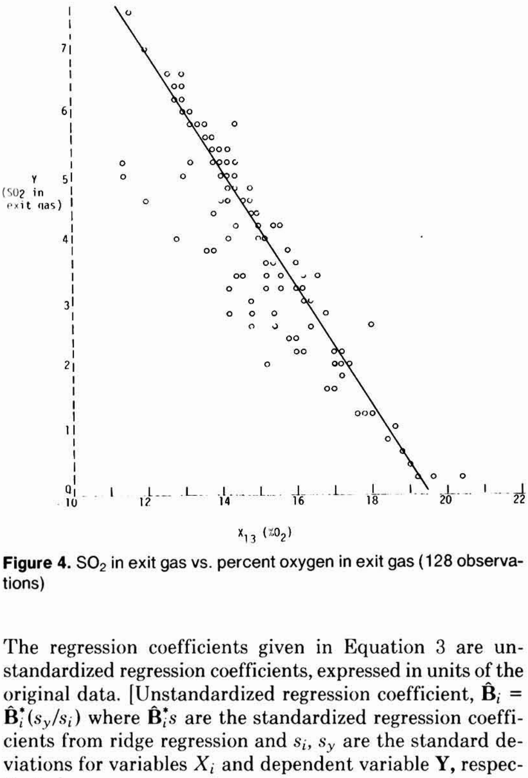

Figure 4. SO_2 in exit gas vs. percent oxygen in exit gas (128 observations)

almost the same as with an orthogonal system of predictors. Having reduced the number of predictor variables to four, several multiple regressions were then computed using these four variables and their subsets. The significant results from these computations are presented below.

Accountability of Regression Models. Table IV presents the percent of the total variation of SO_2 in exit gas accounted for by various linear regression models at $k = 0$. The table shows that the full 12-variable model accounts for 94.7% of the total variance in exit gas SO_2 concentrations; with the four-variable model this percent has only been reduced to 89.6, and with a two-variable model containing X_3 (% S removed) and X_{13} (% O_2 in the exit gas), this percent is 88.2. In addition, 83.8% of the total variation in **Y** is accounted for with a linear model containing only X_{13}. To illustrate the strong relationship between **Y** and X_{13}, Figure 4 presents a plot of these two variables for the 128 observations available for this study. The figure clearly shows a very strong linear relationship between **Y** and X_{13}.

The regression equation with predictor variables X_3 and X_{13} is:

$$\% \; SO_2 = 17.315 - 0.023 \; (\% \; S \text{ removed}) - 0.799 \; (\% \; O_2) \quad (3)$$

$$(\text{for } n = 128)$$

The regression coefficients given in Equation 3 are unstandardized regression coefficients, expressed in units of the original data. [Unstandardized regression coefficient, $\hat{\mathbf{B}}_i = \hat{\mathbf{B}}_i^* (s_y/s_i)$ where $\hat{\mathbf{B}}_i^*s$ are the standardized regression coefficients from ridge regression and s_i, s_y are the standard deviations for variables X_i and dependent variable **Y**, respectively.]

Since percent oxygen in the exit gas (X_{13}) accounts for 83.8% of the total variability in the present data, one is tempted to use only this variable to predict SO_2 concentration. However, an examination of Figure 4 shows that several data points appear to deviate (i.e., for a given percent O_2, their SO_2 values are too small) from the general trend—e.g., at 11.5% oxygen, two points center around a y value for 5%. An investigation of these data points indicated that almost all of them came from tests showing a very high percent sulfur removal (X_3). Thus, the low SO_2 values were attributed to the fact that at such high levels of sulfur removal, a greater portion of the consumed oxygen went to form metal oxides rather than to form SO_2, thus lowering the SO_2 concentration for a given exit gas oxygen level. The fact that the regression model containing both percent sulfur removed and percent oxygen (given in Equation 3) accounts for 88.2% of the total variation (vs. 83.8% for the model with percent oxygen alone) indicates that percent S removed is also an important prediction variable for SO_2 concentration.

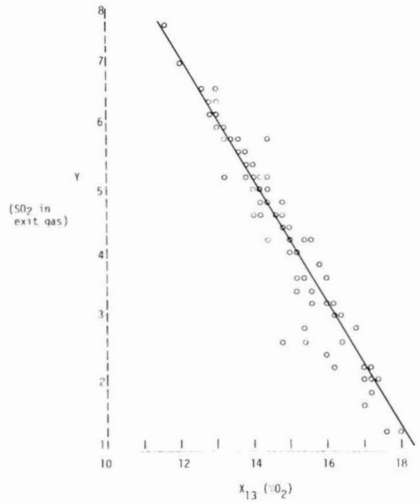

Figure 5. SO_2 in exit gas vs. percent oxygen in exit gas for < 70% sulfur removal (90 observations)

To further investigate the deviations observed in Figure 4, the data were first sorted into two sets, one consisting of those tests with percent S removed < 70%; the other, ≥ 70%. A linear regression model with percent oxygen as the predictor variable was then fitted to each set. The results indicate that the regression models for the two sets are quite different. The two models are:

$$\% SO_2 = 19.21 - 1.008\ (\%\ O_2){:}\%\ S < 70 \quad (\text{for } n = 90) \qquad (4)$$

$$\% SO_2 = 12.56 - 0.624\ (\%\ O_2){:}\%\ S \geq 70 \quad (\text{for } n = 38) \qquad (5)$$

The percent of the total variability accounted for by Equations 4 and 5 is 93.9 and 84.6, respectively. Figure 5 gives the results when percent S removed < 70%.

Conclusions

The analysis identifies the oxygen concentration of the multihearth roaster exit gas as a good predictor to its sulfur dioxide concentration. This factor accounted for 84% of the variance in the exit gas. Of the other 11 predictor variables investigated, the variable that appears to explain more variations in SO_2 concentration after the variation explained by oxygen is eliminated is the percent sulfur removed in roasting. Together, these two variables accounted for more than 88% of the total variation in the SO_2 concentration for the data examined in this report.

Two other variables that appear to explain a small amount of the variation in the SO_2 concentration after the variation explained by oxygen is removed are furnace availability and the iron content of the roaster charge. Furnace availability is simply the percent of time during the tests when all the five roasters of the system were actively roasting. At Bor it appears that the shutdown and startup of a roaster introduced an additional dilution of the exit gases beyond that due to other causes and practices, which was detected in the data analysis. In the modification of a roaster system to achieve high levels of exit gas SO_2, attention should be given to elimination of the particular dilution effects of roaster shutdown and startup. This effect may not exist in a system designed to seal off a roaster when it is taken out of service. Whether it can be eliminated at startup, when fuel is burned to provide heat, requires further investigation. The separate effect of this variable on the exit gas SO_2 concentration is very small, however, compared to that of excess oxygen.

While some excess oxygen must be present to maintain the roasting process, the required lower limit of excess oxygen in the exit gases is not known. During these experiments, a lower limit of 11.6% is attained. If lower limits were shown to be feasible, even higher exit gas SO_2 concentrations could be generated.

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Processes Limiting Oxidation of Sulfur Dioxide in Stack Plumes

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■ A formalism is developed to treat chemical reactions in expanding stack plumes of arbitrary concentration profile to examine the effects of dilution and of oxidant or catalyst depletion upon SO_2 oxidation. The rate and extent of reaction are described in terms of an assumed mechanism and defined measurable properties of the concentration profile. The rate of plume expansion exerts a controlling influence upon reactions that are higher than first order in plume constituents. Quenching of reaction is exhibited at high expansion rates. For the concentration of a conservative tracer diminishing with time proportionately to t^{-n}, a pth-order reaction is quenched for $n(p-1) > 1$ and unquenched for $n(p-1) \leq 1$. The meteorological stability classes that would lead to quenching of second- and third-order reactions are considered. Re-examination of SO_2 oxidation data obtained in studies of the Northport, N.Y., oil-fired plume confirms that the oxidation mechanism is higher than first order and strongly suggests second order. The data are consistent with this mechanism for a wide range of assumed catalyst/SO_2 ratios; it is thus established that no inference may be drawn concerning catalyst depletion. The implications of these new insights are considered relative to the design of plume experiments and to the understanding of SO_2 oxidation mechanisms in plumes and in the ambient atmosphere.

Because of the importance of atmospheric oxidation reactions of sulfur dioxide upon the ultimate fate of this atmospheric pollutant, in the last several years a number of experimental investigations and theoretical analyses of the rate of SO_2 oxidation in power plant and smelter plumes have been conducted. These studies have been motivated by the fact that localized point source emissions of SO_2 represent a substantial fraction of total SO_2 emissions, and by the opportunity afforded by stack plumes as localized, time-resolved "reactors" for the in situ study of the mechanism and rate of these oxidation reactions free from the influence of such uncontrolled laboratory variables as reactor walls. Despite nonuniform plume profiles and rapid dilution of plume constituents with distance, the extent of SO_2 oxidation in a plume may be determined by examination of the ratio of the integrated concentrations of SO_2 and sulfate.

An important feature of reactions in rapidly diluting plumes that are second or higher order in plume constituents is the fall-off in the oxidation rate as a function of distance or time due to the decreased concentration of the reagents with distance. Interpretations of the rate of oxidation of SO_2 in the plumes of the oil-fired Northport, N.Y., plant of the Long Island Lighting Co. (*1*) and of the Sudbury, Ontario, nickel smelting plant [data of Lusis and Wiebe (*2*), as interpreted by Forrest and Newman, (*3*)] have suggested a mechanism that is second order in plume constituents. This dependence has been inferred to represent the contribution of the SO_2 and catalytic particulate concentrations to the overall rate. Freiberg (*4*) also has discussed the effect of plume dilution upon the rates of higher-order reactions.

A second important feature of such is the possibility that rapid dilution may lead to quenching, i.e., that the reagent concentration may asymptotically approach a limit in excess of that dictated by equilibrium considerations. This possibility was suggested in the interpretation of the Northport data (*1*) and was noted as well by Freiberg (*4*) in a model calculation based upon a mechanism that is third order in plume constituents.

A second process that might contribute to the decrease or possible cutoff of the rate of oxidation of SO_2 in plumes is the inhibition of oxidation by depletion as the reaction proceeds, of catalytic or oxidative species present in the plume. Such a process has been suggested to be responsible for the sharply curtailed rate of SO_2 oxidation observed in the early dilution of plumes from coal-fired electric generating plants (*5, 6*) and thus may play a role also in oil-fired and smelter plumes. However, this suggestion has not been quantitatively explored in previous studies, in which the analysis has been confined to the use of the simple rate expression:

$$\frac{\partial(SO_2)}{\partial t} = -k_2(SO_2)^2 \tag{1}$$

that describes the process as pseudo-second order.

In view of the continuing interest in SO_2 oxidation in plumes and of the implications of a limit to the ultimate extent of this oxidation, and in view also of questions that have been raised, e.g. (*7*), concerning the mathematical description of these processes, we consider here, in somewhat greater generality and detail than has been presented previously, the factors that govern the rate and extent of reactions in expanding plumes. We proceed to consider the effects of the two potential processes, dilution and oxidant or catalyst depletion, using the data of the Northport study to examine the degree to which the observed decrease in oxidation rate may be attributed to one or the other of these processes.

General Formalism

In this section we develop equations that describe chemical reactions in an expanding plume, with specific reference to SO_2 oxidation. The treatment is general with respect both to order of reaction in species that dilute with the plume (taking SO_2 as a surrogate for all such species) and to the shape of the distribution of reactive species within the plume, since substantial insight may be developed even at this level of generality.

As is customary we consider the plume to be a steady state reactor. The time dependence of the amounts of the several species, and in turn of the rates of chemical reactions, is inferred from the distance to the stack x through the mean wind speed u as

$$t = x/u \tag{2}$$

where the time variable t represents the age subsequent to emission from the stack of the air parcel at distance x. As previously (*1*) we cast our equations in terms of f, the fraction of sulfur species at distance x that remains as SO_2:

$$f = \frac{\int(SO_2)dA}{\int\{(SO_2) + (SO_4{}^{2-})\}dA} = \frac{\int(SO_2)dA}{\int(S)dA} \tag{3}$$

where (SO_2) and $(SO_4{}^{2-})$ denote the concentrations of SO_2 and sulfate, respectively, and where $(S) = (SO_2) + (SO_4{}^{2-})$ denotes the total sulfur concentration. In Equation 3 the integrals are taken over the entire cross section of the plume $dA = dydz$. We introduce the square bracket notation

$$[S] = \int(S)dA \tag{4}$$

$[S]$ thus represents the number of moles of sulfur per unit extent of the plume in the direction of travel x; we similarly

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define $[SO_2]$ and $[SO_4^{2-}]$. Under the assumption that the sum of the two sulfur species is conservative, i.e., that there is neither fallout of sulfate from the plume nor SO_2 deposition, then $[S]$ is constant and may be evaluated as the quotient of the emission rate of sulfur by the mean wind speed. In the square bracket notation

$$f = [SO_2]/[S] \tag{5}$$

Measurement of f, the ratio of integrated concentrations, may be achieved with aircraft-mounted integrating-type sampling equipment (*1, 8*).

The time rate of change in the amount of SO_2 in the plume (per unit distance in the x direction) may be evaluated as

$$\begin{aligned}\frac{d[SO_2]}{dt} &= u\frac{d[SO_2]}{dx} = u\frac{d}{dx}\int (SO_2)dA \\ &= u\int \frac{\partial(SO_2)}{\partial t}\Big/\frac{dx}{dt}dA = \int \frac{\partial(SO_2)}{\partial t}dA \end{aligned}\tag{6}$$

Here, $\partial(SO_2)/\partial t$ represents the rate of decrease in SO_2 concentration due to chemical reaction, i.e., excluding the decrease due to dilution. For a reaction that is pth order in SO_2, or in other plume species that dilute as SO_2, we denote this rate as

$$\frac{\partial(SO_2)}{\partial t} = -k_p(SO_2)^p \tag{7}$$

Since $[S]$ is constant,

$$\frac{d}{dt}\left\{\frac{[SO_2]}{[S]}\right\} \equiv \frac{df}{dt} = -k_p[S]^{-1}\int(SO_2)^p dA \tag{8}$$

whence

$$\frac{df}{dt} = -k_p[S]^{p-1}f^p\frac{\int(SO_2)^p dA}{[\int(SO_2)dA]^p} \tag{9}$$

In Equation 9 we have used the definitions given in Equations 3–5. This expression for the rate of change of f is useful since all dependence upon dilution introduced by plume expansion is collected in the last factor. Since this quantity has units $(\text{area})^{1-p}$, it is convenient to denote

$$A_*^{p-1} = \frac{[\int(SO_2)dA]^p}{\int(SO_2)^p dA} \tag{10}$$

The effective plume area A_* may in principle be determined from plume SO_2 concentration profiles obtained with real-time sampling apparatus. The ratio $[S]/A_*$ has (Equation 4) units of concentration. Denoting

$$(S)_* = [S]/A_* \tag{11}$$

we may now write Equation 9 as

$$\frac{df}{dt} = -k_p(S)_*^{p-1}f^p \tag{12}$$

Equation 12 is formally identical with that employed in our previous work (*1, 9*), but does not require the previously employed assumption of uniform (top-hat) concentration profile. However, in this equation, which is derived from *arbitrary* concentration profile, the effective sulfur concentration $(S)_*$ defined by Equations 10 and 11 is not an actual concentration that can be measured at a given point but rather is a mathematical construct that can be computed only from a known or assumed (SO_2) profile. Nevertheless, since $(S)_*$ will decrease approximately as a conservative species as the effective area A_* of the plume increases, Equation 12 retains the salient feature of the previous work, viz., that for reactions that are second or higher order in plume species, the effective rate coefficient, $k_p(S)_*^{p-1}$, diminishes as the plume is diluted. In particular, the effective second-order rate coefficient $k_2(S)_*$ exhibits a direct dependence upon plume expansion, whereas the effective first-order rate coefficient k_1 does not. This distinction between first- and higher-order processes has permitted the oxidation of SO_2 to be ascribed to a second-order process both for the Northport oil-fired plume (*1*) and for the Sudbury nickel-smelter plume (*3*).

The differential rate equation in f (Equation 12) may be formally integrated by separation of variables

$$\int\frac{df}{f^p} = -k_p\int(S)_*^{p-1}dt \tag{13}$$

Evaluation of the integral in the right-hand side requires a determination of the time dependence of $(S)_*$ or, alternatively, modeling $(S)_*(t)$ to permit analytical integration.

A significant extension of Equations 12 or 13 may be achieved under the assumption that the SO_2 concentration profile in the plume retains geometric similarity as the plume expands, i.e.,

$$(SO_2)(x,y,z) = (SO_2)_*(x)\chi\left(\frac{y-y_c}{\eta(x)},\frac{z-z_c}{\zeta(x)}\right) \tag{14}$$

Here, χ is a normalized distribution function, $\int\chi d(y/\eta)d(z/\zeta) = 1$, and η and ζ are the scaling parameters of χ in the y and z dimensions, respectively, e.g., σ_y and σ_z for a gaussian distribution; y_c and z_c represent the plume centerline coordinates. This assumption may be expected to apply (*10*), provided that the rate of dilution greatly exceeds that of chemical reaction, as appears invariably to be the case for SO_2 oxidation in stack plumes. With this assumption

$$(S)_* = \frac{[S]}{\eta\zeta}\Gamma^{1/p} \tag{15}$$

where

$$\Gamma = \int\chi^p d\left(\frac{y}{\eta}\right)d\left(\frac{z}{\zeta}\right) \tag{16}$$

is a numerical constant of order unity that depends on the shape function χ. Equation 13 now becomes

$$\int\frac{df}{f^p} = -k_p\Gamma\int\left(\frac{[S]}{\eta\zeta}\right)^{p-1}dt \tag{17}$$

which is formally identical to Equation 13 since $[S]/\eta\zeta$ has units of concentration. The similarity assumption thus permits, for an arbitrary, unspecified shape function, the analysis of the dependence of the reaction rate upon the order of reaction and upon dispersion parameters, *as if this shape function were a uniform box*, since the only effect of a nonuniform shape function χ will be to alter the apparent rate coefficient by the constant factor Γ. We may thus proceed to use Equation 13 as if $(S)_*$ were an actual, uniform concentration. This approach facilitates examination of the mechanism and order of plume reactions.

Equations similar to 17, but restricted to the gaussian shape function and to a specific third-order mechanism, have been presented by Freiberg (*4*) and by Lusis and Phillips (*11*). A similar equation for the time evolution of the concentration in a cloud emanating from an instantaneous, point-source release, expanding in three dimensions, was given by Friedlander and Seinfeld (*10*).

Effect of Plume Dispersion on Rate and Extent of Reaction

To introduce dispersion into Equation 13 or 17, it is convenient to model this process by the usual power-law expression for the concentration of a conservative species in an expanding plume

$$(S)_* \propto t^{-n} \tag{18}$$

It should be emphasized that a simple power-law expression such as Equation 18 is not expected to hold over the entire extent of the plume, but that the effective dispersion index n may change with distance from the stack. This is considered in more detail below. Assuming for the moment that n is constant, we obtain, upon substituting Equation 18 into 13 and integrating, an analytical expression for f_t, the fraction of plume sulfur species remaining as SO_2 at time t, for a reaction of order $p > 1$:

$$\frac{1}{f_t^r} - \frac{1}{f_0^r} = \begin{cases} k_p (S)_0^r t_0 r \left(\dfrac{1}{nr-1}\right) \left[1 - \left(\dfrac{t_0}{t}\right)^{nr-1}\right], & nr \neq 1 \\ k_p (S)_0^r t_0 r \ln\left(\dfrac{t}{t_0}\right), & nr = 1 \end{cases} \tag{19}$$

Here, t_0 represents the plume age at an arbitrary initial time at which Equation 18 is applicable, $(S)_0 = (S)_*$ at t_0, and $r \equiv p - 1$. The initial value f_0 reflects the contributions both of primary sulfate emissions and of oxidation occurring in the plume prior to t_0. Equation 19 represents a generalization to arbitrary reaction order p of the equation we have employed previously in our analyses of SO_2 plume oxidation data (i.e., Equation 16 of ref. *1*). The adherence to the predictions of the model, for given reaction order p and dispersion index n, of a set of experimental measurements of f as a function of plume age t would be indicated by a linear fit of f^{1-p} to the power (or logarithm) of t indicated in the right-hand side (RHS) of Equation 19.

Despite the generality of the assumptions that have been made in the present derivation, we may nevertheless draw important conclusions from this treatment concerning the ultimate extent of SO_2 oxidation in stack plumes. This is facilitated by considering the long-time limiting values of f that are indicated by Equation 19. For low values of the dispersion index n such that $n(p - 1) \leq 1$, the RHS of Equation 19 increases without bound at long times; hence

$$\lim_{t \to \infty} \frac{1}{f_t^r} = \infty, \; n(p-1) \leq 1 \tag{20a}$$

Thus, f_∞ approaches zero, i.e., all of the SO_2 in the plume is ultimately oxidized. On the other hand, for $n(p - 1) > 1$, the RHS of Equation 19 approaches a finite limit,

$$\lim_{t \to \infty} \frac{1}{f_t^r} = \frac{1}{f_0^r} + k_p (S)_0^r t_0 r \left(\frac{1}{nr-1}\right), \; n(p-1) > 1 \tag{20b}$$

In this case, the long-time limit of f is not zero, but is a finite value between zero and one, i.e., for $n(p - 1) > 1$ the reaction is quenched by the expansion. The higher the order of reaction p, the lower is the value of the index of dispersion n that will lead to this dilution quenching. For a second-order reaction, dilution quenching will be manifested for the dispersion index $n > 1$; for a third-order reaction, $n > 1/2$ is sufficient to lead to quenching. This quenching phenomenon depends only on the order of reaction in plume constituents and on the index of dispersion and is independent of the details of the reaction mechanism.

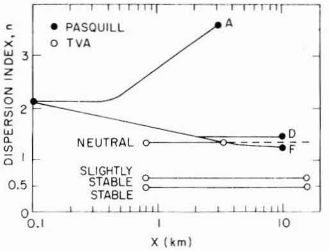

Figure 1. Values of dispersion index n derived by Equation 19 from plots of normalized centerline plume concentrations of Islitzer and Slade (*13*)

A, D, F: Pasquill stability classes. TVA-neutral curve extrapolated beyond 3.2 km. Quenching of second-order reactions expected for values of $n > 1$, and of third-order reactions for values of $n > 1/2$

It may be useful here to consider briefly the values of the dispersion index that may be expected for elevated buoyant plumes in various atmospheric stability classes. The subject of turbulent diffusion has been reviewed, for example, by Gifford (*12*), who emphasizes that no single power law, such as Equation 18, can be expected to fit diffusion data over all down wind ranges. Nevertheless, the approximate linearity over limited ranges of graphs of log σ_y or log σ_z vs. log distance supports the utility of Equation 18. Within that approximation the summary of normalized axial concentration measurements (C) for elevated releases presented by Islitzer and Slade (*13*) is useful for estimating the dispersion index n appropriate for the several atmospheric stability classes. Values of n derived from Figure 4.6 of that paper as

$$n = -\frac{d \log (C)}{d \log x} \tag{21}$$

are shown in Figure 1 for the TVA curves for centerline concentration of stack plumes. Also shown are values of n derived from the Pasquill curves. Briggs (*14*) has described the rise Δh of buoyant plumes as proportional to $t^{2/3}$ and has pointed out as well the proportionality between plume depth and plume rise. Assuming an equivalent rate of expansion in the crosswind dimension leads to $n = 4/3$, identical to the TVA-neutral value in Figure 1.

From estimates of the dispersion index n derived from these several sources, it appears that quenching may be unequivocally predicted for second- and third-order reactions under unstable and neutral conditions, and for third-order reactions even under slightly stable conditions. For slightly stable and stable conditions the considerable variance between the several values of n encompasses the critical values of this parameter and thus precludes an a priori prediction of whether or not quenching of second-order reactions will occur. However, it would appear that the dispersion indicated by the Pasquill curves for slightly stable and stable conditions may be substantially overestimated (*13*), since these curves reflect enhanced dispersion characteristic of low altitude release. Also, the Pasquill curves are based on relatively long-time average plume profiles that include some plume meander, not on instantaneous profiles that would govern the rate of chemical reactions between plume constituents. The diminished rate of dispersion reflected in the TVA measurements may in part be due to the shorter averaging times in those studies (*12*).

On the other hand, the TVA measurements for slightly stable and stable conditions would appear not to reflect near-stack, buoyancy-induced dispersion, which would sharply diminish the rate of second- and third-order reactions. If, however, the rate of dispersion subsequently decreases to the lower values shown, second-order reactions, and under stable conditions, third-order reactions, would ultimately proceed to completion.

The phenomenon of dilution quenching of chemical reactions has been recognized for some time in the somewhat different circumstance of an expanding instantaneous puff that might be suitable for modeling reactions in an urban pall (*10*). The phenomenon was exhibited for a stack plume in a model calculation by Freiberg (*4*) for a mechanism that is third order in plume constituents, with dispersion index $n = 1$, and was indicated as well in the initial Brookhaven paper on the Northport plume oxidation study (*1*). However, in neither of the latter papers is there a description, as displayed here in Equation 20, of the generality of dispersion-induced quenching.

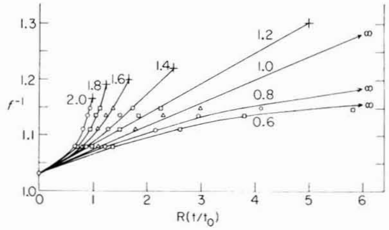

Figure 2. Data of Northport Run 2, ref. *1*, plotted according to Equation 18 for pseudo-second-order mechanism for indicated values of plume dispersion index *n*

f is fraction of SO_2 remaining unoxidized at time of measurement. Dimensionless variable *R*, defined in text, increases with increasing time. Symbol + indicates infinite time extrapolated, or quenched, value of f^{-1}

The Northport study, in fact, provides a useful case for illustrating the sensitivity of the interpretation of the extent of further oxidation of SO_2 within the plume, to rather slight changes in the index n that characterizes the dispersion of the plume. Figure 2 presents the data of Northport Run 2 graphed according to Equation 19 for reaction order $p = 2$ and for several values of the dispersion index n. Unfortunately, the dispersion was not well characterized. For Run 2 the lapse rate at plume altitude (~0.9 °C/100 m) indicated a neutral to slightly stable atmospheric stability (*9*); a value for n of 1–2 was suggested from the decrease in SO_2 concentration with distance. Because of this uncertainty we treat n as an adjustable parameter, constant throughout the run. In Figure 2 f^{-1} is plotted vs. the dimensionless quantity

$$R\left(\frac{t}{t_0}\right) = \begin{cases} \dfrac{1}{nr-1}\left[1 - \left(\dfrac{t_0}{t}\right)^{nr-1}\right], & nr \neq 1 \\ \ln\left(\dfrac{t}{t_0}\right), & nr = 1 \end{cases} \tag{22}$$

that appears to the right-hand side of Equation 19. R is an increasing function of time with the properties that $R(1) = 0$; $R(\infty) = 1/(nr - 1)$ for $nr > 1$ and ∞ for $nr \leq 1$. As in the original paper, values of t, which range from 1.3 to 27 min, were determined from the mean wind speed (Equation 2); t_0 is taken as the value of t at the distance of the initial measurement.

From Figure 2, an acceptable straight-line fit to Equation 19 is obtained for values of n ranging roughly from 0.8 to 1.4; i.e., any value of n within this range would be consistent with the present model. Values of n within this range are consistent as well with the range suggested in Figure 1 for the indicated atmospheric stability. The plot of the oxidation data according to Equation 19 also permits an estimate to be made of the ultimate extent of reaction, by extrapolation of R to its infinite time value. The extent of this extrapolation depends strongly on n. For $n \leq 1$, R is unbounded, f^{-1} increases without bound at long time, and f approaches zero. However, for $n > 1$, R and f^{-1} cannot increase beyond the limits shown in Figure 2; thus, f is interpreted as approaching a limit that, depending on the value of n, may be quite significant compared to unity. For example, for $n = 1.4$ the model predicts the ultimate quenched value of f to be $f_\infty = 0.82$, i.e., only 18% of the sulfur species emitted into the plume would ultimately be oxidized to sulfate by the second-order, in-plume mechanism under consideration. This compares to the measured value of 13% sulfate at 27 min. This strong quenching contrasts with the absence of quenching indicated for $n \leq 1$, and exemplifies the importance of the value of n to the interpretation of plume reaction measurements.

In Figure 3 the data from the same run are plotted according to Equation 19 for a pseudo-third-order mechanism ($p = 3$), in plume constituents has been advanced, for example, by Freiberg (*4*, *15*), representing the contributions of two SO_2 molecules and of iron catalyst to the oxidation rate. An acceptable straight-line fit of f^{-2} vs. R, as required by Equation 19, is obtained for values of n ranging roughly from 0.4 to 0.7, and again the critical value of n that would lead to quenching, $n = 0.5$, falls within this range. As with the second-order mechanism the predicted values of f_∞ range from zero to 0.82 as n is varied throughout the acceptable range. However, it would appear that the pseudo-third-order mechanism may be excluded, since values of n that give a linear fit to Equation 19 seem too low to be consistent either with the measured decrease in SO_2 concentration with distance (*1*) or with the range expected from Figure 1 for the indicated stability. In other words, the rate of oxidation did not decrease fast enough to be consistent both with a third-order reaction and with the rate of plume dispersion.

Effect of Reagent Depletion on Rate and Extent of Reaction

In the preceding discussion consideration has been restricted to a stoichiometric condition in which the several reagents are consumed proportionately. In this section we consider the adequacy of this approach by treating a second process that may preclude the complete oxidation of SO_2 within stack plumes, viz., the depletion of oxidative or catalytic activity of a second reagent as the oxidation of SO_2 proceeds. Such a process might be expected to occur, for example, as the acidity of the aqueous film surrounding catalytic particulates is increased as SO_2 is oxidized to sulfuric acid or as an initially emitted oxidizing species or free-radical precursor (e.g., HONO) is depleted. Since depletion of oxidative capacity by this mechanism would be dependent upon the extent of SO_2 oxidation that has occurred, it seems reasonable to model this process as if the particulate (or other oxidant) P were a reagent that is exhausted during the course of the oxidation,

$$SO_2 + P \rightarrow SO_4^{2-} \tag{23}$$

This mechanism may be represented by the rate expression

$$\frac{\partial(SO_2)}{\partial t} = -k_2(SO)_2(P) \tag{24}$$

where (P) denotes the concentration of particulate (or other oxidant) that is both being diluted as the plume expands and being depleted as the oxidation proceeds. Equation 24 may readily be expressed in terms of f, the fraction of SO_2 remaining unoxidized, by the same procedure as carried out above. By analogy to Equation 5, we introduce the notation

$$[P] = [S](f - e) \tag{25}$$

where e represents the extent, normalized to $[S]$, by which the amount of SO_2 initially present exceeds that of the particulate,

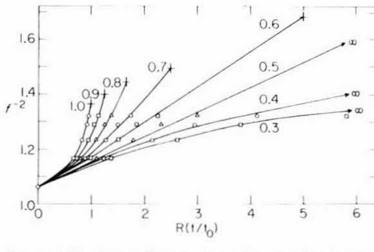

Figure 3. Data of Northport Run 2 plotted according to pseudo-third-order mechanism for indicated values of plume dispersion index *n*

according to the "Reaction" 23. For $0 < e < 1$, the particulate would ultimately become the "limiting reagent", and e represents the normalized fraction of $[S]$ that would remain unoxidized as the reaction proceeds to completion. For $e < 0$, the particulate is present in excess over the amount needed to react completely with the SO_2 present in the plume; here $-e$ represents the amount of particulate, again normalized to $[S]$, that would remain as the reaction goes to completion.

With the introduction of this notation the differential equation for the time dependence of f becomes (cf. Equation 12 for $p = 2$):

$$\frac{df}{dt} = -k_2(S)_* f(f - e) \tag{26}$$

As in Equation 12 the effective rate coefficient depends directly upon plume expansion; the effective plume area A_* is now given by $[\int (SO_2)dA] \times [\int (P)dA]/[\int (SO_2)(P)dA]$ rather than by Equation 10. This dependence on expansion continues to obtain even for large negative e, $-e \gg 1$. In this limit $[P]/[S]$ is effectively constant, as the oxidation reaction proceeds, i.e., the oxidant or catalytic particulate is only conservatively diluted with the plume. Nevertheless, the participation in the oxidation mechanism of a second species, which is continuously being diluted, remains manifested in the effective rate coefficient. Thus, even under this extreme condition the plume dilution still permits an observable distinction between a first-order reaction and the first-order limit of a second-order reaction.

With the assumption of the power-law dispersion expression (Equation 18), Equation 26 may be analytically integrated. We express this result as

$$L(t) - L(t_0) = k_2(S)_0 t_0 R\left(\frac{t}{t_0}\right) \tag{27}$$

where we have introduced

$$L(t) \equiv -\frac{1}{e}\ln\left(1 - \frac{e}{f(t)}\right) \tag{28}$$

and where R was defined in Equation 22. Equation 27 represents an extension of Equation 19 to the general second-order mechanism (Equation 24). The RHS of Equation 27 is identical with that of Equation 19 so that the concept of quenching pertains to the general reaction as well. For $e > 0$ (SO_2 in excess over particulate), whether the long-time value of f approaches e or some greater quenched value depends on the long-time behavior of R, as discussed above. For $e < 0$ (particulate in excess over the amount needed to oxidize the SO_2 completely), f_∞ will approach zero or a finite value, again depending upon the long-time behavior of R. In fact, the quenching phenomenon is quite general and depends only on the overall reaction order in plume constituents, since changes in mechanism, for a given reaction order, will affect only the left-hand side of Equation 13, whereas the quenching arises entirely from the integration of the right-hand side.

Two limiting cases are of interest for the left-hand side (LHS) of Equation 27. For $e \to 0$, i.e., the pseudo-second-order limit, $L \to f^{-1}$, in agreement with the LHS of Equation 19. For large negative e, the conservative reagent limit, the LHS of Equation 27 approaches $e^{-1}\ln(f_t/f_0)$.

To examine whether a given set of experimental data is consistent with the mechanism of oxidant or catalyst depletion, the quantity L may be plotted against R for assumed values of the plume expansion index n and the excess reagent parameter e; a linear relation is expected for appropriate values of n and e. In the treatment that follows, we consider the linearity of the fit of such a plot for the Northport data for e considered as a variable parameter, holding the value of $n = 1$. This value of n is selected here since a substantially lower value appears to be excluded on the grounds noted above, and since a higher value would enhance the role of plume dilution over that of reagent depletion in controlling the rate and extent of oxidation in the plume.

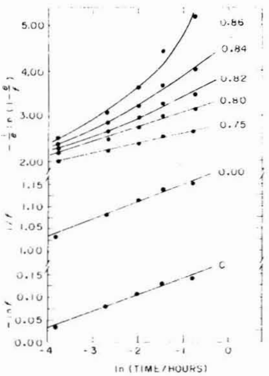

Figure 4. Data from Northport Run 2 plotted according to general second-order mechanism under plume dilution ($n = 1$) for indicated values of excess reagent parameter e

C denotes conservative particulate or large negative limit. Adherence to model is indicated by fit of data to straight line

Figure 4 shows the quantity L computed from the data of Northport Run 2 (*1*) plotted for values of the excess reagent parameter e ranging from 0.86 to the "large negative", conservative reagent, limit. (Since the extent of reaction was followed in this study to 13% of the SO_2 oxidized, values of e greater than 0.87 are summarily excluded.) For values of e greater than 0.82, a significant departure from linearity is observed, but for all values of e less than 0.82 including negative values (i.e., particulate in excess of SO_2), an acceptable straight-line plot is obtained. Thus, the fit to the function f^{-1} corresponding to the pseudo-second-order mechanism treated above, is not a unique description of the SO_2 oxidation rate, but is one of a family of equally adequate descriptions corresponding to the general second-order mechanism for various values of the parameter e.

The more general analysis given here sustains the interpretation given above that oxidation was occurring by a second-order mechanism. The insensitivity of the linearity of these graphs to the value of e, due largely to the limited extent of oxidation represented in the data, supports the use of the pseudo-second-order mechanism ($e = 0$) in the consideration of the effects of dispersion on the rate and extent of reaction. This insensitivity also precludes the precise determination of e. At one extreme ($e = 0.82$) the data are consistent with an amount of oxidative or catalytic activity sufficient to oxidize as little as 18% of the SO_2 initially present; the observed 13% oxidation would, at this extreme, correspond to depletion of roughly three-fourths of the catalyst. At the other extreme the data are consistent with an interpretation that requires no depletion of catalytic activity whatsoever, with the decrease in the observed oxidation rate due entirely to plume dilution. This more detailed analysis thus, while confirming the role of dilution in diminishing the oxidation rate, does not support the heuristic suggestion of Newman et al. (*1*) that the oxidation was limited by catalyst depletion and that conversions much greater than 20% are not to be expected. Rather, this analysis demonstrates that the data under examination cannot provide information relative to the question of exhaustion of particulate activity as the oxidation reaction proceeds.

Discussion and Conclusions

Perhaps the strongest conclusion to be derived from this analysis is that for higher than first-order reactions in dispersing plumes, the value of dispersion index n plays a controlling role in determining the rate and ultimate extent of reaction. This dependence follows naturally from two assumptions of the model by which the reaction was described, specifically: The dispersion of plume constituents occurs according to the nth power of the time following emission, Equation 18; and the oxidation of SO_2 takes place entirely by a mechanism that is pth order in plume constituents, Equation 7. While we consider these features of the model to be approximately correct in regions relatively close to the stack where in-plume reactions would be most important, ultimately we would expect each of these assumptions not to hold. We consider here the implications of these assumptions upon the interpretation of plume experiments and upon the design of future studies.

Because of the demonstrated strong dependence of the rate and extent of plume reactions upon the index of dispersion n, it would appear mandatory in future studies that this parameter be determined independently of the oxidation measurements, and with a degree of precision consistent with the important role of this parameter. Alternatively, in view of the strong influence of the rate of dispersion upon the rate of chemical reactions in expanding plumes and upon mechanistic interpretations derived from these measurements, it would appear highly worthwhile to carry out experiments in which the SO_2 *profile* is actually determined at various distances, by real-time, fast-response instruments. This would permit a direct determination of A_* (Equation 10) and S_* (Equation 11) and in turn would permit the SO_2 oxidation data to be interpreted via Equation 13 without the imposition of a model for the plume dispersion. Additionally, such measurements would permit interpretation of quenching of faster reactions for which the similarity assumption would be inapplicable because of flattening of the concentration profile due to reaction. This flattening would enhance the rate of increase of A_* with time and thus contribute further to quenching of reaction.

With respect to the assumption that SO_2 is oxidized only by reactions between plume constituents, we would note that in addition to this process, oxidation may be expected to occur as SO_2 in the plume is admixed with constituents present in the ambient atmosphere. This may occur either by a heterogeneous mechanism involving aerosol particles or by a homogeneous mechanism involving active intermediates. Either process would be first order *in plume constituents,* and hence would be expected to dominate the SO_2 oxidation at long times. Thus, the continuously diminishing oxidation rate implied in Equation 12 or 19 will ultimately level off at a nonzero value characteristic of the local burden of catalytic or active species; therefore, the final measured value of the oxidation rate in a plume may be taken as an upper limit to this ambient oxidation rate. From the Sudbury plume data (*2, 3*), we may take this upper limit as $\sim 0.5\%\ h^{-1}$; the low rates of SO_2 oxidation measured in coal-fired plumes (*5, 6*) suggest a similar upper limit to this rate. Oxidation of SO_2 at the low, ambient rate will then continue, along with deposition processes, until the SO_2 is entirely consumed.

Note that the picture of SO_2 oxidation described here differs substantially from that depicted, for example, by Wilson et al. (*16*). According to that picture, SO_2 is oxidized principally by species present at low concentrations in the ambient atmosphere, and this oxidation is suppressed in concentrated plumes by the large excess of plume constituents. An example of such a mechanism would be oxidation of SO_2 by free radicals whose concentration is coupled to the ambient ozone concentration, which is strongly diminished by nitric oxide present in the plume. Similarly, if ammonia were required to neutralize sulfuric acid formed during the SO_2 oxidation before oxidation could proceed further, the depletion of this species in the concentrated plume might suppress the reaction until the plume became sufficiently diluted with ambient air. If SO_2 oxidation were occurring by such a process, one might expect an *increase* in the oxidation rate until the ambient level was attained. This increase might be gradual and continuous or, alternatively, might be characterized by a more or less abrupt onset at some distance downwind from the stack at which a critical plume constituent, e.g., NO, has become "titrated" by admixture with the ambient air. In fact, a limited amount of evidence for a process of the latter sort has been presented (*16*). While ultimately the choice between the two pictures must await further experimentation, we feel at the present time that there is substantial evidence demonstrating the absence of any increase in the SO_2 oxidation rate out to distances upward of 60 km, and plume ages in excess of 3 h, for oil-fired (*1, 17*), coal-fired (*5, 6*), and smelter plumes (*3*), and consequently that the ambient oxidation rate must be of the order of $0.5\%\ h^{-1}$ or less.

With regard to the examination of a possible oxidant on catalyst depletion mechanism for limiting SO_2 oxidation in oil-fired and smelter plumes, we conclude that the observed decrease in the SO_2 oxidation rate as a function of time subsequent to emission from the stack does *not require* the assumption of such a mechanism, despite plausible arguments that have been presented previously (*1*), based upon the relative mass emissions of particulates and SO_2, that such a mechanism might be expected. Rather, the decrease in oxidation rate may be due entirely to plume dispersion, and the data are entirely consistent with the SO_2 surrogate, pseudo-second-order mechanism.

The oxidation measured in the Northport plume contrasts with the results of the studies of SO_2 oxidation in certain other oil-fired plumes (*17*) and in coal-fired plumes (*5, 6*), where the oxidation is not interpretable in terms either of a second- or a first-order mechanism. In those studies the extent of oxidation seldom exceeded 5% and was generally only 1–3%. Furthermore, any oxidation subsequent to emission was quite minimal and appeared to be arrested within the first 5 km. We thus continue to feel that the ascription of the arrest of oxidation in coal-fired and certain oil-fired plumes to catalyst poisoning remains plausible, although an alternative interpretation might be that the observed sulfate is largely produced prior to stack emission and that the emitted particulates are essentially catalytically inactive.

Note Added in Proof

Since completion of this work, we have learned of a study by J. Freiberg, to be published in the proceedings of the International Symposium on Sulfur in the Atmosphere, that reaches similar conclusions concerning the quenching of SO_2 oxidation in plumes.

Acknowledgment

We thank Paul Michael for his valuable suggestions and continued interest in this work, Ronald Meyers for incisive discussion, and Robert Brown for his careful reading of the manuscript. We thank a referee for pointing out the applicability of Briggs' treatment to the discussion of quenching.

Nomenclature

( ) = concentration of the indicated species as a function of x, y, and z in the plume

[ ] = amount of the indicated species per unit extent of the plume in the x-direction; a function of x only

(S) = total sulfur concentration = $(SO_2) + (SO_4^{2-})$

$(S)_*$ = effective sulfur concentration, Equation 10; a function of x only

$(S)_0$ = effective sulfur concentration at initial time t_0
$(SO_2)_*$ = effective SO_2 concentration, Equation 13
(P) = concentration of catalytic particulates
(C) = plume centerline concentration of conservative tracer
$dA = dydz$ = differential area element of plume cross section
A_* = effective cross-sectional area of plume, Equation 10; a function of x
χ = normalized (SO_2) distribution function, Equation 14; a function of y and z only
$\eta(x)$, $\zeta(x)$ = scaling parameters of χ in y and z dimensions
Γ = shape factor, Equation 15, a constant for a given reaction order and plume distribution function
x, y, z = distance variable in the directions of plume travel, cross-wind, and vertical, respectively
u = mean wind speed in the x direction
t = plume age, Equation 2
f = fraction of sulfur present as SO_2, a function of x or t
f_0 = fraction of sulfur present as SO_2 at initial time t_0
f_∞ = fraction of sulfur ultimately remaining as SO_2
e = excess reagent parameter, Equation 24
p = order of reaction in plume constituents
$r = p - 1$
n = index of plume dispersion, Equation 18
k_p = reaction rate coefficient for pth order reaction
R = dimensionless, increasing function of time, Equation 21
L = measure of extent of reaction, for general second-order mechanism, Equation 28

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Measurement of Cu and Zn in San Diego Bay by Automated Anodic Stripping Voltammetry

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■ Cu and Zn values were measured in San Diego Bay by anodic stripping voltammetry with a specially built, automated instrument. During 1975–1977, trace metal surveys were conducted in the bay from a small vessel. Samples were collected and analyzed aboard the craft while under way. Cu and Zn concentrations were less than 0.1 and 0.6 μg/L, respectively, at the mouth of the bay and increased toward the center of the bay to approximately 2.5 and 2.9 μg/L, respectively. Also, synoptic measurements made at a stationary pier location showed that Cu and Zn concentrations coincided precisely but inversely with tidal cycles. Cu and Zn measurements made by automated anodic stripping voltammetry were compared to measurements made by extraction on Chelex 100 followed by analysis by flame atomization atomic absorption spectrophotometry. The two methods produced values that were indistinguishable within experimental error.

Cu and Zn are of interest in the study of marine environments because these elements are necessary to living organisms at trace concentrations, while at higher levels they rapidly become toxic. The concentrations and distributions of Cu and Zn in the waters of metropolitan bays and harbors are of particular concern because of potential industrial and urban discharges and because circulation in these basins is restricted. Antifouling paints and cathodic protection devices used on ships are also potential sources for these metals. We have measured Cu and Zn in surface waters in and around San Diego Bay, Calif., with an automated anodic stripping voltammetry (AASV) device which enabled us to make a determination for either Cu or Zn every 10–20 min. We made hundreds of determinations at a stationary pier location and conducted a general study of the surface distributions of the metals in the bay from aboard a small vessel. We also wished to compare Cu and Zn concentrations obtained by AASV with those obtained by a spectrophotometric procedure. Therefore, in parallel with our voltammetric determinations we collected discrete samples of bay water and measured their Cu and Zn content by extraction on Chelex 100 followed by analysis by flame atomization atomic absorption spectrophotometry.

This report discusses new improvements to the voltammetric system, presents the results of the voltammetric surveys and those of the intercomparison of methods, and attempts to relate these measurements to the circulation pattern of the bay and to speciation models proposed by other investigators.

Experimental

Voltammetry. *Cell Modifications.* All measurements were made with a tubular mercury graphite electrode (TMGE),

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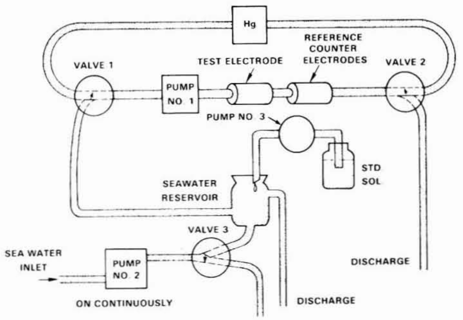

Figure 1. Schematic of electrolysis cell

previously described (*1*), which is part of an automated anodic stripping voltammetry system. The original system consisting of a solid state programmer, which controls a PAR 174 polarographic analyzer, two peristaltic pumps, and five solenoid valves has been described in detail (*2*). In this work we modified the electrolysis cell by eliminating the recycling of the sample through the electrodes, replacing the reference electrode with a new Ag/AgCl–Pt reference-counter electrode, eliminating the analysis of an independent solution, which was a procedure previously included in the automated sequence, and installing a third peristaltic pump to dispense a standard solution into the sample. A diagram of modified cell is shown in Figure 1. The new cell configuration contains two solution loops: a closed loop for the mercury solution which, as previously, can be passed through the electrodes by pump No. 1 and returned to the reservoir; and an open loop in which seawater is taken from its reservoir, passed through the electrodes, and discharged through valve 2. Because the seawater sample travels through the electrodes only once, it was necessary to increase the volume of the test cell to 1 L and to increase the pumping rate accordingly. Thus, a 4-min electrolysis required a seawater flow of 240 mL/min. We found that passing the sample through the electrode only once eliminated the recycling of possible contaminants and rendered the system essentially self-cleaning.

Reference electrode. The Ag wire reference electrode used originally (*1*) was replaced by a newly designed, tubular Ag/AgCl–Pt reference-counter combination electrode. This electrode was constructed as follows: an anodized Ag wire covered with AgCl was obtained from the reference element of a broken combination pH electrode (Corning No. 476050) and wound around a 2.5-cm-long porous polyethylene tube (0.32 cm i.d., 0.64 cm o.d.). The Ag wire was fastened around the tube with Teflon heat shrink tubing, and a portion of Ag wire was allowed to extend beyond the polyethylene. This piece was then folded over the heat-shrink tubing. A 2-cm portion of a thin strip of Pt foil, 4 cm long and 0.2 cm wide, was placed against the interior wall of the polyethylene tube. A 2.5-cm-wide Pt gauze was then rolled into a cylinder, inserted into the polyethylene tube, and pressed into the wall, firmly entrapping the foil strip. The remaining 2 cm of foil were then bent over the Teflon tubing. The Ag wire and Pt foil were then fixed in place with epoxy adhesive, with a small length of bare wire or foil left exposed for electrical connections. The polyethylene tube was then impregnated with KCl-saturated agar by immersing it in warm agar solution under vacuum. Finally, the Ag wire was soldered to the "reference" lead of the PAR 174, and the Pt foil was soldered to the corresponding "counter" connection. Figure 2 is a diagram of the electrode. Soon after construction, we measured the potential of the reference electrode against a saturated calomel electrode at room temperature and found it to be −47 mV. We remeasured this potential after using the electrode for a year and found it to be essentially unchanged.

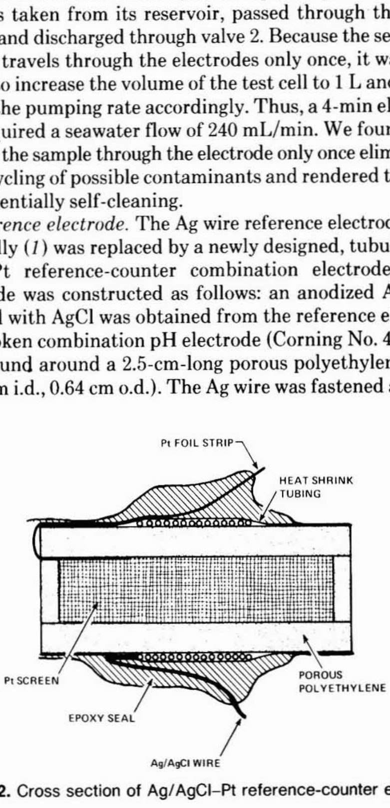

Figure 2. Cross section of Ag/AgCl–Pt reference-counter electrode (*13*)

Procedure. The TMGE, stock solutions, and standards were prepared as described previously (*1, 2*). Standard additions, however, were performed automatically by coupling a third peristaltic pump to the controller. The pump was a SAGE Model 371 tubing pump with 1-mm i.d. silicone rubber tubing which delivered 0.62 ± 3% mL/min of standard. Sampling and analysis procedures have already been described (*2*) but will be briefly summarized here for completeness.

The sample is collected from the sea by means of a peristaltic pump (No. 2 in Figure 1) which draws unfiltered seawater to the instrument through a 17-m length of Tygon tubing. The seawater flows through a three-way valve (No. 3 in Figure 1) and ordinarily is discharged. When valve 3 is activated, the sample is diverted into the test reservoir and purged of oxygen with Coleman grade CO_2. This brings the pH of seawater to $\simeq 4.9$. The height of the discharge port in the test reservoir controls the sample volume, while the volume of flow into the reservoir determines the degree of rinsing. When a sample has been collected, valve 3 is deactivated, $Hg(NO_3)_2$ solution is circulated through the electrode assemblage via valves 1 and 2, and a potential is applied to the electrode to deposit the Hg film. The potential for deposition of the sample is also the potential for deposition of Hg. We chose −1.6 V vs. Ag/AgCl for the determination of Zn and −1.0 vs. Ag/AgCl for the determination of Cu. This lower electrolysis potential eliminates the interference of Zn on Cu. After the film has been deposited, the sample is introduced into the electrodes by energizing valves 1 and 2 and is then discarded. Constant potential electrolysis is carried out for 4 min, and then the flow is stopped. The metals accumulated in the film, as well as the film itself, are oxidized by applying a pulsed potential ramp to the electrode. The cell current is recorded and the anodic scan is terminated after the oxidation of the Hg. Flow is then resumed, Hg solution is reintroduced into the electrodes, the potential is reapplied, and the sample cell is refilled. The process is continuous and a standard addition is made to every third sample. The differential pulse scan was made with a 50-mV pulse at a rate of 10 mV/s.

The AASV instrument was initially placed at the Naval Ocean Systems Center (NOSC), San Diego, in a building with a bay front location. This location corresponds to position D in Figure 6. The sampling tube, which extended from the instrument to the collection point, was secured to a weight by a 1-m line and to a float and placed in the water approximately 1 m above the bottom and approximately 17 m from the shore. Analyses for Cu and Zn in the unfiltered water were made irregularly by the following procedure. A freshly prepared electrode was placed in the instrument. Freshly prepared $Hg(NO_3)_2$ solution and standard solutions (if required) were placed in their respective containers, and the instrument was turned on. The controller then directed all instrument functions, and the device was left unattended for about 24 h at which time the electrode was reexamined for sensitivity, replaced if required, and the determinations were either continued for another day or terminated. The instrument was programmed to perform an analysis every 20 min and to make a standard addition to every third sample. A strip chart recorder registered the trace metal peaks from which concentrations could be computed later. No corrections for "blanks" were made (*2*).

When measurements were made from a small boat, a similar procedure was used, and the sampling line was towed approximately 17–50 m behind the vessel, with the intake just below the water's surface. No contamination from the boat was detected under these sampling conditions (*2*). For comparison with ASV values, 4-L samples would occasionally be taken from the main discharge line and collected in acid-washed LPE bottles for subsequent analysis by atomic absorption spectrophotometry.

Extraction and Atomic Absorption Spectrophotometry. Cu and Zn were determined in seawater by atomic absorption spectrophotometry (AA) after extraction with a chelating resin of the imino diacetic type (Chelex 100, Bio-Rad Laboratories, Richmond, Calif.). Our procedure is a modification of the method of Riley and Taylor (*3*).

Apparatus and Instrumentation. The resin was packed in 1.5 cm diameter × 30 cm long Pyrex glass columns. These columns are similar to those commonly used for the determination of NO_3^- (*4*). The upper part of the column was expanded into a reservoir capable of receiving the neck of a narrow mouth 4-L polyethylene bottle. The lower portion of the column was connected with silicone rubber to a length of 1-mm i.d. capillary tubing which was extended upward beyond the top of the resin. A u-bend was then made, and the tip of the capillary was cut off at the level of the resin. Flow was controlled with a screw clamp placed across the silicone tubing. Eluate from the columns was received in 250-mL Teflon FEP wide mouth bottles.

Atomic absorption measurements were performed with a Perkin-Elmer Model 306 instrument. Samples were atomized using an air–acetylene flame. Radioactivity was measured in a 7.6 × 7.6 cm well-type NaI (Tl activated) gamma ray detector coupled to a gross gamma counter.

Reagents. Four-liter stock solutions of 2 N HCl and 2N NH_4OH were prepared by diluting appropriate volumes of a reagent grade HCl and NH_4OH with quartz distilled deionized water (D2I H_2O). Chelex 100 (Bio-Rad Laboratories, Richmond, Calif.) acquired in the 50–100 and 100–200 mesh size was sieved and cleaned prior to being packed into columns. A stock oxine solution was prepared by dissolving 5 g of oxine in 46 mL of glacial acetic acid and diluting to 100 mL.

Procedures. A slurry composed of resin D2I H_2O was poured into the column and allowed to settle until the resin filled the bottom 15 cm. A plug of glass wool was placed atop the resin to act as a coarse filter. A resin was then cleaned and regenerated by the addition of reagents in the following order: 100 mL D2I H_2O, 60 mL 2 N HCl, 140 mL D2I H_2O, 60 mL NH_4OH, and 150 mL D2I H_2O. Freshly collected 4-L samples of seawater (pH ≃ 8.1) were passed through the resin bed by simply inverting the collection vessels over the top of the column (the 4-L bottles were supported by the shoulder on a ring which was itself connected to a stable laboratory rack). The flow of seawater through the column was not allowed to exceed 5 mL/min, and approximately 24 h were required for the passage of the sample. The column was then rinsed with five bed volumes of D2I H_2O for a total volume of 150 mL. Cu and Zn were eluted with 60 mL of 2 N HCl followed by another 150 mL of D2I H_2O. The first 100 mL of eluate were collected in a 250-mL Teflon bottle and reduced to dryness by lyophilization. The crystalline residue was then redissolved by pipeting 5 mL of 2 N HCl into the Teflon bottle. Direct analysis by flame atomization AA then followed. Concentrations were calculated by comparison with standard solutions prepared in 2 N HCl. Lieberman (*5*) has shown that the same response to standard additions was achieved in both the sample matrix and in the pure 2 N HCl matrix. Columns were then regenerated with 60 mL of 2 N NH_4OH followed by 150 mL of D2I H_2O.

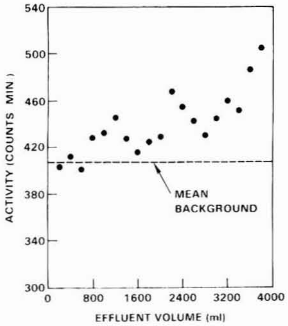

Figure 3. ^{65}Zn remaining in seawater after extraction with Chelex 100 in NH_4^+ form

Analyses Blanks. Blanks were estimated according to the procedure of Riley and Taylor (*3*). For each determination 4 L of seawater were processed through Chelex 100 as described and collected. The column was then eluted and regenerated. The collected Cu and Zn "free" seawater was then passed through the column once more and discarded. Finally, the resin was eluted and the elute lyophilized, redissolved in 5 mL of 2 N HCl, and analyzed by atomic absorption.

For Cu, individual analysis blanks were determined for each column. For 50–100 mesh Chelex 100, blanks for the five columns were 0.24, 0.21, 0.24, 0.24, and 0.36 μg Cu/L, respectively. A sixth column packed with 100–200 mesh resin measured 0.4 μg Cu/L. Zinc blanks were determined similarly. However, 22 determinations were made in all, and up to five blank determinations were made for each of five columns. Because no significant difference could be detected between individual columns, all of the data were pooled and a grand mean and standard deviation were computed. Two of the 22 blank determinations were found to lie beyond three standard deviations of the mean and were assumed to have been contaminated. The remaining determinations computed to a mean blank of 0.4 ± 0.2 μg Zn/L. This value was then subtracted from the Zn concentrations obtained from individual samples.

Column Retention and Recovery. Column retention for Zn was estimated by adding carrier-free ^{65}Zn with a total activity of 72 000 counts/min to a freshly collected, unfiltered 4-L sample of San Diego Bay water. The radioisotope was allowed to equilibrate with the water for 2 h and then was passed through the column. The effluent and succeeding 150 mL of D2I H_2O rinse were collected in sequential 200-mL aliquots. Each aliquot was reduced to a volume of 10 mL using the oxine cocrystallization procedure described by Weiss and Shipman (*6*). Each effluent fraction was then counted. The column was then eluted with 60 mL of 2 N HCl followed by a 150-mL D2I H_2O wash, and the initial 100 mL of eluate were then collected and counted. The results of this experiment are presented in Figure 3 which shows that there is a trend toward higher activity in the later effluent fractions. However, even the most active fraction (approximately 100 counts/min above background) represented less than 3% of the activity expected if breakthrough was fully developed. A total of 97.9% of the ^{65}Zn added to the 4-L seawater sample was recovered in the initial 100 mL of eluate. Since the resin has a higher affinity for Cu than it does for Zn, it was reasoned that Cu should also be extracted and recovered quantitatively. This was further investigated by adding $\mu g/L$ quantities of Cu to 1-L aliquots of San Diego Bay water that had been previously passed through Chelex 100 and then treating the spiked water as a normal sample. As determined by this procedure, the mean recovery was 99%.

To verify that both Cu and Zn could be collected quantitatively in the first 100 mL of eluate, we spiked 4 L of seawater with Zn and Cu, collected the eluate in 10-mL fractions, and subsequently analyzed each fraction by flame atomization AA spectrophotometry. The results are presented in Figure 4 which indicates that Cu and Zn are primarily eluted as two narrow concentration peaks. All of the Cu was recoverable in the first 100 mL. However, 2% of the Zn was lost in the tail of the peak. This loss was correctable and not significant. We cannot explain the smaller "Zn peak" centered at 30 mL.

Results and Discussion

Initial measurements of Cu in San Diego Bay were made while participating in a three-day study of southern California coastal waters sponsored by the Food Chain Research Group of the Scripps Institute of Oceanography (SIO). The AASV instrument was placed on the *R/V Ellen B. Scripps,* and the Tygon tubing intake hose was attached to the boat boom and towed behind the ship just below the water's surface (*2*). On 6 March 1975, as the vessel returned to San Diego, measurements for Cu, Cd, and Pb were made outside of the bay, in the shipping lane, and at the ship's berth at the SIO Nimitz facilities next to NOSC. The instrument was programmed to make measurements every 20 min, and the sampling locations reflect the position of the vessel at the time the sample was collected. These measurements are summarized in Figure 5 which reproduces the strip chart record as obtained from the analyzer. The letters refer to locations in Figure 6. Cu is not measurable in the water outside of the bay (A) and is first detected about 1.6 km inside the channel bounded by Pt. Loma and the North Island jetty (C). Cu values are very high at the docking facilities (D). This last sample was collected with the sampling hose dangling directly against the side of the vessel and probably includes trace metal contributions from the ship itself as well as from the ambient water. Cd and Pb, simultaneously obtained with Cu by the analyzer, also showed a marked gradient as we entered the bay, but their distribution will not be discussed at this time. They are shown here to demonstrate the general covariance between the several metal distributions that we have studied.

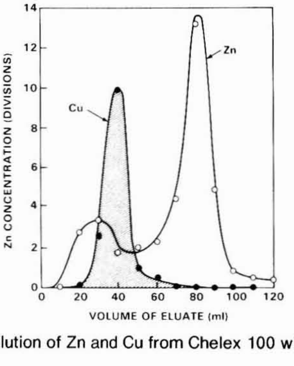

Figure 4. Elution of Zn and Cu from Chelex 100 with 2 N HCl

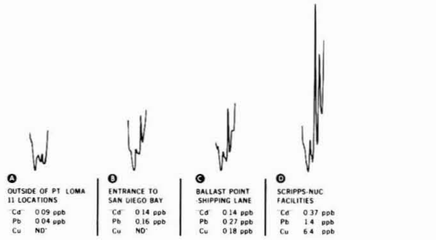

Figure 5. Strip chart record of Cd, Pb, and Cu in seawater obtained while entering into San Diego Bay

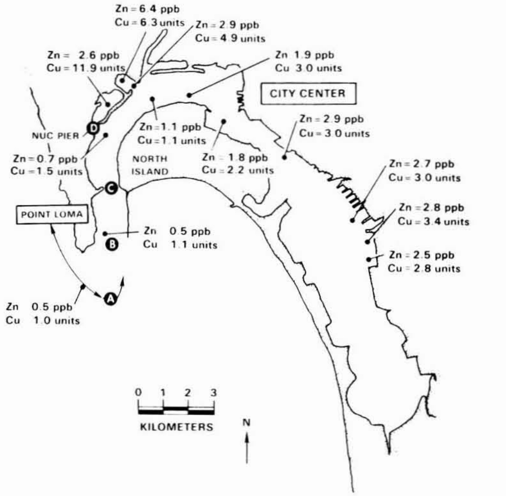

Figure 6. Cu and Zn levels in San Diego Bay surface waters during 10–14 Oct. 1975

The first survey directed to the study of metals in the bay occurred on 9 and 14 October 1975. The AASV analyzer was placed on a small vessel, a converted flat-bottomed landing craft. The Tygon tubing was towed with the intake approximately 17 m from the stern. Initial measurements were made outside of Pt. Loma. The boat then returned to make a rapid survey of the surface waters inside of the bay. Many of these measurements are shown in Figure 6. Other measurements similar to those shown have been omitted for clarity. Because this survey was primarily conducted to study Zn, and the determination of Zn hinders that of Cu, only Zn values are given in ppb. Cu values are presented only in relative units (u). Although these cannot be directly translated to concentrations, they give an indication of the Cu gradients present in the bay.

Overall, this survey confirmed the earlier observation that the surface waters of the bay were considerably higher in Cu and Zn than those outside of Pt. Loma. Pockets of high concentration existed along the shore. These pockets are probably maintained by a source of metal input along with limited flushing. The most obvious of these is the pocket formed by Shelter Island, an artificial construction which serves as a pleasure boat harbor. The north and south embayments of Shelter Island are high in both Cu and Zn with the south cove (the Municipal Yacht Harbor) very high in Cu, while the north (the commercial basin) is very high in Zn. Values of Cu and Zn are higher on the northern (industrial and urban) side of

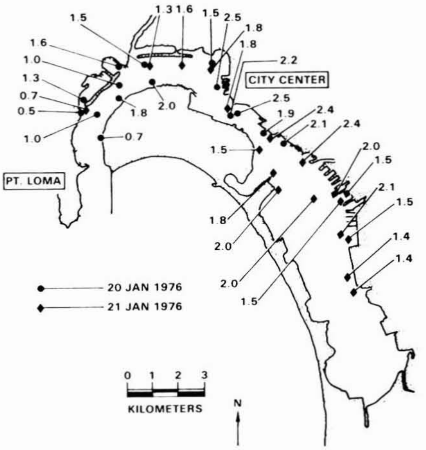

Figure 7. Cu levels in San Diego Bay surface waters during 20–21 Jan. 1976. All values in parts per billion

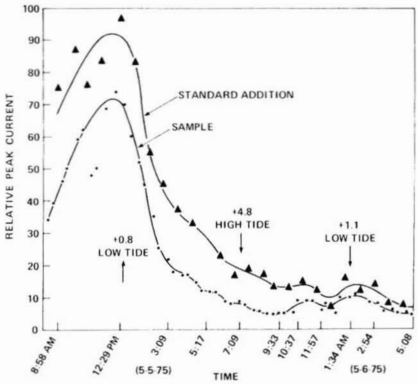

Figure 8. Peak currents for Cu in seawater and seawater plus standard addition of Cu

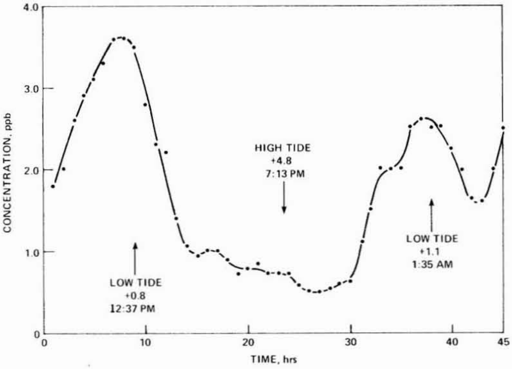

Figure 9. Tidal fluctuations of Cu concentrations in San Diego Bay 5–6 May 1975

the bay than at the center of the channel where incoming surface water dilutes the ambient bay water.

A second survey directed primarily to the study of Cu was conducted during 20–21 January 1976. The results of that work are presented in Figure 7. As noted earlier, Cu concentrations are lower (<1.0 μg/L) near the bay mouth and increase into the bay. The highest concentrations, from 2.0 to 2.5 μg/L, are found near and south of the city's center, where industrial concerns and extensive shipping and berthing facilities are located.

In general, the Cu and Zn concentrations found inside of the bay are only slightly higher than the generally accepted values for open water (7) and are not deemed toxic. Nevertheless, the small but positive gradient from the mouth to the central side of the bay suggests a slow but continuous source for Cu and Zn. It is also notable that we did not locate any point sources of high concentration. Because of the multiple potential sources located at the north-central side of the bay, it is at present impossible to single out individual polluters. Nevertheless, it appears that ships' antifouling paints and cathodic protection devices are plausible sources for at least some of the observed Cu and Zn. Such an explanation would also apply to the Municipal Yacht Harbor and commercial basin which are baylets of very high density berthing and restricted circulation. Although we have presented only a few days' data, other surveys conducted generally confirmed the overall surface distribution pattern presented in Figures 6 and 7.

Tidal Variations in Cu and Zn Concentrations. Between surveys the AASV instrument was placed at the NOSC waterfront location. Cu data collected on 5 and 6 May 1975 are typical of the information that has been collected at this location. The raw data were obtained from the strip chart recorder as a series of peak heights which could then be plotted vs. time as two distinct curves: the locus of points of the peak heights obtained from the analyses of seawater and the locus of points of the peak heights obtained from seawater to which a standard had been added. These two plots are presented in Figure 8. The seawater plus standard plot automatically compensates for the gradual variations in electrode response and eventual loss of sensitivity caused by the accumulation of "contaminants" in the film (2). Abrupt spikes and uneven behavior are also corrected because a "smooth fit" curve is drawn through all the points. Trace metal concentrations are computed from the difference in the heights of the curves by direct proportion. Following this procedure, Cu concentrations were plotted as a function of time to yield the curve presented in Figure 9. Over the two-day period, Cu concentrations are seen to vary from 3.6 μg/L to a low of approximately 0.5 μg/L. Values collected at low tide are much higher than those collected at high tide, presumably because a wedge of bay water, high in metals, has moved southward past our stationary inlet. Toward the end of the measurements the electrode has lost sensitivity, and the error in the computed concentrations is high. Nevertheless, the differences between low and high tide are obvious.

Similarly, Zn was measured at the same location between 10 and 15 June 1975. One electrode was used for all 380 determinations. The results are presented in Figure 10. The lower plots represent the loci of the points obtained from the seawater and seawater plus standard. The upper plot represents the calculated concentrations plotted vs. time of sampling. For the five days the concentration of Zn varies between 0.6 and 3.8 μ/L, and it follows the semidiurnal tidal fluctuations characteristic of San Diego Bay. As in the case of Cu determinations, some resolution is lost on the last day because the electrode has lost sensitivity.

Our trace metal results confirm the observation made by McDermott and Heesen (8) that at the entrance to San Diego Bay, Cu levels increased at the end of the outflowing tidal cycle. We propose to explain our observations as follows: San Diego Bay is a tidally flushed basin with Mediterranean characteristics; from spring to fall there is virtually no inflow of fresh water, and the rate of evaporation is high. Surface

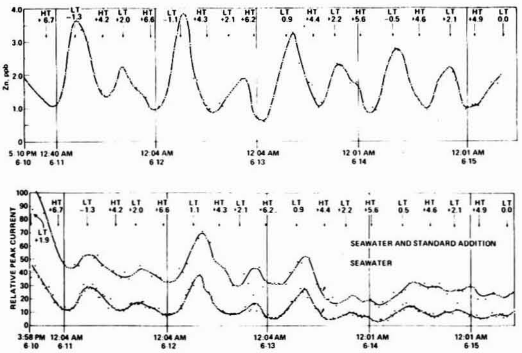

Figure 10. Upper: Tidal fluctuations of Zn concentrations in San Diego Bay during 10–15 June 1975. Lower: Peak currents for Zn in seawater and seawater plus standard addition (*13*)

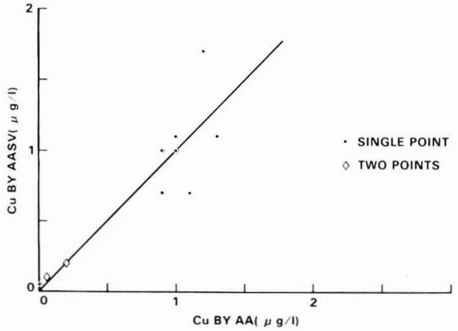

Figure 11. Correlation between Cu values obtained by AASV and Chelex 100-AA

evaporation and pronounced night cooling produce cold saline water which flows out of the bay along the bottom. This outflowing water is replaced with surface water from outside of the channel. In the spring and early summer a thermal gradient, which can be approximated by a two-layer system, develops (*9*). The depth of this gradient increases out of the channel where the ratio of bay water to ocean water is reduced. Tidal forces cause the position of the density interface to oscillate in the channel. The outflowing, colder, saline water which is formed throughout the bay has by virtue of its formation resided longer in the basin than the surface ocean water and therefore has also been exposed longer to the sources of trace metal pollution within the bay. Thus, at our stationary pier location we can observe Cu and Zn concentrations increase at ebb tide when the outflowing bay water passes our sampler. Conversely, during flood tide, relatively uncontaminated ocean water reaches our intake. The motion of water in the channel has been well documented by Smith (*9*) who for a year made measurements of tidal height, current speed, current direction, and temperature and salinity at the same pier location where we made our trace metal measurements. Our observations and our model of the trace metal circulation correspond to his findings.

Results of Intercomparison of Cu and Zn Concentrations Obtained by AA and ASV. Twelve 4-L seawater samples were collected from the outflow line of the AASV instrument at various times and locations and analyzed for Cu by extraction on Chelex 100 followed by analysis by atomic absorption. The result of this study is presented in Figure 11. A linear regression of the 12 points yields a slope of 1.00 and an intercept of −0.01. The coefficient of correlation is 0.92. Thus, within experimental error the values obtained by the two methods are identical. Similarly, 22 samples were collected over a five-month period, and their Zn concentrations were measured by the two methods. The results are plotted in Figure 12. As for Cu there is no systematic difference between the results obtained by either method. A linear regression of the data yields a slope of 1.07 and an intercept of −0.20. The coefficient of correlation is 0.89. The findings are in excellent agreement with those obtained by Fukai and Huynh-Ngoc (*10*) who conducted a similar experiment under comparable conditions. Similarly, the data of Florence and Batley (11) can be interpreted to show that the Cu value obtained by extraction with Chelex 100 in the NH_4^+ form is identical to the Cu value obtained by ASV at pH 2.2, the so-called labile fraction. Because of differences in procedure, however, only one of their samples could be directly compared with our results.

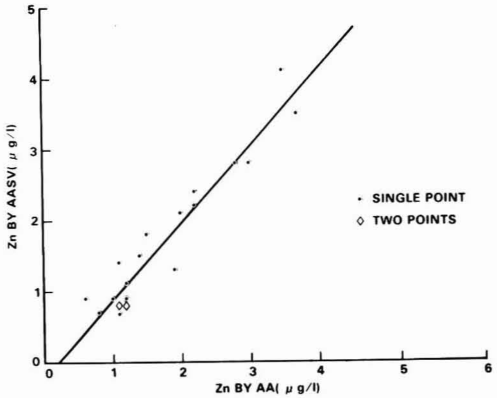

Figure 12. Correlation between Zn values obtained by AASV and Chelex 100-AA

Fukai and Huynh-Ngoc (*10*) and Florence and Batley (*11*) found that both methods measure only a portion of the total metal present in the sample. For Zn in Mediterranean coastal water the fraction measurable by ASV-Chelex 100 varied between 80 and 85% of the total. Total Zn was the quantity measured after the seawater sample had been treated with H_2SO_4–$K_2S_2O_8$ and heated. Florence and Batley (*11*) found that extraction on Chelex 100 (comparable to our ASV method) measured only 64% of the total Cu in coastal waters near Sidney, Australia. Again, total was defined as the quantity of metal measurable after the sample had been treated with hot HNO_3. At present it cannot be determined conclusively whether those fractions readily measurable under our conditions are a constant percentage of the total. Under differing conditions Fukai et al. (*12*) noted that the relative concentrations of chemical forms of Zn may vary over a wide range, depending on the time and place of water collections. These investigators observed that the fraction of dithizone extractable Zn (comparable to ASV at pH 8) in Mediterranean coastal water varied widely with time even though the total Zn often stayed relatively constant. Fukai et al. (*12*) noted that inputs of Zn occurred in the extractable form and then decreased rapidly. These findings can be extended to our own work. Sources of Cu and Zn in San Diego Bay introduce these metals into the water in labile forms which can be easily detected by our methods. The concentrations of these labile forms decrease with time and distance from the sources by dilution with oceanic water and by possible in situ transformation into refractory forms which are not measured in our survey work. Thus, we can detect concentration gradients near sources of trace metal input.

Acknowledgment

We thank Paul R. Kenis for carrying out some of the AA–AASV intercomparisons, Sachio Yamamoto for his continuing support of this project, and P. M. Williams for reviewing the manuscript.

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Ozonation of Water: Kinetics of Oxidation of Ammonia by Ozone and Hydroxyl Radicals

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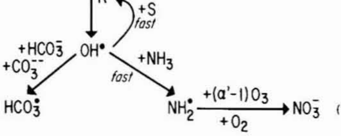
■ Ozone initiated oxidation of ammonia in water can result from the direct reaction of O_3 with NH_3 as well as from the reactions of $OH^{\cdot}$ radicals formed upon O_3 decomposition. The direct reaction of O_3 predominates at pH <9. In the presence of low concentrations of free NH_3, it is a slow reaction; the rate constant for O_3 depletion by reaction of O_3 with NH_3 is $20 \pm 1\ M^{-1}\ s^{-1}$. At pH values >9, OH^- and radical-catalyzed decomposition of O_3 to the very reactive intermediate, $OH^{\cdot}$, determines the kinetics of the NH_3 oxidation. The reaction rate constant of $OH^{\cdot}$ with NH_3 is relatively small. Whenever the $OH^{\cdot}$ mechanism is involved, NH_3 is easily protected by other solutes which also consume $OH^{\cdot}$ radicals. Even carbonate and bicarbonate ions may act as efficient $OH^{\cdot}$ scavengers. Because carbonate and organic solutes affect the lifetime of O_3 in water, they consequently shift the pH range in which either the direct O_3 or the $OH^{\cdot}$ mechanism predominates. A comparison with reactions initiated by gamma irradiation proves helpful in elucidating the reaction mechanisms.

In water and wastewater treatment, elimination of ammonia and interference of ammonia with water treatment processes often present a problem. In spite of this, available data are not yet sufficient to describe the process parameters which affect the ozonation process. In some publications, however, overall yields for the oxidation of ammonia are described. Singer and Zilli (*1*), Kirk et al. (*2*), Ikehata (*3*), Huibers et al. (*4*), and others have concluded from their studies that some oxidation of ammonia can take place in ozonation processes. Oxidation seems evident above pH 7, that is, only in the pH range in which free NH_3 is present. In carbonate-containing systems the yield of the ammonia oxidation declines when the pH is raised above 9. It also appears that the yield improves after preliminary lime clarification (*2, 4*).

In this study we have attempted to separate the individual parameters which affect ammonia oxidation. Based on observations reported in previous studies (*5, 6*), the hypothesis presented in Reaction Sequence 1 is proposed: O_3, which is an electrophile, does not oxidize NH_4^+, but it can oxidize free NH_3. Above pH 9, where the ratio of NH_3/NH_4^+ is significantly shifted toward NH_3, the decay of O_3 in water is quite fast (compare Figure 1A and B) and results in unfavorable conditions for slow direct reactions of molecular O_3 with solutes. However, the decomposition of O_3 leads to free radicals, one of which, $OH^{\cdot}$, is an extremely reactive oxidant (*5*). Radiolytic and gas-phase studies indicate that $OH^{\cdot}$ can also oxidize NH_3 but not NH_4^+ (*7–10*). Reactions of $OH^{\cdot}$ with NH_3 proceed with relatively low reaction rate constants (Table I); therefore, it must be assumed that many solutes, even in low concentrations, consume the oxidant in competition with NH_3. Selected examples of rate data given in Table I show that even carbonate and bicarbonate ions, whenever present in a concentration comparable to that of NH_3, may protect NH_3 from oxidation by reducing the $OH^{\cdot}$ radical. They thereby become oxidized to $HCO_3^{\cdot}$ ($CO_3^{\cdot-}$), i.e., to a radical of low oxidation reactivity (compare Reaction Sequence 1).



(1)

Since $OH^{\cdot}$ reacts with CO_3^{2-} much faster than with HCO_3^-, the protecting effect of a given amount of total carbonate (ΣCO_2) should increase in the pH range above 9 where the dissociation

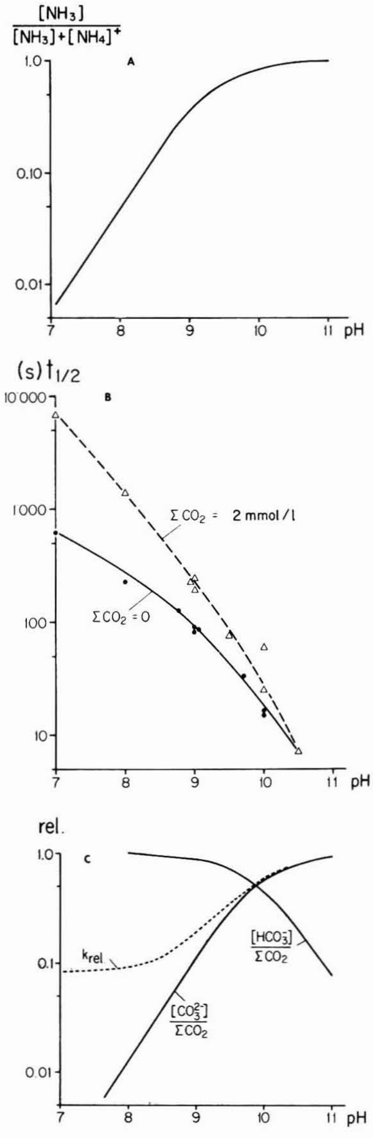


Figure 1. pH dependence of parameters influencing oxidation of ammonia

A: Relative amount of oxidizable free NH_3 existing in equilibria with NH_4^+. Calculated for p*K*a = 9.27 (ionic strength = 0.12). B: Halftime of O_3 decay in absence of NH_3. Measured values for $[O_3] \sim 0.3$ mM $\Sigma CO_2 = [HCO_3^-] + [CO_3^{2-}]$. C: Relative concentration of CO_3^{2-} resp. HCO_3^- species in solution of const. total carbonate, $\Sigma CO_2 = [HCO_3^- + CO_3^{2-}]$. (Calculated for p*K*a = 9.9; ionic strength = 0.12). Relative rate by which OH· radicals are consumed by $HCO_3^- + CO_3^{2-}$ present in solution = $k_{HCO_3^-} \times [HCO_3] + k_{CO_3^{2-}} \times [CO_3^{2-}]$. Calculated for = $k_{CO_3^{2-}}/k_{HCO_3^-} = 12$ (*6*)

of HCO_3^- to CO_3^{2-} becomes effective (Figure 1C). Such pH-dependent oxidation inhibitions by carbonates have been described for organic solutes before (*6*).

Since the O_3 decomposition is initiated by OH^- ions and accelerated by a chain reaction in which free radicals act as chain carriers, the rate of O_3 decomposition also depends on the solutes present in water which interfere with radicals. Some solutes accelerate the chain reaction by forming efficient secondary radicals (e.g., benzene), and some inhibit the reaction by inactivating the OH· radical (e.g., HCO_3^-, see Reaction Sequence 1). Solutes of the latter class stabilize O_3 and provide the molecular O_3 more time to react directly with NH_3.

Table I. Reaction Rate Constants for OH· Radicals in Water (22–25 °C)[a]

Solute	*k*, $(M^{-1} s^{-1}) \cdot 10^{-7}$
NH_3	8.7[b] (*8*), 1.7[b] (*9*)
Benzene	670[b] (*11*)
Methanol	85[b] (*12*)
Methanol-d_3	42[b] (*12*)
Acetate ion	7[b] (*13*)
H_2O_2	3.5 (*14*)
HCO_3^-	1.5 (*15*)
CO_3^{2-}	38[b] (*16*)

[a] Values are selected for easy comparison. For lists comprising a few hundred solutes, compare Dorfman and Adams (*17*). [b] Values corrected for $k_{ethanol} = 1.85 \cdot 10^9\ M^{-1} s^{-1}$ or $k_{ferrocyanide} = 9.3 \cdot 10^9\ M^{-1} s^{-1}$ used as a reference basis (*17*).

The purpose of this study was to test the hypothesis postulated in Reaction Sequence 1 by experiments and to determine the reaction rate constants of the direct reaction of O_3 and of the radical-type reactions involved in the oxidation of NH_3. The anticipated results would indicate how the chemical composition of the water affects the NH_3 oxidation and to what extent the presence of NH_3 in water may interfere with other oxidations. To analyze the part of the oxidation reaction which is entirely due to the preliminary decomposition of O_3 to radicals, some measurements were repeated by generating radicals by high-energy irradiation instead of by using O_3. In O_2 containing water high-energy irradiation produces the same types of intermediate radical species as those which are formed upon O_3 decomposition in water (OH·, $HO_2^·$) (*18, 19*).

Experimental

Ozonation Procedures. Batch reactions were carried out in 10- or 25-mL bottles which, for final cleaning, were kept filled with O_3 containing water for a few hours before use. Water of known O_3 concentration was added to the buffered solutions containing the solutes to be ozonated. The bottles were filled close to the top to eliminate head space. They were only opened when the decomposition of O_3 was complete. For details see ref. *5*.

Gamma-Irradiation Initiated Oxidations. γ-irradiation was performed in a Gammacell 220 in an O_2-saturated solution (compare refs. *5* and *19*). The samples were prepared as described above.

Analytical Methods. *NH_3* was determined by the indophenol method by measuring the absorption of indophenol blue at 700 nm (*20*). In samples containing H_2O_2, excess H_2O_2 was destroyed by catalase added before the NH_3 was determined.

NO_2^- was measured according to Standard Methods (*21*). The absorbance of a dye produced by the coupling of diazotized sulfanilic acid with α-naphthylamine was measured at 510 nm.

NO_3^- was determined by UV absorption at 220 nm after elimination of ΣCO_2 by acidification with HCl and air stripping (*22*). Results were also checked on the Technicon Autoanalyzer (reduction of NO_3^- to NO_2^- and determination as described above for NO_2^-) or by the formation of nitrososalicylic acid, which was determined by absorption at 420 nm. All three methods gave similar results and were therefore chosen

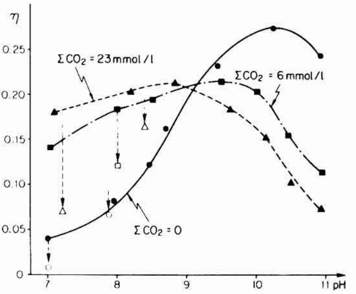


Figure 2. Yield of oxidation of NH_3 to NO_3^- vs. pH for different carbonate concentrations

$\eta = -\Delta NH_3/-\Delta O_3$; dashed arrows indicate yields measured when reaction was stopped after 15 min. $[NH_4^+ + NH_3]_o = 1.4$ mM. ΣCO_2: $[H_2CO_3 + HCO_3^- + CO_3^{2-}]$

according to need and convenience in different parts of the studies.

O_3 was determined by its UV absorption at 258 nm after calibration against similar samples determined by the iodide reaction and titration with thiosulfate at pH 6–7. (Apparent molar extinction coefficient for aqueous solution at 20 °C: 2900 M^{-1} cm^{-1}.) Decay rates of O_3 were measured by recording the 258-nm absorbances vs. time at 20 °C in thermostated 1-cm cells.

Organic solutes were determined by gas-liquid chromatography (*5, 6*).

Materials. *pH adjustments* were generally performed by sodium phosphate "buffers" (0.05 M phosphate in final solution).

Tap water was from the city of Dübendorf. The carbonate hardness was determined on each lot. Carbonate precipitation was performed by adding $CaCl_2$ and raising the pH to 10.5 with NaOH. After a settling time of 16 h, the clear water was withdrawn with a pipet.

Other materials are as described in refs. *5* and *6*.

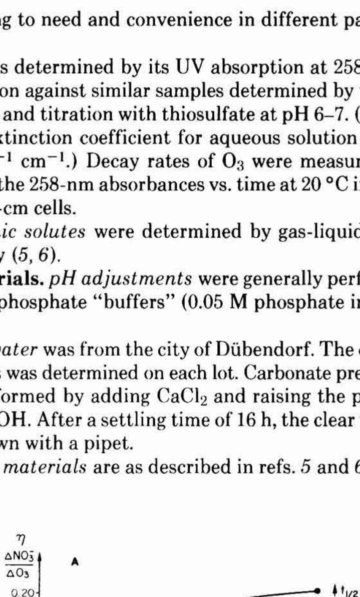


Figure 3. Yield of oxidation of NH_3 to NO_3^- and halflife ($t_{1/2}$) of O_3 vs. bicarbonate concentration

$[NH_3 + NH_4^+]_o = 1.4$ mM

Stoichiometry of Nitrate Formation. Results from experiments with ammonia solutions (0.1–1.5 mM total ammonia) and O_3 (doses to yield 6–80% conversion) were in agreement with observations of Singer and Zilli (*1*) in that ammonia depletion by ozonation always resulted in formation of a corresponding amount of NO_3^- (±5%). No significant buildup of NO_2^- was detected. It is concluded that the oxidants initiate a sequence of oxidations leading to NO_3^- and that only the initial step is a rate-limiting reaction.

Ozonation Experiments Covering Broad pH Range. Figure 2 summarizes the efficiency of the oxidation of ammonia by ozonation between pH 7 and 11 in the presence and absence of carbonate. Each point given in the figure was determined from the slope of a linear plot of the nitrate formed vs. the amount of O_3 added. Typically five different O_3 doses were used per yield determination, the maximal O_3 doses being limited to give not more than 10% ammonia depletion. Because the fraction of ammonia present as free NH_3 assumes very low values at low pH values (compare Figure 1A), traces of arbitrary contaminants could compete with NH_3 in consuming oxidants in an ill-defined manner. Therefore, some measurements were repeated after adding 10^{-5} mol/L acetate before ozonation to limit and define the lifetime of $OH^{\cdot}$ radicals. The yields of oxidation were not altered significantly as a result of this precaution.

The optimum yield for the oxidation of ammonia to nitrate is observed between pH 9 and 10. The presence of carbonate increases the yield at low pH values but decreases the yield at pH >9. The reaction at low pH values is slow as shown by the results of experiments in which excess O_3 was destroyed by adding 2-butenol after a period of reaction of 15 min. These results show that the reactions leading to oxidation of ammonia are regulated by different mechanisms and process parameters when performed at high or at low pH values.

Measurements at pH Values Below 9. *Ammonia Oxidation as a Function of Bicarbonate Concentration.* Motivated by the results presented in Figure 2, we measured the oxidation yield, $\Delta NO_3^-/\Delta O_3$, at pH 7 and 8 as a function of the bicarbonate concentration. In addition, the decay rate of O_3 was followed in solutions similar to those used for the yield measurements. Results presented in Figure 3 show that at both pH values the lifetime of O_3 and the yield, $\Delta NO_3^-/\Delta O_3$, increase in a similar way with higher bicarbonate concentration. We therefore postulate that oxidations observed in this pH region are due to direct reactions of molecular O_3 and not to decomposition products of O_3. The comparison of the time scale in Figure 3A and B indicates that the reaction rate is increased by about a factor of 10 when pH is increased from 7 to 8. As shown below, this has to be correlated to the 10 times increased concentration of free NH_3 at the higher pH (compare Figure 1A).

Oxidation Initiated by Gamma-Irradiation. Similar samples as used in the ozonation experiments but saturated with oxygen, were irradiated by γ-radiation (pH 7; 30–60 krad). At these low pH values the radiation-initiated oxidations had a very low radiolytic yield of only 0.07 molecule NO_3^- formation per 100 eV absorbed energy. This corresponds to only 5% of the $OH^{\cdot}$ radicals evolved by radiolysis from the aqueous solution. In similar samples, but containing 16 mM bicarbonate, the NO_3^- formation per $OH^{\cdot}$ radical formed was even depressed to 1.5%. Consequently, we conclude that $OH^{\cdot}$ radicals produced by irradiation of aqueous solutions do not contribute significantly to the initiation of ammonia oxidation at these reaction conditions. In addition, $HCO_3^{\cdot}$ radicals, which are produced as secondary radicals in aqueous solutions containing bicarbonate, do not contribute to the oxidation of NH_3 either. A decomposition of O_3 in aqueous solutions would

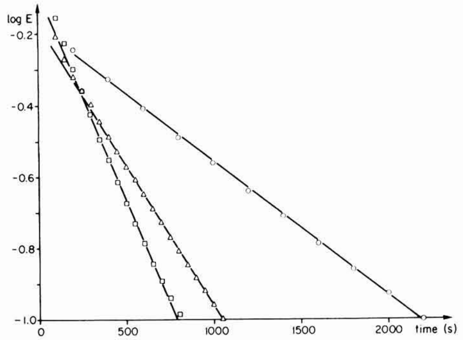


Figure 4. Consumption of O_3 vs. time for different concentrations of NH_3 (examples)

$[O_3]_o \sim 0.3$ mmol/L; $[HCO_3^-] = 22$ mM. NH_4Cl added: □ 12 mM (pH: 7.6); △ 6 mM (pH: 7.3); ○ 3 mM (pH: 7.2). E: UV extinction measured at 258 nm

lead to the same types of radical species as the radiolysis ($OH^\cdot$, $HO_2^\cdot$, $HCO_3^\cdot$). Therefore, in ozonation processes the radical reactions do not contribute to the initiation of the oxidation of ammonia when performed at low pH values, where the concentration of free NH_3 is very low.

Rate Constant for Direct Reaction of O_3 with NH_3. In the pH region below 8, O_3 may be stabilized by addition of bicarbonate to an extent that, at high ammonia concentrations of more than 0.3 mM, the rate of O_3 depletion becomes predominantly regulated by the kinetics of the direct reaction of molecular O_3 with free NH_3. Figure 4 shows examples of O_3 depletion vs. time when a large excess of NH_4^+ provides a small but practically constant concentration of free NH_3 over the whole duration of the reaction. The depletion of O_3 was measured by following the UV absorption. The linearity of the log of the UV extinction vs. time shows that the reaction is of first order in O_3 concentration, and the following expression can be used to described the rate of ozone depletion:

$$\frac{-d[O_3]}{dt} = k' \times [O_3] \times [NH_3]^n \qquad (2)$$

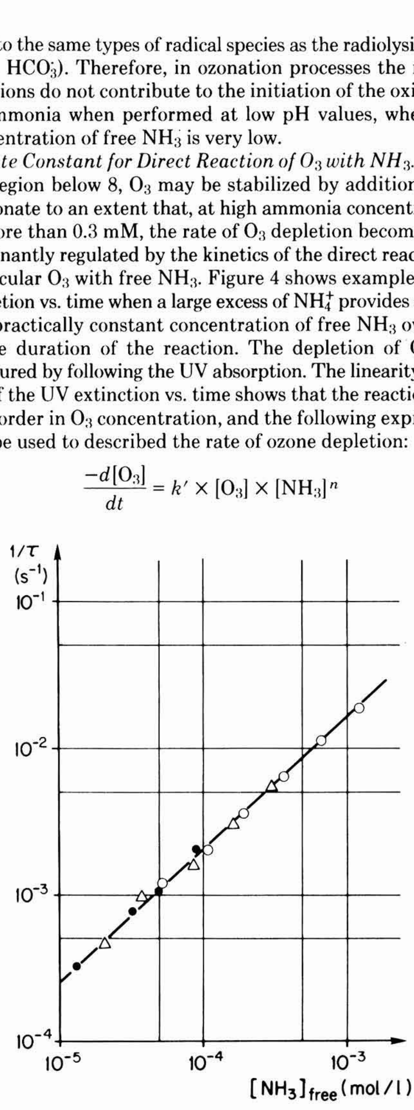


Figure 5. Inverse lifetime of O_3, $1/\tau$, vs. concentration of free NH_3

$[O_3]_o \sim 0.7$ mM. ○ pH range: 8.1–8.2; △ pH range: 7.2–7.6; ● pH range: 6.8–7.0

and the lifetimes of O_3, τ_{O_3}, becomes:

$$(\tau_{O_3})^{-1} = k' \times [NH_3]^n$$

A log-log plot of measured τ_{O_3} values vs. the concentration of free NH_3 yields a straight line relationship from which the reaction constants k' and n can be calculated:

$$-\log \tau_{O_3} = \log k' + n \times \log [NH_3] \qquad (3)$$

For measurements the free NH_3 concentration was varied by adding various amounts of NH_4Cl to the solution and by setting the pH to approximately pH 7, 7.5, or 8. The amount of free NH_3 was calculated from the concentration of NH_4Cl added, the measured pH of the solution, and by assuming a pKa (NH_4^+) value of 9.27 (20 °C) ($I = 0.12$). This pKa value is corrected for the ionic strength by applying the Güntelberg approximation. Figure 5 indicates that the linear relation given by Equation 3 holds over a wide (hundredfold) range of NH_3 concentration. The slope of the line is 0.88 ± 0.04. Therefore, the reaction is practically first order in NH_3. The rate constant k' becomes $20.4 \pm 1.0\ M^{-1}$ for $[NH_3] = 10^{-4}$ M. Only the concentration of free NH_3 is relevant: the NH_4^+ concentration does not have an effect as is seen by the good fit of the results found for different pH values, by which the NH_3/NH_4^+ ratio was varied from 4×10^{-3} to 7×10^{-2}.

The rate constant for O_3 depletion, k' in Equations 2 and 3, corresponds to the overall consumption of O_3. However, more than one ($\alpha \geq 1$) O_3 molecule is consumed in one oxidation sequence leading from NH_3 to NO_3^-:

$$NH_3 \xrightarrow[k]{+1\ O_3} (N\text{-oxidation}) \xrightarrow[+O_2]{+(\alpha - 1)O_3} NO_3^- \qquad (4)$$

Thereby k denotes the rate constant with which NH_3 is oxidized to NO_3^-. Because only the first oxidation step is rate limiting, we may write for the rate of O_3 depletion and for the rate of nitrate formation (ammonia oxidation).

$$\frac{-d[O_3]}{dt} = \alpha \times \frac{d[NO_3^-]}{dt}$$

$$= k' \times [O_3] \times [NH_3] = \alpha k \times [O_3] \times [NH_3] \qquad (5)$$

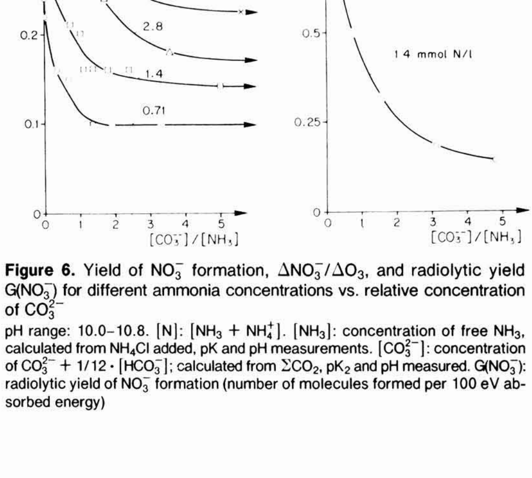


Figure 6. Yield of NO_3^- formation, $\Delta NO_3^-/\Delta O_3$, and radiolytic yield $G(NO_3^-)$ for different ammonia concentrations vs. relative concentration of CO_3^{2-}

pH range: 10.0–10.8. [N]: $[NH_3 + NH_4^+]$. $[NH_3]$: concentration of free NH_3, calculated from NH_4Cl added, pK and pH measurements. $[CO_3^{2-}]$: concentration of $CO_3^{2-} + 1/12 \cdot [HCO_3^-]$; calculated from ΣCO_2, pK_2 and pH measured. $G(NO_3^-)$: radiolytic yield of NO_3^- formation (number of molecules formed per 100 eV absorbed energy)

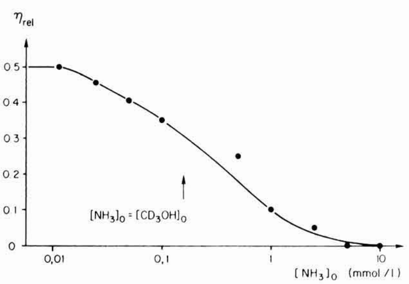


Figure 7. Oxidation of methanol (CD_3OH) and its protection by NH_3 $[CD_3]_o$ = 0.16 mM; O_3 added for 25–40% conversion. pH: 10.3–10.5. rel = $-\Delta[CD_3OH]/a\,\Delta[O_3]$

Based on the stoichiometry of measured O_3 consumption vs. the oxidation of NH_3 to NO_3^-, we estimate that $\alpha \sim 5$. However, this α-factor, the specific ozone consumption, may vary with NH_3 concentration.

Measurements at pH Values Above 10. *Protection of NH_3 by Carbonate Ions.* The nitrate yield, $\Delta NO_3^-/\Delta O_3$, measured for different ammonia and carbonate concentrations at pH 10.5, is shown in Figure 6. The yields were again determined on the basis of five different ozone doses giving less than 10% ammonia depletion. The nitrate formation was again linear with the ozone added.

The inhibiting effect of carbonate in this pH range is evident. Already a carbonate-to-ammonia mole ratio of 2 decreases the oxidation yield to less than 40% in samples of low NH_3 concentrations. The lower levels of carbonate concentrations used in these experiments are comparable to those encountered in natural water and wastewaters. The results presented in Figure 6, however, indicate that the quenching effect of CO_3^{-2} tails off at high CO_3^{-2} concentrations whenever high concentrations of NH_3 are present. Such an effect was not found in our earlier studies on the oxidation of more inert solutes (*6*) or when the formation of oxidative radicals was initiated by γ-irradiation (compare Figure 6B). This remaining NH_3 oxidation, still observed even at highest concentrations of radical scavengers, can be due to some underlying contributions of a direct reaction of molecular O_3: a critical reaction time, τ_{crit}, which would be necessary for 63% of the available molecular O_3 to react with ammonia in a direct reaction, can be estimated from Equation 2:

$$\tau_{crit} = 1/(k'[NH_3]) \qquad (6)$$

Using the values $[NH_3] = 10^{-2}$ M and $k = 20\ M^{-1}\ s^{-1}$, τ_{crit} becomes 5 s. Such lifetime values of O_3 are measured even at pH 10.5 when systems are stabilized with CO_3^{-2} and when organic solutes are absent (compare Figure 1B).

Protection of NH_3 by H_2O_2. The effect of H_2O_2 on the yield of the ozonation was tested because H_2O_2 is a known scavenger for OH·. H_2O_2 transfers OH· to the O_2^-species:

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot}$$

$$HO_2^{\cdot} \rightleftarrows H^+ + O_2^- \ (pKa = 4.4)$$

O_2^- species may also be formed by irradiating aqueous aerated solutions (*18, 19*).

Ozonation experiments in the presence of H_2O_2 should show whether the O_2^- species initiates a NH_3 oxidation and what inhibitory effect a buildup of H_2O_2 in the ozonized solution would have on the oxidation.

At pH 10.5, a strong protection of NH_3 could be observed already when the ratio of the concentration of H_2O_2 to NH_3 reached 2:1 mol/mol. From data in Table I the relative rate constant with which OH· reacts with NH_3 and H_2O_2, $k_{NH_3}/k_{H_2O_2}$ becomes 2.5. This value can fairly well explain the concentration pattern of the yield curve found in this experiment. This shows again that the secondarily formed O_2^- species is not involved in the initiation of NH_3 oxidation and therefore cannot influence the kinetic data determined in the foregoing sections.

Protection of NH_3 by Organic Solutes. Protection of NH_3 by solutes such as methanol, acetone, acetic acid, and benzene was in fair agreement with the effects to be expected from the relative rate constants and relative concentrations of the organic solutes which consume OH· radicals in competition (compare values in Table I and ref. *17*). It can therefore be assumed that the secondary radicals formed from the organic solutes by ozonation, e.g., peroxy radicals, do not initiate appreciable amounts of NH_3 oxidation.

Protection of Organic Solutes by NH_3. Figure 7 shows the inhibition NH_3 exhibits on the oxidation of methanol–d_3 at pH 10.3. It amounts to about 50% when the molar concentration of NH_3 reaches about twice that of methanol–d_3. At this pH the ozone-initiated oxidation of an inert organic solute such as methanol also proceeds, only via the action of OH· formed as an intermediate and not via the direct reaction of molecular O_3 (*6*). The experimentally determined degree of competition is tantamount to what is expected from the relative rates with which OH· is consumed by these two solutes. However, an exact value for the degree of protection cannot be calculated, because the stoichiometric factor $\alpha - 1$ in Reaction Sequence 4 may also depend on the availability of other oxidants, such as organic peroxides formed from organic solutes. For these experiments methanol–d_3 was used because other solutes, even methanol–h_4, react faster than methanol–d_3 (compare Table I). These would therefore have to be limited to too low concentrations in order not to inhibit completely all NH_3 oxidation.

Oxidation of Ammonia in Treatment of Natural Waters. Table II summarizes the yields of the ammonia oxidation, $\Delta NH_3/\Delta O_3$, as found in distilled water containing 40% tap water of 3 mM HCO_3^-, and water in which the carbonate was eliminated by $CaCO_3$ precipitation before ozonation. In all samples, the pH was raised to 10.9 by adding sodium hydroxyde. The oxidation yields were calculated from duplicate determinations involving depletions of up to 30% of the ammonia initially present. The results reflect the protective effect of carbonate on ammonia oxidation and that this effect can be overcome by a preliminary elimination of carbonate. Experiments using a flow-through reactor showed the same effect of the carbonate.

All these results agree well with the inhibiting effect of carbonate we observed in our studies on the ozonation of organic micro pollutants in natural water (*6*).

Conclusions

All the observed yields and kinetics on ozonation of ammonia can now be explained by separating the initiating reactions into a direct reaction of molecular O_3 and an OH·

Table II. Yield of NH_3 Oxidation in Water of Different Carbonate Hardnesses (pH = 10.9)[a]

Type of water	η (%)	η (%) after CO_3^{2-} eliminated
Bidistilled	9 ± 1	11 ± 2
Bidistilled + 0.8 mM CO_3^{2-}	6	12
Bidistilled + 4 mM CO_3^{2-}	1	11
40% tap water (2.5 mM CO_3^{2-})	2	8

[a] $\eta = -\Delta NH_3/-\Delta O_3$; $[NH_3]_o = 0.11$ mM; $[O_3]_o = 0.31$ mM.

radical-type reaction. The oxidation of NH_3 in ozonation processes can only be of importance when relatively high concentrations of free NH_3 prevail; NH_4^+ cannot be oxidized.

At pH values below 9, it is predominantly the selectively reacting molecular O_3 which initiates the oxidation of ammonia. Because in this pH range only a small fraction of the ammonia is present as free NH_3 and because the rate constant of the reaction $NH_3 + O_3$ is only 20.4 $M^{-1}\,s^{-1}$, this oxidation reaction is slow. In ozonation processes with a long reaction time, bicarbonate ions may improve somewhat the NH_3 oxidation by quenching the radical chain reaction which would accelerate decomposition of O_3.

At pH values above 9, the fast decomposition of O_3 to radicals mostly precedes the oxidation of free NH_3. Of the radicals formed, only $OH^\cdot$ is of relevance for the oxidation initiation. A rate constant for the reaction of $OH^\cdot$ with NH_3 of $8.7 \cdot 10^{-7}$ $M^{-1}\,s^{-1}$ (*8*) gives results consistent with those found in all the systems tested. Carbonate ions as well as all types of organic solutes and H_2O_2 may protect NH_3 from oxidation by consuming the $OH^\cdot$ radicals in fast reactions. The protecting effect of the different solutes can be estimated by comparing their rate constants (Table I) and their concentrations.

Ozonation processes for drinking water or wastewater are typically designed for reaction periods of less than 1000 s. Based on the rate constant of 20.4 $M^{-1}\,s^{-1}$ for the direct reaction of $O_3 + NH_3$, we estimate from Equations 5 and 6 the critical concentrations of NH_3, $[NH_3]_{crit}$, which would be necessary to consume 63% of the O_3 added during this reaction time (this means that 37% or the $1/e$ fraction of the O_3 applied survives reaction with NH_3):

$$[NH_3]_{crit} = (20.4\ M^{-1}\,s^{-1} \times 1000\ s)^{-1} = 5 \cdot 10^{-5}\ M$$

This critical concentration of free NH_3 corresponds to 2.5 mM total ammonia at pH 8 and to 25 mM total ammonia at pH 7 ($pKa(NH_4^+ = 9.7)$). We therefore expect an interaction of NH_3 with other reactions of molecular O_3 only when relatively high concentrations of total ammonia are present.

For the contribution of the $OH^\cdot$ radical mechanism to the NH_3 oxidation, we may make the following estimate for a typical surface water (pH ~ 8): A concentration of 1 mg/L total ammonia-N corresponds to about 10^{-5} M free NH_3. If this reacts with $OH^\cdot$ with a rate constant of $8.7 \cdot 10^7$ $M^{-1}\,s^{-1}$, it consumes $OH^\cdot$ at a rate of $8.7 \cdot 10^2$ s^{-1}. Compared with this rate, the sum of all solutes present in waters, such as from Lake Zürich or from sources around Zürich (all pH 8), scavenges $OH^\cdot$ radicals about 40 times faster [$2 \cdot 10^4$ s^{-1} (*6*)].

NH_3 could also interfere with other oxidations of organic pollutants by consuming $OH^\cdot$. However, because NH_3 consumes $OH^\cdot$ in a reaction with a relatively low rate constant, comparable for instance with that known for carbonate ions, free NH_3 can significantly inhibit other oxidations only when present in concentrations at least comparable to those of carbonate and the sum of organic solutes. Therefore, the protecting effect of ammonia toward other solutes can be neglected in the case of drinking water and even in the case of most domestic secondary effluents.

The ammonia system investigated here exemplifies an ozonation where a solute of intermediate reactivity toward O_3 is involved. The results should also assist when evaluating experimental methods for studying other systems of solutes.

The methodology applied in this study has recently been applied to the determination of many rate constants of reactions of O_3 with organic trace impurities. Relevant for the system studied here is the result that methylamines or amino acids (free amines) react 10^3 to 10^5 times faster than ammonia at comparable pH values (*23*).

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Separation of Gaseous Fission Products from Reactor and Reprocessing-Plant Off-Gases

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■ Considerable amounts of gaseous radioactive fission products krypton and xenon result from nuclear power generation, thus creating a radiation hazard in the event of their uncontrolled release to the environment. The most efficient method for treating off-gas streams appears to be low-temperature distillation, the efficiency of which depends on an exact knowledge of vapor-liquid equilibrium data. Isothermal data are measured for mixtures of Kr and Xe between 145 and 170 K and for their mixtures with components of air between 100 and 125 K, which make possible the exact design of a distillation column suitable for effective removal of the fission products. The solubilities of Kr in the components of air and of Xe in liquid krypton are studied, and possible applications for the safe separation and fixation of Kr are discussed.

The growth of the nuclear power industry has resulted in an increasing awareness of possible cumulative effects on the environment by the release of even very low levels of long-lived radionuclides. Whereas high-level radioactive wastes have always been carefully stored under the earth, it has been customary to either discharge low-level streams directly to the environment or to give them minimal treatment to decrease the radioactivity below specified levels.

With an increasing number of nuclear power plants and other nuclear facilities, more efficient removal of radioactive components from the off-gases will be necessary to meet national regulations (*1*) and to prevent buildup of the long-lived radionuclides in the environment. Kr-85 is one of the long-lived radionuclides dispersed in significant quantities worldwide from the nuclear fuel cycle. Within the nuclear fuel cycle, the fuel reprocessing plants offer great potential for significant impact on the environment. A second noble gas, xenon, is also produced in nuclear fission and released together with krypton. Although the absolute molar quantities of fission-produced xenon are about five times higher than those of krypton, its radiological burden is negligible due to the short half-lives of all Xe radioisotopes produced. They decay to harmless stable nuclides prior to reprocessing of the fuel elements.

During the reprocessing of spent fuel, gaseous fission products are released mainly during the dissolution of the fuel in the nitric acid. They are strongly diluted with air. The percentage of noble gas amounts is only about 0.3% (Table I). Economic management of noble gas fission products will probably require up to 99% or better separation of noble gases from the mentioned off-gases. Only about 1% of the total volume of noble gases is Kr-85, but it represents the dangerous radioactivity of the noble gas fraction. To avoid local release and long-term buildup in the atmosphere, Kr-85 with a half-life of 10.7 years must be separated and stored for a long period of about 100 years to allow a substantial decay. To keep the radiation dose to the population as low as possible, the Commission for Radiation Protection of the Federal Republic of Germany recommends a limitation of Kr-85 release for a reprocessing plant to a value of 10^6 Ci/year (*1*). This limitation requires a decontamination factor of ⩾100 for any Kr-85 separation process being applied.

Table I. Design Flow Rate and Composition of Off-Gas Stream Routed to Cryogenic Unit

	1 (STP)/h	Ci/h	Vol %
Nitrogen	3900	...	96.6
Xe (stable)	83	...	2.1
Kr (stable)	14	...	0.3
Argon	40	...	1.0
Krypton-85	1	1430	0.02

The most suitable procedure to accomplish this task is low-temperature distillation. The principal advantage of this method is its present high level of technology. Air liquefaction plants have been in operation worldwide for many years with high capacities and reliability. Considerable knowledge has thus been obtained on construction materials, compressors, auxiliary control systems, valves and other remote control elements. It is surprising, however, that equilibrium data necessary for the precise design and operation of a distillation plant are scarce.

Experimental

To make reliable calculations for the design and construction of technical cryogenic facilities, knowledge of isothermal or isobaric equilibrium data for the pairings of the components of air and noble gases krypton and xenon is required. This knowledge would allow determination of deviations in the behavior of real gas mixtures from the ideal gas law.

According to the evaluation method of Prausnitz and Chueh (*2*), measurements of individual binary gas mixtures suffice for a description of the real gas behavior of a mixture of all these gases. Consequently, the thermodynamic data of the binary systems Kr–N_2, Kr–Ar, and Xe–Kr are of utmost importance.

Apparatus. A series of experimental measurements on vapor-liquid equilibria was made, and the liquidus lines for solid krypton in the liquid-air components and solid xenon in the liquid krypton were determined. A dynamically operated measuring device shown schematically in Figure 2 and equipped with an external vapor circuit was used. The major advantage of the dynamic measuring procedure over a static (*3*) one is the short time required to reach the equilibrium state in a measuring cell. Also, withdrawing of samples during measurement to analyze their composition does not disturb the accuracy of the measurements. A direct interconnection of a gas chromatographic analyzing device (GAS) is thus possible and allows on-line measurements of gas compositions.

Data. In a series of experimental measurements on vapor-liquid equilibria and determinations of liquidus lines of solid krypton and solid xenon, the following isothermal systems were studied.

Argon–Nitrogen. The Ar–N_2 equilibrium data at temperatures of 80, 85, 90, 95, and 100 K are shown in an isothermal McCabe-Thiele diagram (Figure 2). They are compared to previously reported results by Fastovskij and Petrovskii (*4*) and Thrope (*5*). Figure 2 shows the results in the system

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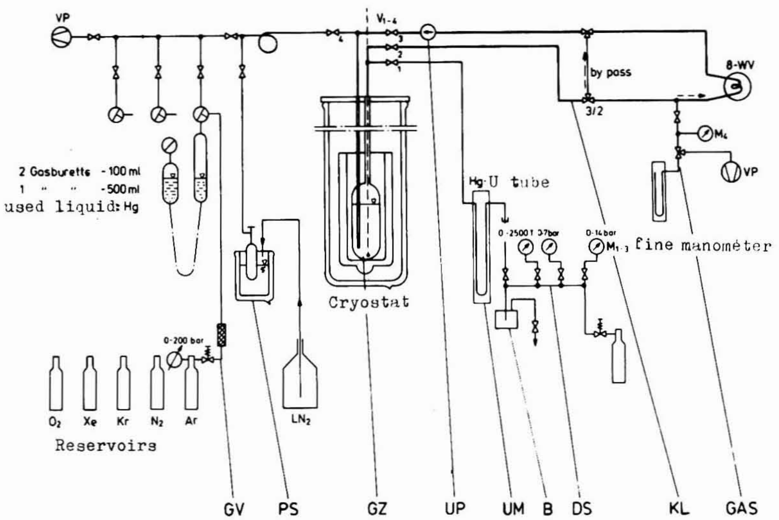

Figure 1. Schematic of measuring apparatus

GV, gas reservoirs; PS, sampling cylinders; GZ, glass equilibrium cell; UP, circulation pump; UM, U-tube with mercury; B, reservoir (capacity); DS, pressure measurement device; V, valves; KL, external gas circuit; VP, vacuum pump; GAS, pressure control system for chromatographic investigation

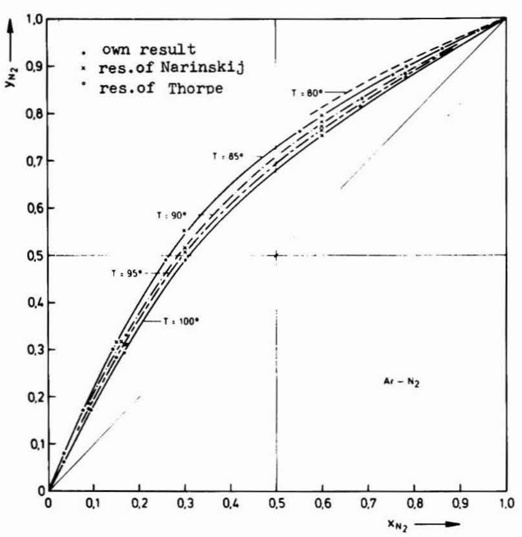

Figure 2. Ar–N_2 isothermal equilibrium curves

Ar–N_2 in an x-y diagram. The consistency of the measured equilibrium data was checked by applying a computer program, called SYMFIT, developed by Prasnitz and Cheuh (2). A fairly good agreement was obtained between experimental and theoretical data. The numerical agreement was better in the region of higher pressure than at lower pressure.

Figure 3 shows the calculated activity coefficients from the experimental results, and Figure 4 shows the fugacity coefficients at temperatures of 85, 90, 95, and 100 K in the Ar–N_2 system. The results for the known system Ar–N_2 and comparison with our data demonstrate that the apparatus functions objection free. Next, measurements were carried out on mixtures which had not previously been systematically investigated, in particular:

Krypton–Argon. The Kr–Ar equilibrium data at temperatures of 115, 116.5, 120, and 125 K are shown in an isothermal McCabe-Thiele diagram (Figure 5). Previous measurements of Seemayer (6) at 116.5 K may be compared with our data and show good agreement. Figure 5 shows the results in the system Kr–Ar in an x-y diagram.

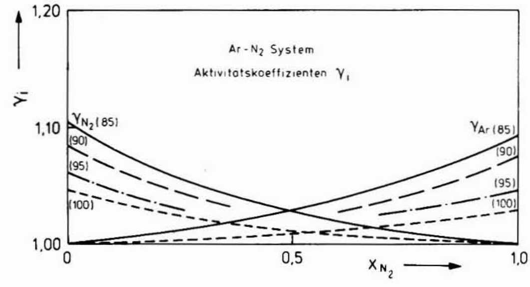

Figure 3. Ar–N_2 activity coefficients

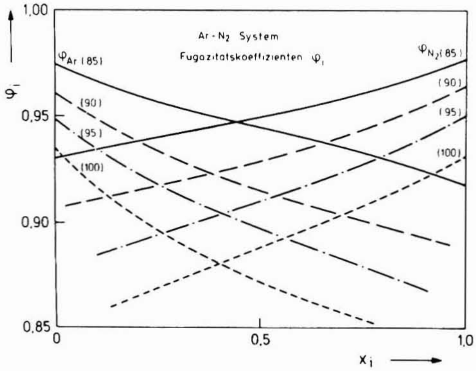

Figure 4. Ar–N_2 fugacity coefficients

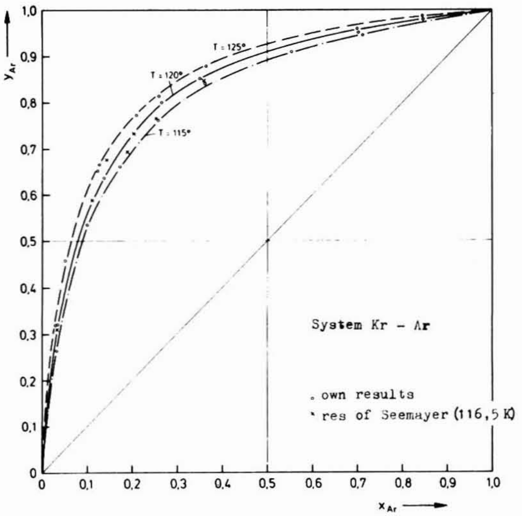

Figure 5. Kr–Ar isothermal equilibrium curves

Krypton–Nitrogen. The Kr–N_2 equilibrium data at temperatures of 115, 120, and 125 K are shown in Figure 6, along with the equilibrium data in the nitrogen-rich region of the liquid Kr–N_2 mixture above the liquidus line of solid krypton, below its triple point, at temperatures of 110, 105, and 100 K.

Figure 7 shows the results in the system Kr–N_2 in an x-y diagram. These very important equilibrium data are also presented in Figure 6 in the form of a pressure-mole fraction (p-x, -y) diagram, which gives the experimental results for equilibrium states at 115 K and below, combined with the liquidus line (= 3 phase boundaries) for solid krypton below the temperature of 115.9 K.

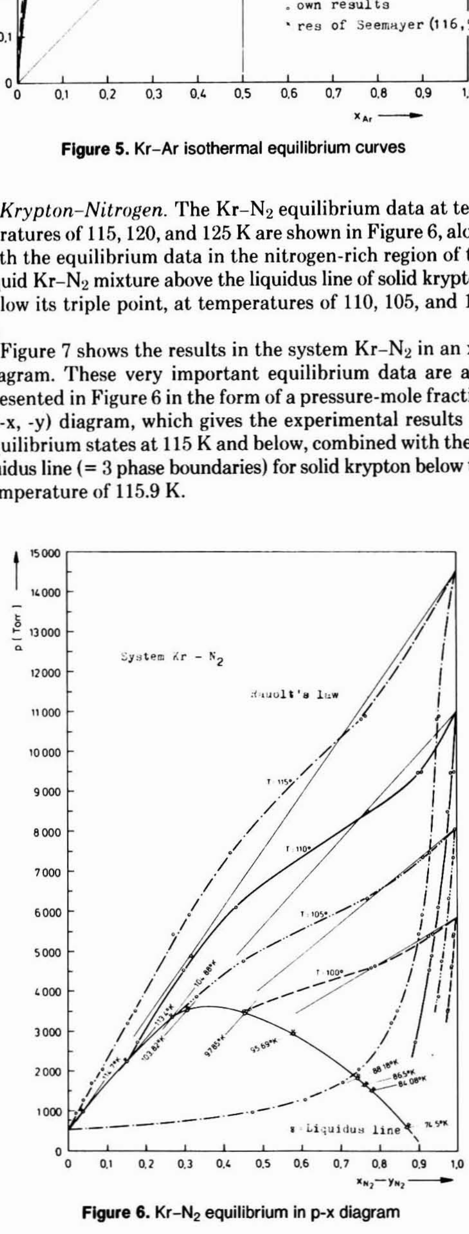

Figure 6. Kr–N_2 equilibrium in p-x diagram

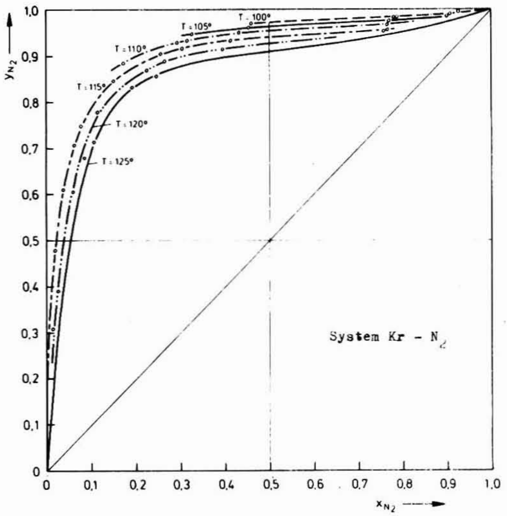

Figure 7. Kr–N_2 isothermal equilibrium curves

Xenon–Krypton. In Figure 8 the Xe–Kr equilibrium data between 150 and 170 K, at 5 K steps are shown in an isothermal McCabe-Thiele diagram. Previous experimental data of Seemayer (*6*) at 166 K can be compared with our results. In addition, the liquidus lines of solid krypton in a liquid Kr–Ar and a liquid Kr–N_2 mixture were systematically studied (*9*).

Summary and Results

The available experimental data now make possible the transition from binary vapor-liquid equilibria to multicomponent mixtures by means of suitable computer programs (*2*). However, a consistency check of the data shows that as already mentioned some of the thermodynamic data entering into the calculations, in particular the pure component data (*8*), are not known to the desired accuracy in the critical region (*8*).

However, independently of their exact evaluation, a few important conclusions can already be drawn, which have

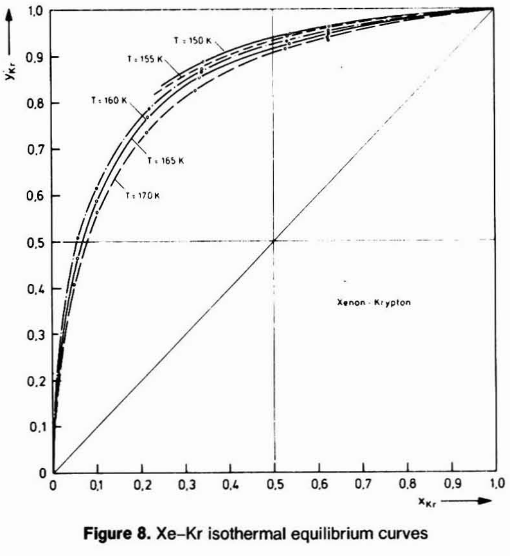

Figure 8. Xe–Kr isothermal equilibrium curves

consequences for its construction. If the process is carried out in such a way that the greatest of the xenon is removed before the low-temperature separation, the separation of the system $Kr-N_2$ in the first column is determined. If the column is operated at constant pressure, pressures between 6 and 8 bar can be maintained. The temperature in the collection vessel must then rise with increasing enrichment of krypton to around 125 or 130 K. If it is desired to operate at a constant temperature for the collection vessel, the temperature must be maintained at about 115–120 K, which would result in pressures in the range of 20 bar and below for the nitrogen-rich region. The xenon fraction is only very slightly contaminated with krypton (Kr-85) when a preseparation is performed. One is then in the xenon-rich range. In this case, the column can be operated at temperatures of 160–165 K and pressures about 2–3 bar.

If the xenon is not separated before the low-temperature distillation, a Xe–Kr mixture becomes enriched in the collector vessel of the first column. For reliable estimation of operating conditions, above all the complete gas data for the systems with xenon and the multicomponent system $(Xe + Kr)-N_2$, as well as the corresponding liquidus lines, are still missing. However, from our last experiments and calculations, a high degree of enrichment of noble gases in the collection vessel requires temperatures to above 155 K and pressures far in excess of 20 bar. Furthermore, the xenon–krypton separation in the second column will also be able to function at relatively low pressures.

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Organic Compounds in an Industrial Wastewater: A Case Study of Their Environmental Impact

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■ The wastewater and receiving waters and sediments from a specialty chemicals manufacturing plant are extensively analyzed for organic compounds. The concentrations of anthropogenic compounds range up to about 15 ppm in the wastewater and 0.2 ppm in the river (receiving) water, but up to several hundred ppm in the sediments. The composition of the river water reflects the composition of the wastewater except that some of the compounds appear to degrade or volatilize in the river. Many compounds accumulate in the sediments where they appear to be stable and build up to high concentrations. Some of the compounds are modified in situ. Various phenols are easily oxidized to quinones; these may be partially reduced back to phenols depending on the redox nature of the environment. Several compounds of known biological activity (herbicides, bacteriostats, and disinfectants) as well as some potentially toxic chemicals such as dichlorodibenzodioxin are present in the water. The long-term, low-level exposure to this wide variety of chemicals may have contributed to the lack of biota in this part of the river.

Industrial wastewaters are a major source of anthropogenic organic chemicals which enter the environment. Recently, the detailed organic analyses of the wastewaters of tire (*1*), paper (*2*), and dye (*3*) manufacturing plants have been reported. In addition, the Environmental Protection Agency will be analyzing the wastewaters of many other types of industries (*4*) with the goal of identifying potentially toxic organic compounds so that possible serious chronic effects due to long-term, low-level exposure to dangerous organic chemicals may be averted.

This paper reports on the detailed organic analysis of the wastewater and the receiving waters and sediments of a specialty chemicals manufacturing plant, i.e., a plant that manufactures a broad range of chemicals, many of which are used by other chemical companies. Since little is known about the eventual fate of specific organic compounds after leaving a manufacturing plant, we have studied, in detail, the interaction of this plant with its environmental setting. Thus, we have been concerned with the identities of compounds entering the receiving waters and sediments, the compounds already present, and others that may be formed through in situ transformations.

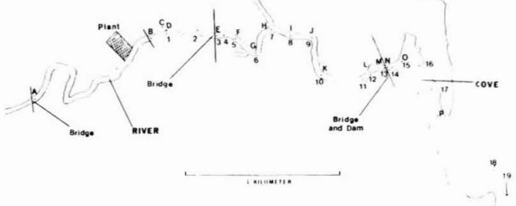

Figure 1. Map of the plant and its environmental setting
Sampling sites indicated; letters: water samples; numbers: sediment samples. Point C: clarifier at plant

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Many different analytical techniques were required to separate and identify the organic compounds found in these complex samples. The techniques included vapor stripping of volatile organic compounds, direct aqueous injection gas chromatography, computerized gas chromatographic mass spectrometry (GC/MS), high-pressure liquid chromatography (HPLC) with subsequent mass spectral analysis of the collected fractions using the direct introduction probe, and high resolution mass spectrometry (HRMS).

Plant Description and Setting. A map showing the details of the plant location is presented in Figure 1. The plant location lends itself to a detailed study because the plant is the last on a small freshwater river which drains into a small brackish cove, then into a large brackish river which empties into an estuary.

The plant operates in a batch production mode, generally following a weekly schedule. A wide range of compounds including pharmaceuticals, herbicides, antioxidants, thermal stabilizers, ultraviolet light absorbers, optical brighteners, and surfactants is produced. Water is used in synthesis processes, in the recovery of solvents, in steam jets, and in vacuum pump seals. The wastewater is neutralized in either of two 1 million-gal equalization tanks, passed through a trickling filter for biological degradation, and clarified in a 150 000-gal tank with a residence time of 3 h. The water spills over from the clarifier at a rate averaging 1.3×10^6 gal/day and enters the river through an underground pipe about 100 yards away. Only about one-fourth of the total BOD, which averages 12 000 lb/day, is removed by the waste treatment system, and much of this is in the form of low molecular weight solvents.

Experimental

Sampling. The water and sediment sampling sites in the vicinity of the plant are shown in Figure 1. Several samples were taken at some of the more convenient locations such as at the plant (site C) and at bridges. Wastewater samples were collected on November 6, 1975, January 27, 1976, July 13, 1976, and September 8, 1976; river water samples were collected on November 6, 1975, January 27, 1976, March 8, 1976, June 12, 1976, June 23, 1976, July 13, 1976, and September 8, 1976; sediment samples were collected on January 27, 1976, March 8, 1976, June 12, 1976, June 23, 1976, and September 8, 1976.

Water samples were collected in 1-gal amber glass bottles with Teflon-lined caps. Wastewater samples were collected as the water spilled over from the clarifier. River water samples were collected both upstream and downstream from the plant by use of a small boat. Sediment samples were collected with a dredge-type sampler from the boat and also with the aid of a diver. About 300 mL of nanograde (Mallinckrodt) dichloromethane and 15 mL of 12 M hydrochloric acid were added to the water samples at the collection site (except those used for volatile organic analysis) to minimize biological degradation and to start the extraction.

One-quart glass jars were used for the sediment samples. They were covered with aluminum foil before replacement of the screwcap lids and placed in a box containing dry ice. The composition of the river bottom sediments varied from large gravel to an organic-rich black ooze. Generally, the bank area was quite silty, whereas the bottom became more gravelly toward the center of the river.

Procedures. When returned to the laboratory, the sediment samples were placed in a freezer, and the water samples to be used for volatile analysis were placed in a refrigerator. A Teflon-covered magnetic stirring bar was added to each of the water samples containing dichloromethane for overnight extraction on a magnetic stirrer. Then most of the water was poured into another clean bottle, and the dichloromethane extract was separated from the remaining aqueous phase in a separator funnel. A plug of preextracted glass wool was used to aid in phase separation for those samples developing emulsions. Much of the emulsion remained on the glass wool which was then washed with additional aliquots of dichloromethane. These extracts and washings were combined and rotary evaporated to the desired volume. The decanted water from the acidic extraction was rendered alkaline with a preextracted, concentrated KOH solution and extracted with an additional 200 mL of dichloromethane to recover the basic compounds.

The exact concentrations of some of the volatile solvents in the wastewater were determined using direct aqueous injection of 2-μL aliquots onto a 2 m × 0.32 cm i.d. stainless steel column packed with 0.4% Carbowax 1500 on Carbopack C (Supelco, Inc.).

Qualitative analyses of the volatile organic compounds were performed using vapor stripping. About 2 L of a river water sample or about 200 mL of a wastewater sample were put into a 3-L glass stripping vessel similar to that described by Novotny et al. (*5*). The water temperature was maintained at about 80 °C. Purified helium was passed through the sample from a glass frit located at the bottom of the apparatus at a rate of 120 mL/min. Helium and the stripped organics were passed through a water-cooled condenser into two glass sampling tubes connected in parallel. These tubes were glass injection port liners from the gas chromatographs and were packed with about 40 mg of precleaned 60/80 mesh Tenax-GC porous polymer adsorbent. The liners were conditioned at 250 °C for at least an hour in the injection port of the gas chromatograph prior to use. After vapor stripping for the desired length of time, the precolumns were removed and stored in Teflon-lined screw-cap test tubes until analysis by GC and GC/MS.

The sediment samples were allowed to thaw at room temperature and then sieve-washed through a 2-mm stainless steel screen to remove pebbles and extraneous debris. Excess water was decanted, and the wet sediment was Soxhlet extracted for several hours with nanograde isopropyl alcohol. A further extraction with nanograde benzene was then necessary to isolate the polycyclic aromatic hydrocarbons. The isopropanol extract was evaporated to dryness on a rotary evaporator at 30–40 °C; the benzene extract was freed of elemental sulfur by passage through a column of colloidal copper (*6*).

Some of the sediment and water samples were also liquid chromatographically separated into hexane, benzene, and methanol fractions on a column containing about 1 g of 5% water–deactivated silica gel.

Instrumentation. Preliminary gas chromatographic analyses were carried out on a Perkin-Elmer 900 gas chromatograph equipped with a flame ionization detector and on a Hewlett-Packard 5730A gas chromatograph equipped with flame ionization and electron-capture detectors. The columns used were 180 cm × 2 mm i.d. glass columns packed with 3% SP-2100 (a methyl silicone fluid) on 80/100 mesh Supelcoport; we also used 25 m × 0.25 mm i.d. glass capillary columns statically coated (*7*) with SE-52. Approximate quantitation was based on external standards made with the compounds identified.

Liquid chromatographic separations were performed on a Waters Model ALC/GPC 204 liquid chromatograph equipped with two Model 6000 pumps, a Model 660 solvent programmer, and a Model 440 dual absorbance detector.

Low resolution (~800) mass spectra were obtained with a Hewlett-Packard 5982A GC/MS system with a dual EI/CI source and interfaced with a HP 5933A data system. The quadrupole mass spectrometer was coupled to the gas chromatograph via a glass-lined jet separator held at 300 °C. The mass spectrometer was operated in the electron impact mode,

Table I. Summary of All Compounds Found in Wastewater, River Water, and Sediment

Compound no.	Compound name	Concn range, ppm			Present in tar ball[a]
		Wastewater	River water	Sediment	
	N-Containing heterocyclics				
1	Acetylpyridine	0.05[b]	ND	ND	No
2	Dibenzo[b,f]azepine*	<0.01	ND	ND	No
3	10,11-Dihydrodibenzo[b,f]azepine*	<0.01	ND	ND	No
4	5-(3-Dimethylaminopropyl)-10,11-dihydrodibenzo[b,f]azepine*	3.7[b]	ND	ND	No
5	4-*n*-Butyl-1,2-diphenylpyrazolidine-3,5-dione*	0.02–0.5	0.001–0.006	ND	No
6	2-(2′-Hydroxy-5′-methylphenyl)-2H-benzotriazole*	0.5–7	0.006–0.10	2–670	Yes
7	2-(Hydroxy-*t*-butylphenyl)-2H-benzotriazole*	ND	ND	60	Yes
8	2-(Hydroxy-di-*t*-butylphenyl)-2H-benzotriazole*	ND	ND	40	Yes
9	2-(Hydroxy-butyl-*t*-amylphenyl)-2H-benzotriazole*	[d]	<0.001	[e]	Yes
10	2-(2′-Hydroxy-3′,5′-di-*t*-amylphenyl)-2H-benzotriazole*	0.55–4.7	0.007–0.085	1–100	Yes
11	2-(Hydroxy-*t*-butylphenyl)-chloro-2H-benzotriazole*	ND	ND	2–50	Yes
12	2-(2′-Hydroxy-3′,5′-di-*t*-butylphenyl)-5-chloro-2H-benzotriazole*	ND	ND	2–300	Yes
13	2-Methoxy-4,6-bis-isopropylamino-*s*-triazine*	2–7.5	0.015–0.35	0.3[b]	No
14	2-Chloro-4,6-bis-isopropylamino-*s*-triazine*	0.5–3.5	0.01–0.45	4.5–12	No
15	Benzothiazole*	ND	0.002[b]	ND	No
	Nitrogen-containing compounds				
16	Aniline	0.02[b]	ND	ND	No
17	Acetanilide	0.2[b]	ND	ND	No
18	Di-*t*-butylcyanophenol	ND	ND	[e]	Yes
19	Azobenzene	0.03[b]	ND	ND	No
20	*N*-phenyl-1-naphthylamine	[d]	[d]	[d]	Yes
	Oxygen-containing compounds				
21	Methanol	17–80[h]	ND	ND	No
22	Stearyl alcohol	1–4	0.007–0.16	0.5	Yes
23	Acetone	200–230[h]	ND	ND	No
24	2-Butanone	8–20[h]	ND	ND	No
25	2-Methyl-3-heptanone	[f]	ND	ND	No
26	Phenol	0.01–0.30	0.01–0.10	ND	No
27	Cresol	0.07–0.15	0.001–0.01	ND	No
28	*t*-Butylphenol	0.001–0.15	0.003[b]	0.2–7	Yes
29	C_8-Alkylphenol (two isomers)	0.001–0.075	ND	5[b]	Yes
30a	2,6-Di-*t*-butylphenol	0.6–0.8	0.001–0.006	0.1–150	Yes
30b	2,4-Di-*t*-butylphenol	0.5–0.6	0.001–0.005	0.1–100	Yes
31	2,6-Di-*t*-butyl-4-methylphenol (BHT)	<0.01	0.001–0.002	1–60	Yes
32	2,4-Di-*t*-amylphenol	0.13–0.40	0.001–0.005	0.3–10	Yes
33	Tri-*t*-butylphenol	0.125[b]	ND	0.2–25	Yes
34	Methoxy-di-*t*-butylphenol	ND	ND	[e]	Yes
35	3,5-Di-*t*-butyl-4-hydroxybenzaldehyde	ND	ND	[e]	Yes
36	Nonylphenol	0.05[b]	ND	ND	No
37	Phenylphenol	ND	0.001–0.003	ND	No
38	Tetra-*t*-butyl-dihydroxydiphenyl*	ND	0.001–0.002	0.5[b]	Yes
39	Methylene-bis-(di-*t*-butylphenol)*	ND	ND	0.1–3	Yes
40	Ethylene-bis(di-*t*-butylphenol)*	ND	ND	[e]	Yes
41	Tetra-*t*-amyldihydroxydiphenyl*	ND	ND	[d]	Yes
42	Di-*t*-butylhydroxycinnamic acid*	[d]	[d]	[d]	No
43	Methyl-di-*t*-butylhydroxycinnamate*	[d]	0.010[b]	[e]	Yes
44	Ethyl-di-*t*-butylhydroxycinnamate*	ND	0.010[b]	[e]	Yes
45	3-(3′,5′-Di-*t*-butyl-4′-hydroxyphenyl)propionic acid*	[d]	[d]	[d]	No
46	Methyl-3-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)propionate*	0.6–11	0.025–0.20	1.5–170	Yes
47	Ethyl-3-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)propionate*	<0.02	<0.002	2.5[b]	Yes
48	*i*-Propyl-3-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)propionate*	0.02–0.30	<0.002	3.5[b]	Yes
49	Hexadecyl-3-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)propionate*	0.040–1.4	0.002–0.04	ND	No
50	Octadecyl-3-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)propionate*	1.6–6.0	0.008–0.2	8–220	Yes
51	$C_{22}H_{34}O_5$ (see footnote *c*)	0.06–0.9	0.006–0.012	0.6[b]	Yes
52	Di-(2-ethylhexyl)phthalate	ND	0.001–0.05	0.2–56	Yes
53	Di-octyl-phthalate	ND	0.001–0.02	1.5–25	Yes
54	Diphenyl ether	0.01–0.20	0.001–0.005	ND	No
55	Phenyl tolyl ether	ND	ND	[e]	Yes
56	$C_{29}H_{44}O_3$ (see footnote *g*)	0.06–0.20	<0.001	0.4–0.8	Yes
57	2,6-Di-*t*-butylbenzoquinone	0.01–0.02	0.001–0.011	0.1–40	Yes

Table I. Continued

Compound no.	Compound name	Concn range, ppm			Present in tar ball[a]
		Wastewater	River water	Sediment	
	Oxygen-containing compounds				
58	Tetra-*t*-butyldiphenoquinone*	0.02–0.30	<0.001	0.2–0.5	Yes
59	Tetra-*t*-butylstilbenequinone*	ND	ND	[d]	Yes
60	Binaphthylsulfone	ND	ND	[d]	Yes
	Halogenated compounds				
61	Dichloromethane	3–8[h]	[f]	ND	No
62	Chloroform	[f]	ND	ND	No
63	Trichloroethane	[f]	ND	ND	No
64	Trichloroethylene	[f]	[f]	ND	1no
65	Tetrachloroethylene	[f]	[f]	ND	No
66	Chlorobenzene	[f]	[f]	ND	No
67	Dichlorobenzene	[f]	[f]	[e]	Yes
68	Chlorotoluene	[f]	[f]	ND	No
69	Chlorobiphenyl	ND	ND	[e]	Yes
70	Chlorophenol	0.01–0.02	[f]	ND	No
71	Dichlorophenol	[f]	[f]	ND	No
72	Chloroaniline	ND	ND	1–2	Yes
73	Chlorotrifluoromethylaniline	ND	ND	0.2–180	Yes
74	Chlorophenylisocyanate*	ND	ND	0.1–2	Yes
75	Chlorotrifluoromethylphenylisocyanate*	ND	ND	0.1–13	Yes
76	4,4′-Dichlorocarbanilide*	ND	ND	[d]	Yes
77	4,4′-Dichloro-3-trifluoromethylcarbanilide*	ND	ND	[d]	Yes
78	4,4′-Dichloro-3,3′-bis-trifluoromethylcarbanilide*	ND	ND	[d]	Yes
79	Chlorotrifluoromethyldinitrobenzene	ND	0.002[b]	ND	No
80	Trichloro-amino-diphenylether	0.025–0.075	0.002–0.005	ND	Yes
81	2,4,4′-Trichloro-2′-hydroxydiphenylether*	6–14	0.012–0.30	1.2–5	No
82	Dichlorodibenzodioxin	[d]	[d]	ND	No
83	Trichlorodibenzofuran	[d]	[d]	ND	No
84	Bis-(dichlorophenoxychlorophenyl)-ether	[d]	ND	ND	No
	Aromatic hydrocarbons				
85	Benzene	[f]	[f]	ND	No
86	Toluene	13–20[h]	[f]	ND	No
87	Xylenes	[f]	[f]	ND	No
88	C_3-Alkyl-benzenes	[f]	[f]	30[b]	No
89	C_4-Alkyl-benzenes	[f]	[f]	[e]	Yes
90	C_5-Alkyl-benzenes	ND	ND	[e]	Yes
91	C_6-Alkyl-benzenes	ND	ND	[e]	Yes
92	C_7-Alkyl-benzenes	ND	ND	0.5[b]	Yes
93	C_8-Alkyl-benzenes	ND	ND	[e]	Yes
94	Biphenyl	ND	0.001–0.015	1–2	Yes
95	Terphenyl	ND	ND	[e]	Yes
96	Naphthalene	1–4	0.006–0.01	1.5[b]	No
97	Di-*t*-butylnaphthalene	ND	ND	[e]	Yes
98	Di-*t*-butyldihydroxynaphthalene	ND	ND	1[b]	Yes
99	Acenaphthylene	ND	ND	0.2–5	Yes
100	Fluorene	ND	ND	2–10	No
101	Methylacenaphthylene	ND	ND	5[b]	No
102	Methylfluorene	ND	ND	[e]	Yes
103	Hydroxyfluorene	ND	ND	0.1[b]	No
104	Phenanthrene	ND	ND	0.2–25	Yes
105	Methylphenanthrene	ND	ND	0.4–20	Yes
106	C_2-alkyl-phenanthrene	ND	ND	[e]	Yes
107	Fluoranthene	ND	ND	1–60	Yes
108	Pyrene	ND	<0.001	0.5–75	Yes
109	Methylpyrene (3-isomers)	ND	ND	0.2–15	Yes
110	Cyclopenta[c,d]pyrene	ND	ND	1–4	No
111	$C_{18}H_{12}$ PAH[i]	ND	ND	0.5–25	Yes
112	$C_{19}H_{14}$ PAH[i]	ND	ND	4–6	No
113	$C_{20}H_{12}$ PAH[i]	ND	ND	0.5–120	Yes
114	$C_{22}H_{12}$ PAH[i]	ND	ND	4–100	No
115	$C_{24}H_{14}$ PAH[i]	ND	ND	5–20	No

(*Continued on page 92*)

Table I. Continued

Compound no.	Compound name	Concn range, ppm Wastewater	 River water	 Sediment	Present in tar ball[a]
	Alkanes				
116	C_6 alkanes	[f]	ND	ND	No
117	C_8 alkanes	[f]	[f]	ND	No
118	C_9 alkanes	[f]	[f]	ND	No
119	C_{10} alkanes	[f]	[f]	ND	No
120	C_{11} alkanes	[f]	[f]	73[b]	Yes
121	C_{12} alkanes	0.3[b]	[f]	ND	No
122	C_{13} alkanes	[f]	ND	ND	No
123	C_{17} alkanes	0.1[b]	ND	ND	No

[a] The tar balls were small pea-size globules consisting of a complex mixture of anthropogenic compounds and were completely soluble in dichloromethane. They were found only at points 11 and 12 in the gravelly bottom just above the dam (Figure 1). Some of the tar balls were extracted along with the gravelly matrix material resulting in very concentrated samples, the quantitation of which would be meaningless. [b] Compound was detected in only one sample. [c] This compound has a molecular formula of $C_{22}H_{34}O_5$ as determined by high resolution mass spectrometry. Tentative identification is methyl isopropyl (3′,5′-di-*t*-butyl-4′-hydroxybenzyl)malonate. [d] The compound was isolated in a HPLC fraction and identified by mass spectrometry. Thus, quantitation was not possible. [e] The compound was only present in the tar ball-containing extract and thus could not be quantitated. [f] The compound was only identified through vapor stripping experiments and thus could not be quantitated. [g] This compound has molecular formula of $C_{24}H_{44}O_3$ from high resolution mass spectrometric data; a very tentative identification is dihydroxy-tetra-*t*-butyl-methyl-diphenyl ether. [h] Accurate compound quantitation based on direct aqueous injection. [i] A polycyclic aromatic hydrocarbon isomer. ND: Compound was not detected in the sample. * For structure, see Figure 2.

and spectra were obtained by continuous scanning under control of the data system. The instrument was also operated in the continuous scanning mode during analysis of collected liquid chromatographic fractions introduced with the direct insertion probe. Even when the LC fractions contained more than one compound, some fractionation of the compounds due to differential volatility allowed collection of relatively clean mass spectra for individual components.

High resolution (~20 000) mass spectrometric data were obtained on a Du Pont 21-110B instrument with photographic plate detection. These plates were read on an automatic densitometer operated on line to an IBM 1800 computer (*8*).

Compound Identification. Our analyses resulted in the accumulation of thousands of spectra. These were initially compared to those published in the Eight Peak Index (*9*). Nearly all of the solvents, phenols, and hydrocarbons were found in this source, but the spectra of only a few of the remaining compounds were found here. Standard interpretation procedures were used to identify the remaining compounds. Unfortunately, due to the normally high degree of aromaticity, the mass spectra of many of the unknowns consisted of only a few peaks, making identification difficult. However, a single high resolution mass spectral analysis of an extract provided the exact masses for most of the major molecular and fragment ions observed during a low resolution GC/MS analysis. Thus, we were able to assign probable formulas to the various ions. This information often enabled us to identify structures related to other compounds already identified in the samples. When this was not successful, the Formula Index of Chemical

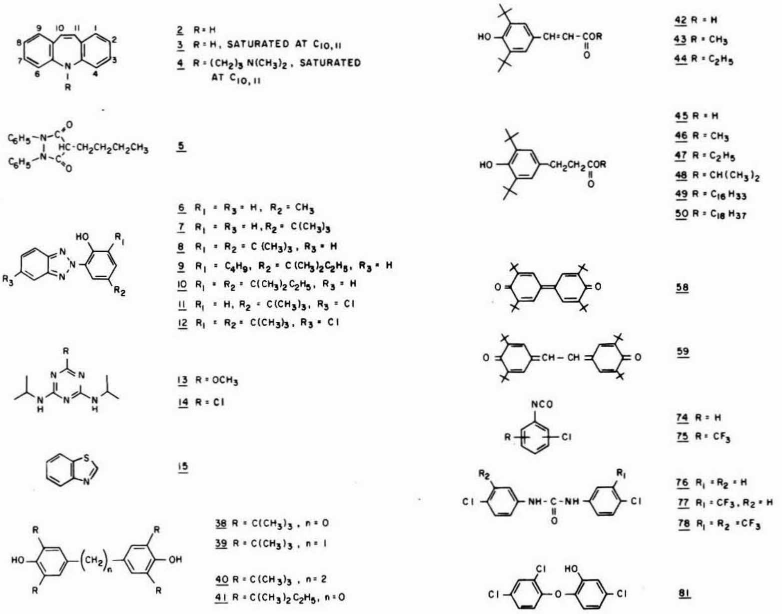

Figure 2. Structures of some of the compounds found in this study (Table I)

Abstracts and the Trade Commission Report (*10*), which lists production data for individual and classes of compounds, were searched for related compounds produced by the company. The company advertising literature, which presented use and toxicity data for some of its products, was also useful in identifying a few compounds. Computer-assisted library search routines (*11*) were not generally used. Because the Eight Peak Index contained most of the compounds in these data bases, time could be more economically utilized in performing the manual procedures described above.

Although the company officials and plant personnel cooperated fully in acquiring wastewater samples for analysis, they provided little information concerning identities of reactants or company products. Specific ring substitution patterns are not easily derived from mass spectrometric data and are included here only for cases where the literature specifies the isomer or in cases where we have purchased standards and observed identical mass spectra and gas chromatographic retention times.

Results and Discussion

All of the compounds identified in the wastewaters, river water, and sediment samples are listed in Table I along with their concentration range. The individual concentrations have an estimated error of 20%. A compilation of the concentration of each of the compounds at each of the sampling locations is presented elsewhere (*12*). The structures of several of the compounds in Table I are given in Figure 2.

The identification of these 123 compounds (see Table I) was made possible only by the synergistic application of several analytical techniques. For example, the very high concentrations of a few compounds in most of the samples (e.g., no. 6, 10, 46, 81) precluded identification of many of the minor components during a single GC/MS analysis and also caused problems with their quantitation. This dynamic range problem was solved at least qualitatively by HPLC followed by mass spectrometry. By way of illustration, a liquid chromatogram of one of the tar ball-containing extracts is shown in Figure 3.

The best separations were achieved using the reverse phase conditions as shown in Figure 3. For example, under these conditions, the slightly different polarity of 2-(2′hydroxy-3′,5′-di-*t*-amylphenyl)-2H-benzotriazole (no. 10) and 2-(2′-hydroxy-3′,5′-di-*t*-butylphenyl)-5-chloro-2H-benzotriazole (no. 12) was sufficient to separate them. By gas chromatography the high resolution of a glass capillary column was required to separate this pair of compounds (Figure 4). Many compounds that had not been observed during GC/MS analysis but absorbed strongly in the UV during HPLC analysis were collected and identified in this manner.

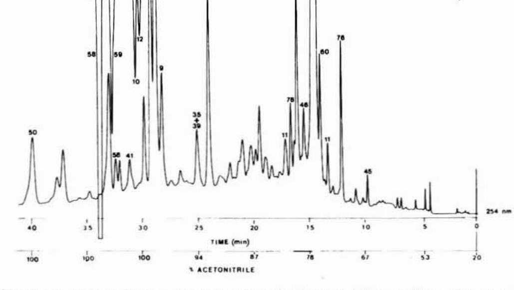

Figure 3. Liquid chromatogram of tar ball-containing sediment extract taken from Point 12 (Figure 1)

Column: 30 cm × 2 mm i.d. packed with C_{18}-μ-Bondapak. Solvent programmed from 20 to 100% acetonitrile in water with flow rate of 2.0 mL/min. Numbers identifying peaks are keyed to Table I

Commonly Observed Compounds. Two of the substituted benzotriazoles (no. 6, 10) were generally the most abundant anthropogenic compounds in the water and sediment samples. They are used as ultraviolet light absorbers in plastics and possess antitoxidant and thermal stabilization properties. No. 12 is apparently a former product found only in the sediments. The other benzotriazoles, present in much lower concentrations, are probably impurities in the major products. These benzotriazoles are characterized by resonance-stabilized internal hydrogen bonding of the phenolic hydroxyl to the benzotriazole ring; this results in compounds with a high degree of environmental stability.

The phenols (no. 30a, 30b, 32) are used as reactants to synthesize several of the company's products, including the benzotriazoles. The 2-chloro-4,6-bis-isopropylamino-*s*-triazine (no. 14) and 2-methoxy-4,6-bis-isopropylamino-*s*-triazine (no. 13) are herbicides; the chloro compound is used to control weeds and grass in corn and in milo, and the methoxy compound is used for general plant control. Several esters of 3-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)propionic acid were identified, the most abundant being the octadecyl and methyl esters (no. 46 and 50).

Some ethers found in the wastewater and river water included diphenyl ether (no. 54), phenyltolyl ether (no. 55), and 2,4,4′-trichloro-2′-hydroxy diphenylether (no. 81) which is a bacteriostat. The diphenyl ether became relatively more concentrated compared to other river water compounds in the brackish cove; this suggests high environmental persistance or its formation in situ from another compound. Some other very interesting compounds, apparently resulting as by-products during the synthesis of 2,4,4′-trichloro-2′-hydroxy diphenyl ether, were trichlorodibenzofuran (no. 83), dichlorodibenzodioxin (no. 82), and a hexachlorinated compound of MW 558 (no. 84) which apparently results from condensation of two molecules of the ether with concomitant loss of water. We do not believe these compounds are artifacts produced from the ether during analysis because they were separated and collected as LC fractions, and the mass spectra were obtained with the direct insertion probe. These compounds have been detected in the wastewater and river water.

Small quantities of 4-*n*-butyl-1,2-diphenyl-pyrazolidine-3,5-dione (no. 5), an antipyretic, anti-inflammatory, and uricosuric drug, and 5-(3-dimethylaminopropyl)-10,11-dihydro-5H-dibenz[b,f]azepine (no. 4), an antidepressant drug, were also found.

Chlorotrifluoromethylaniline (no. 73) was found in the sediment samples. This compound is used as a reactant with chloroaniline (no. 72) in the preparation of 4,4′-dichloro-3-trifluoromethylcarbanilide, a disinfectant. Two other related compounds also found in some of the sediments were chlorophenylisocyanate (no. 74) and chlorotrifluoromethylphenylisocyanate (no. 75). This suggests that some of the 4,4′-dichloro-3-trifluoromethylcarbanilide may, in fact, exist in the sediment extracts but is decomposed in the injection port of the gas chromatograph, since it was very doubtful that the easily hydrolyzable isocyanates exist as such in the sediments. To strengthen this hypothesis, some 3,4,4′-trichlorocarbanilide [none of the 4,4′-dichloro-3-trifluoromethylcarbanilide was available] was analyzed by GC/MS. The injection port temperature was 300 °C. As expected, none of the parent compound eluted from the column. However, mass spectra were obtained for chlorophenylisocyanate, dichlorophenylisocyanate, chloroaniline, and dichloroaniline. The presence of the carbanilides themselves (no. 76, 77, 78) was confirmed with the help of HPLC and mass spectral identification.

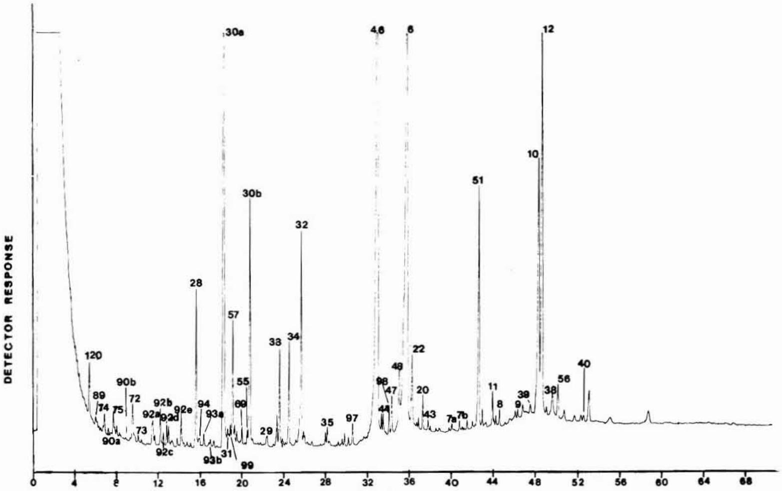

Figure 4. Gas chromatogram of tar ball-containing sediment extract taken from Point 12 (Figure 1)

Column: 20 m × 0.25 mm i.d. glass capillary coated with SE-52 (methyl silicone phase). Column held at 60 °C for 2 min and then temperature programmed to 240 °C at 4 °C/min. Numbers identifying peaks are keyed to Table I

Compounds present in the upstream river water extracts, but not in the plant wastewater included benzothiazole (no. 15), phenylphenol (no. 37), alkanes, and phthalate esters (no. 52, 53). Their source is apparently another manufacturing plant.

Sedimentary Accumulation. The most striking result of this study is the high accumulation of anthropogenic compounds in the sediments. An estimation of the degree of sediment accumulation was gained by calculating a sediment accumulation factor, which is the average sediment concentration divided by the average river water concentration. Typical results are shown in Table II. The mechanism of this accumulation is not yet clear, but one possibility may be the gradual settling out of extremely fine-grained particulate matter with a high organic load. Another possible explanation is that the organic compounds in the wastewater form micelles, thus enhancing the water solubility of normally water-insoluble compounds. As the micelles are diluted by the river, they break up, inducing precipitation of the large, normally water-insoluble compounds.

Extraction of the coarse sediment yielded rather high concentrations of anthropogenic compounds leaving clean sand and gravel. It seemed that the finer-grained material was more conducive to accumulation of large quantities of organic compounds, including polycyclic aromatic hydrocarbons (no. 96–115) and phthalate esters (no. 52, 53).

A small dam creates a falls (between Points 14 and 15, Figure 1) where the river empties into the brackish cove. Just above the dam, the rocky sediment samples contained small tar balls consisting entirely of a mixture of anthropogenic compounds. These tar balls were generally smaller than a pea, but one was knucklesized. Some of these tar balls were discovered in the samples from Points 11 and 12 (Figure 1) and were extracted along with some of the sediment. Quantitation of these samples would be meaningless, but they provided convenient samples for identifying large numbers of anthropogenic compounds in the sedimentary environment.

The sediment concentrations of anthropogenic compounds in the brackish cove were somewhat higher and less variable than upstream; this probably reflects the greater bottom uniformity of the cove. Fewer of the plant's compounds were detected in the channel where the brackish cove leads into the brackish river (Point 18, Figure 1). Found at this location were various phenols (no. 28, 30a, 30b, 31, 33, 38, 39), 2,6-di-*t*-butyl-benzoquinone (no. 57), 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (no. 35), three benzotriazoles (no. 6, 10, 12), chlorotrifluoromethylaniline (no. 73), and 2-chloro-4,6-bis-isopropylamino-*s*-triazine (no. 14). The only compounds from the plant detected in the sediment sample from the brackish river (Point 19) were the two high molecular weight benzotriazoles (no. 10 and 12) and methyl 3-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl)propionate (no. 46).

Some compounds are *not* accumulated into the sediment. The two triazine herbicides (no. 13 and 14) were in most of the wastewater and river water samples, but only as very minor components in a few sediment samples. The greater water solubility (methoxy, 750 ppm, chloro, 8 ppm) of these compounds (*13*), compared to most of the other compounds found in this study, probably prevents them from being incorporated into the sediments. In addition, the methoxy triazine (no. 13) is about two orders of magnitude more volatile (*13*) than the chlorotriazine (1.12×10^{-6} mm Hg vs. 2.9×10^{-8} mm Hg), and it may be lost through volatilization from the river water, especially during the summer months. Another compound of high river water concentration, but of low propensity for

Table II. Sediment Accumulation Factors for Some of the Anthropogenic Compounds from the Plant[a]

	ppm			Accumulation factor
Compound	Wastewater	River water	Sediment	
6	2	0.02	40	2000
10	2	0.02	10	500
12	ND	ND	10	. . .
13	4	0.07	ND	0
14	2	0.07	7	100
30a	0.7	0.002	4	2000
30b	0.5	0.002	3	1500
31	ND	0.002	8	4000
38	ND	0.002	0.5	250
39	ND	ND	0.5	. . .
46	3	0.07	20	300
57	0.02010.003	2	700	
58	0.08	ND	0.3	. . .
80	0.04	0.003	ND	0
81	9	0.06	2	30

[a] The water and sediment concentration values are geometrical averages of the high and low values given in Table I.

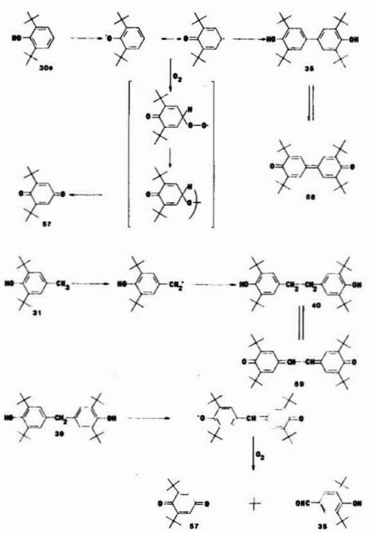

Figure 5. Scheme for environmental oxidation, reduction, and coupling of phenols to produce some of the compounds found in this study. Compound numbers refer to Table I

sediment accumulation, having only been found in minor quantities in a few sediments, was 2,4,4′-trichloro-2′-hydroxydiphenyl ether (no. 81).

Chemical Transformation of Some of the Anthropogenic Compounds in the Environment. The fate of the di-*t*-butyl phenols is quite interesting. In the wastewater 2,6-di-*t*-butyl benzoquinone (no. 57) gives a very minor peak between 2,6-di-*t*-butylphenol (no. 30a) and 2,4-di-*t*-butylphenol (no. 30b). However, as the river water samples were taken further downstream from the plant, the relative intensity of the two phenol peaks gradually decreased and that of the benzoquinone increased. Two other quinones, tetra-*t*-butyldiphenoquinone (no. 58) and tetra-*t*-butyl-stilbenequinone (no. 59), have also been identified. All of these quinones seem to be formed in the wastewater and river water by oxidation and coupling of the phenols (*14, 15*). However, in the reducing environment of the sediment, these quinones seem to be converted to the corresponding bisphenols (Figure 5). This is consistent with geochemical studies which indicate that the phenol/quinone ratio of humic materials (*16*) appears to be sensitive to redox potential (*17*), and the conversion between the two forms is rapid and reversible (*18*). Another compound identified in the sediment extracts, probably resulting from oxidation of substituted phenols or substituted bis-phenols (*19*) is 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (no. 35) (Figure 5).

Environmental and Health Hazards. At this time it is difficult to specify whether the receiving water and sediments present an environmental or human health hazard. Toxicological information is not known for many of the compounds. The wastewater flows into an estuary which is quite contaminated with sewage, and of course, the water is not used for drinking.

The very abundant benzotriazoles exhibit acute oral LD_{50}'s of >5000 mg/kg for oral doses to rats and mice, and no irritation or sensitization was observed during patch tests on humans (*20*). The phenols also do not seem to be particularly toxic; almost all have LD_{50} values of >2500 mg/kg (*20*). Only 2,4-di-*t*-amyl phenol is potentially toxic with an LD_{50} of 330 mg/kg for oral administration to rats (*20*). Similarly, studies on the toxicity of the esters of 3-(3′,5′-di-*t*-butyl-4′-hydroxyphenyl) propionic acid show no significant effect. Male and female rats showed acute oral LD_{50}'s that were greater than 5000 mg/kg body weight (*20*).

The *s*-triazine herbicides are excreted so rapidly from animals that only monodealkylation and some hydrolysis occur (*13*). Apparently no toxic effects occur in animals; 2-chloro-4,6-bis-isopropylamino-*s*-triazine has an LD_{50} in rats and mice of >5000 mg/kg (*13*) and 2-methoxy-4,6-bis-isopropylamino-*s*-triazine of 2350 mg/kg (*20*).

However, another point to consider in determining the environmental effect of these chemicals was brought to light in the studies of Schober and Lambert (*21*). The reproduction rates of daphnia were studied in water with *s*-triazine herbicides at concentrations ranging from 1 to 20 ppm. Although these concentrations had no effect on the life span of the animals (65 days), their reproduction rate decreased steadily with increasing concentration (*21*). In the ecosystem of the specialty chemicals plant, the *s*-triazine concentrations, at least in the water, are much lower than used in the daphnia experiment. However, solvents and a great number of other compounds are also present which may produce synergistic effects. Thus, the acute toxicity levels determined from experiments with laboratory animals probably have little relevance in estimating the long-term ecological consequences of low-level exposure to industrial chemicals.

Summary and Conclusions

The wastewater from a specialty chemicals manufacturing plant and its receiving waters and sediments have been extensively analyzed for organic compounds. The concentrations of anthropogenic compounds range up to about 15 ppm in the wastewater and 0.2 ppm in the river water, but up to several hundred ppm in the sediments. The composition of the river water in general reflected the composition of the wastewater except that some of the compounds appeared to degrade or volatilize in the river water while others accumulated into the sediments where they appear to be stable and build up to a high concentration. The sediment concentrations are all high but depend greatly on sediment characteristics. Thus, the distribution and transport may depend on the dynamics of fine-grained suspended materials.

Some of the compounds are modified in situ. Various phenols seem to be easily oxidized to quinones; these may be reduced back to the phenols depending on the redox nature of the environment.

Several compounds of known biological activity (herbicides, bacteriostats, and disinfectants), as well as some potentially toxic chemicals such as dichlorodibenzodioxin, are present in the water. A human health hazard is difficult to assess, but the long-term, low-level exposure to this wide variety of chemicals may have contributed to the lack of biota in the area.

Acknowledgment

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NOTES

Electrofluidized Bed in Filtration of Smoke Emissions from Asphaltic Pavement Recycling Process

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■ The electrofluidized bed (EFB), a device recently proposed for high efficiency collection of submicron particles, is tested on the emissions from an asphalt recycling plant. The largely hydrocarbon pollutant is collected on sand that is then easily removed from the bed in its fluidized state and subsequently added to the asphalt product. Efficiencies of collection in excess of 98% are reported for submicron particles in beds having unfluidized depths of 8–12 cm using sand having a mean diameter of 2 mm. Superficial velocities range from 1.5 to 2 m/s, with a typical bed pressure drop of 12 cm H_2O. Electrical energization of the bed requires less than 80 W/1000 cfm. Estimates of the EFB capital and operating costs are favorable compared to other devices that could conceivably serve this application. The EFB promises to make an essential contribution toward making possible the recycling of asphaltic highway using existing asphaltic processing equipment.

Motivated by the oil shortage, the Federal Government has been investigating ways of recycling asphaltic pavement. Warren Brothers Co. has been cooperating with this effort by trying to devise ways of adapting conventional plants to operate in a recycle mode. A major impediment to this conversion is the formation of fine particulate smoke that occurs when crushed pavement is subjected to the temperatures necessary for recycling. In the course of this study it was found that, upon heating, the asphalt begins to crack and release hydrocarbon vapor that subsequently condenses into droplets. These submicron droplets are poorly collected in the devices currently in use on asphalt plants, the baghouse and Venturi scrubber.

Even if they are designed for submicron collection, currently available devices are ill suited to the asphalt cleanup problem. Electrostatic precipitators collect the oil on electrode plates from which it is difficult to remove. Fabric filters appropriate for submicron collection must incorporate a large pressure drop that increases significantly as collection of materials proceeds. In addition, bags fouled with oil tend to clog and are at best difficult to clean. Wet wall electrostatic precipitators, charged-droplet scrubbers, and high-energy Venturi scrubbers, all create a water pollution problem and require both a substantial capital investment and a high operating cost.

The electrofluidized bed (EFB) recently proposed by Zahedi and Melcher (*1*) is well suited to the asphaltic smoke cleanup problem. Its efficient collection of submicron particles in a short residence time (about 50 ms), together with the unique feature of collecting the pollutant on easily handled fluidized sand, makes the EFB an attractive device for this application. After being used as a collection surface, the oil-coated sand can be conveniently incorporated into the asphalt product. In fact, an "oiled" sand is desirable for use in asphalt. In the EFB the sand particles are stressed by an ambient electric field creating poles of positive and negative charge on each particle. For the apparatus described in this paper, the electric field is imposed parallel to the gas flow (co-flow), that is, with horizontal screens of alternate potential spaced vertically through the sand bed. It is possible to design a bed with the electric field perpendicular to the gas flow (cross-flow), although this type is somewhat more difficult to build for a large-scale application. The dominant mode of collection is for charged pollutant to be collected by the oppositely charged poles of the sand. Other modes of collection exist, such as microfield collection, inertial impaction, and interception, but these are shown to be of secondary importance by Zehedi and Melcher (*1*).

Fundamentals of Submicron Particle Collection

A remarkably good model for plug-flow beds pictures the bed particles as being much like the electrodes of an ESP, with the electric field terminating over one side of each particle and originating on the other. Instead of the Deutsch model used

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for turbulent flow ESP's (2), the "local mixing model" is invoked with the assumption that on the average the fluid mechanics supplies the full surface of a bed particle with the gas-entrained pollutant. The electric field simply brings the pollutant from the local volume to the bed particle surface. According to this model (*1*), a bed having unfluidized height l_o, bed particles of mean radius R, a superficial gas velocity U, and an imposed electric field E collects particles of mobility b with the efficiency

$$\eta = 1 - \exp(-K_1);\ K_1 \equiv \frac{3\pi}{8} c \frac{l_o}{R} \left(\frac{bE}{U}\right) \qquad (1)$$

where c is a coefficient of order unity.

This model is valid provided that reentrainment and bubbling are not substantial. The first of these conditions is not a problem for liquid aerosols such as asphaltic smoke.

Unless baffled to promote bubble breakup, gas fluidized beds do not expand uniformly as the fluidizing velocity increases, and the resulting effects of nonuniformity in the gas-solid distribution are not accounted for in the plug-flow model. This is especially true in the cross-flow beds where the screen electrodes are not used. In the co-flow configuration, the screens used to impose the electric field tend to prevent the growth of bubbles. Models have been developed and correlated with experiments for bubbling electrofluidized beds (*3*). These combine the particle-scale collection model tested in the plug-flow experiments (*1*) with two-phase models that have been developed for the transfer characteristics of conventional fluidized beds (*3*). It is important to recognize that the structure of beds can be strongly influenced by an applied electric field. In what will be termed the "bed electromechanics", particles tend to form "chains" or "strings" while gas flow causes a fluttering motion instead of the typical bubbling one (*4*). These effects have important implications for bed mixing and particle elutriation. However, high submicron collection efficiencies can be obtained at relatively low electric field intensities where electromechanical effects are not of significance. Thus, the Davidson model is adopted for a conventional bubble having the diameter D_b (in which the particle density is low) interacting with the dense phase. Part of the gas passes through a dense region at about the minimum fluidization velocity U_{mf}, while the remainder bypasses the system in the form of bubbles. There is a continual exchange of particles between phases accounted for by the Davidson model.

Two possible extremes can be used to model the penetration of pollutant through the bed as a whole. The dense phase can be viewed as evolving uniformly in the flow direction (the plug-flow model). Because of bubble agitation a complete mixing model is also plausible. Both models have been studied with the dense phase plug-flow model clearly found to be more representative of what happens.

The plug-flow bubbling model shows how parameters not represented in the collection coefficient K_1 come into play. The predicted efficiency is

$$\eta = 1 - \frac{1}{m_2 - m_1} \left\{ m_1 e^{m_2 l_f} \left[1 + \frac{m_2 l_f U_{mf}}{c_q U} \right] - m_2 e^{m_1 l_f} \left[1 + \frac{m_1 l_f U_{mf}}{c_q U} \right] \right\} \qquad (2)$$

where m_1 and m_2 are the roots of

$$m^2 + \left[\frac{(c_q + K_1)U}{l_f U_{mf}} \right] m + \frac{K_1 c_q U}{l_f^2 U_{mf}} = 0$$

and

$$c_q = \frac{9}{2} \frac{(l_f - l_{mf})}{D_b} \frac{U_{mf}}{U - U_{mf}}$$

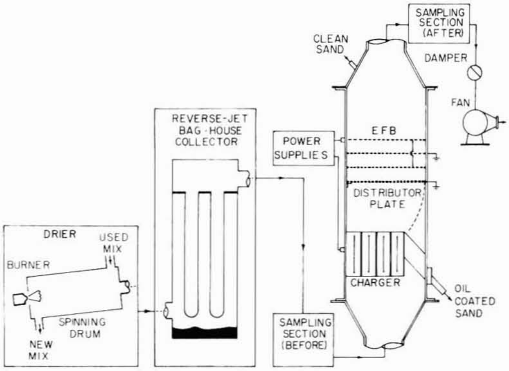

Figure 1. Schematic of EFB test system

The collection coefficient K_1 is the same as defined with Equation 1; U and l_f are, respectively, the superficial velocity and fluidized bed height under the conditions of interest; and U_{mf} and l_{mf} are these quantities under conditions of minimum fluidization. The most important parameter is D_b, the bubble diameter. The quantities necessary to evaluate these expressions are, of course, averages. The bed height is a fluctuating quantity, and even in the shallow beds of interest here, bubbles grow significantly as they pass through the bed.

If the rate of gas interchange between the bubbles and the dense phase is large, which according to Davidson's model means that $c_q \rightarrow \infty$, the efficiency predicted by Equation 2 reduces to that for the single-phase plug-flow model, Equation 1. The most important aspect of the bubbling model is its prediction of efficiencies less than 100%, no matter how large the collection parameter. In the limit $K_1 \rightarrow \infty$, the efficiency approaches the limiting value

$$\eta \rightarrow 1 - \left[1 - \frac{U_{mf}}{U} \right] e^{-c_q} \qquad (3)$$

Using experiments to evaluate c_q, over a wide range of fluidization states, this parameter is mainly a function of the bubble diameter D_b.

Experimental Tests

A prototype EFB of cross-sectional area 1 ft^2 was built and tested on both a small-scale asphalt recycling system and on a bypass to a full-scale asphalt plant operating in the recycle mode. The EFB, together with the small-scale recycling system, is shown schematically in Figure 1. The test unit was constructed of metal plate in the shape of a rectangular box. A wall of fireglass afforded visual observation. The distributor plate was constructed of ¼-in. perforated plate with approximately 9% open area. This plate was covered with a 16-mesh screen. Three screens of ½-in. hardware cloth were used to impose the electric field. In addition, these upper screens helped promote bubble breakup. Because bed particles tended to polish metallic and insulating surfaces within the bed, these screens remained free of pollutant buildup. The distributor plate structure exhibited a pressure drop of about 2 cm of H_2O under 400 cfm operating conditions. (It is important to use a distributor plate that minimizes excessive bubbling at a reasonable pressure loss.) For all small-scale tests, sand with median diameter of 2 mm was employed. Utilizing such a large size sand enables operation of the fluidized bed at a high superficial flow velocity, about 2 m/s, and therefore a small bed cross section. A sand removal system was devised with a hinged distributor plate. The tests were performed on a batch basis, with fresh sand fed at the top.

Table I. Summary of Collection Performance of EFB; Comparison of Experimental and Predicted Efficiencies

EFB operating parameters				Efficiency (%)		
					Theoretical	
Particulate loading (mg/s·m^3)	U (m/s)	l_o (cm)	E (kV/m)	Exptl	Plug-flow model	Bubbling model
167	1.7	10	465	96	99	96
82	1.8	10	250	93	94	91
44	1.8	13	500	94	99	92

After each test the sand was removed by releasing the distributor plate.

The charger used was of the plate and wire type. Pollutant spent on the average 50 ms in the corona region, providing sufficient time for the particles to acquire a saturation charge (2). The test system was designed to stand temperatures up to 500 °F, while the sampling system was capable of dealing with a humid environment and rapid variations in gas loading. The miniature drier was capable of processing 500 lb/h of crushed pavement, containing approximately 3% asphalt. The baghouse was used for removing large (10–100 μm) road dust entrained in the drier and displayed very little deposition of submicron oil. Field tests were also conducted on a bypass from a full-scale asphalt plant operating in the recycle mode (Warren Brothers plant #135, Richmond, Va., with production maintained at 45 tons/h). Washed river sand with a mean diameter of 4 mm was employed, with the EFB operated after a bag filter.

Two Andersen 2000 "nonviable" cascade impactors were used to isokinetically measure the pollutant mass concentration both before and after the bed and to subsequently infer the device collection efficiency. Separately controlled heating systems prevented condensation in the devices. The two impactors were kept at the same temperature to maintain the same volume flow rate and cut diameter in both. All impactor results are shown in terms of the aerodynamic diameter.

Results

The results of three separate tests of the collection efficiency of the EFB on the small-scale recycling system are reported in Table I. Experimental results are shown along with the theoretical efficiencies predicted by the plug-flow model and the more complete bubbling model, Equation 2, which accounts for the effect of bubble bypass. Both the bubble model and the plug-flow model are independent of pollutant loading, a result confirmed in previous experiments (*1*). The deviations from the bubble model in the second and third tests are well within experimental error.

A typical size distribution of the sampled aerosol is reported in Figure 2. After removal of dust by the bag filter, the aerosol displays a mass median diameter of 0.3–0.5 μm, with a geometric standard deviation of about 2. This extremely small particle size accounts for the poor collection efficiency of conventional devices such as the baghouse and venturi scrubber.

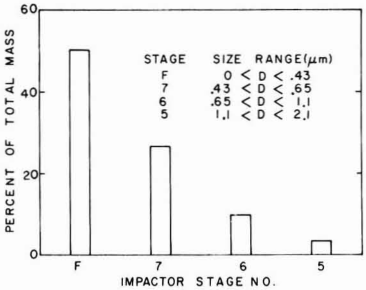

Figure 2. Asphaltic smoke size distribution, by mass

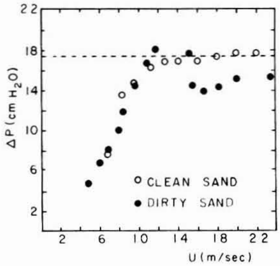

Figure 3. Pressure drop as a function of superficial flow velocity for 12-cm bed

Dirty sand contains 0.7% asphaltic oil. Dashed line: theoretical pressure drop based on density of sand

An important parameter is the amount of time that sand can be used before it must be replaced because of a drop in collection efficiency. The mechanism for this loss of efficiency seems to be channeling of the gas through spouts in the bed, caused as the bed becomes sticky from excessive oil collection. In Table II, tests with similar operating parameters are shown side by side; in one case with clean sand and in the other, oil-coated sand. In the two cases for which the oil loading is 0.7%, the measured efficiency for the oily sand is essentially the same as for the clean sand. In the case of 1.2% oil loading, a drop in efficiency is observed.

Pressure drop accounts for the largest share of EFB operating costs. Figure 3 reports the experimental pressure drop across the sand as a function of flow velocity for both fresh and oil-coated sand. Theoretically, the pressure drop of a fluidized bed is equal to the weight per area of the bed, shown in Figure 3 as a dashed line. The 15% reduction in pressure drop reported for oil-coated sand in Figure 3 is due to the spouting characteristic of the bed (5). This reduction in pressure drop provides a simple test for when sand should be replaced due to its poor collection characteristics. Electrical energization

Table II. Comparison of Collection Performance of Fresh and Oil-Coated Beds

			Efficiency (%)				
			Fresh bed		Oil-coated bed		
EFB operating parameters							
U (m/s)	E (kV/m)	l_o (cm)	Particulate loading (mg/s·m^3)	Exptl	Particulate loading (mg/s·m^3)	Oil loading[a] (%)	Exptl
1.8	500	13	44	94	107	0.7	94
1.8	500	13	44	94	200	0.7	95
1.7	465	10	167	96	233	1.2	85

[a] Oil loading is defined as the ratio of the weight of collected oil to the bed total weight.

Table III. Summary of Collection Performance in Richmond

Efficiency measuring device	EFB operating parameters			Efficiency (%)
	E (kV/m)	U (m/s)	l_o (cm)	
Mass monitor	400	1.9	10	99.3
Andersen impactor	400	2.1	11	99.1

represents a much smaller share of EFB operating costs than pressure drop. Both the bed and the charger were energized at 20 kV with a total current of about 1 mA. This represents a power consumption of about 20 W for 400 cfm.

Test results from Richmond, Va., are reported in Table III, where 400 cfm of flue gas is filtered through the EFB. Pollutant loadings varied between 4 and 41 mg/m^3, the higher levels being used for measuring the device collection efficiency. Particles had a mass median diameter of 0.35 μ with a geometric standard deviation of 1.4. The collection efficiency was determined using both a Thermo System Inc., Mass Monitor 3200 A and the Andersen impactors. The higher Richmond test efficiences reflect the use of a somewhat larger grade of sand, and hence a bed that was incipiently fluidized.

Discussion

The tests show that the EFB provides a viable and perhaps uniquely attractive solution to the asphaltic smoke cleanup problem. High submicron collection efficiency is combined with the unique material handling capability of collecting the oil droplets on sand and then making the oily sand a part of the product. For other applications, reprocessing of sand outside of the collection device should prove to be a more attractive alternative than trying to remove the material from plates or separating the material from an excessive volume of water.

From the experience gained with the 400 cfm prototype EFB, a 35 000 cfm unit has been designed for the conversion of a full-scale asphalt plant to recycling. This bed is designed to operate with fresh sand continuously introduced at the top and dirty sand overflowing out through the center. It is anticipated that the sand will have to be cycled once for each 50 h of plant operation; consequently, fresh sand will be fed at a rate of 80 lb/h. Different modes of asphalt plant operation could create higher pollutant levels which would dictate that the sand be cycled proportionately faster.

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CORRESPONDENCE

SIR: Photochemical reactivity of volatile organic compounds has been measured by a number of parameters, chief among which has been total oxidant or maximum oxidant produced in smog chamber experiments. While secondary effects of photochemical smog such as visibility reduction, eye irritation, and plant damage have also been used in reactivity comparisons, oxidant has retained primary interest because of its direct relation to human health effects.

Weinstock et al. (*1*) demonstrated the key role of hydroxyl radicals in smog chamber reactions, and Pitts et al. (*2, 3*) proposed a five-category photochemical reactivity classification based upon hydroxyl reactivity. Pitts and coworkers measured the relative rates of reaction of hydroxyl radicals with a large number of organic compounds and published the resulting rate constants. These covered a range of five orders of magnitude, hence the proposed five-category reactivity classification. This sound technical approach relates closely to oxidant production from the same organic compounds, as discussed below.

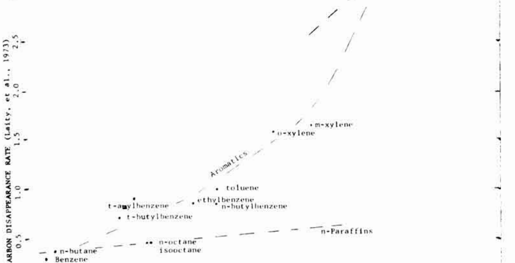

Figure 1. Hydrocarbon disappearance vs. oxidant maximum

However, before discussing the relationship between hydroxyl reactivity and oxidant production, a few observations need to be made about hydrocarbon disappearance rate. While Pitts and coworkers (*2, 3*) implied a relationship between hydroxyl reactivity and hydrocarbon disappearance rate, this has not been borne out by data from our earlier work (*4*). We measured disappearance rates for hydrocarbons and other volatile organic compounds in smog chamber studies but showed no particular relationship with oxidant formation. A recent plot of these hydrocarbon disappearance rates vs. oxidant maxima from the WOGA reactivity classification (*5*) shows a wide scatter of the data (Figure 1). However, closer examination according to class of compounds shows a wide variation between paraffinic, aromatic, and olefinic hydrocarbons. Aromatic hydrocarbons show the best correlation with oxidant maxima, and paraffins the worst. Figure 2 compares hydroxyl reaction rates (*6*) with hydrocarbon disappearance rate. Again, different correlations are apparent for paraffinic, aromatic, and olefinic hydrocarbons. It seems that this evidence would indicate that mechanisms in addition to hydroxyl radical attack are involved, viz., one each for paraffinic, aromatic, and olefinic hydrocarbons. Further studies of the mode of attack by hydroxyl radicals seem to be indicated.

However, when hydroxyl reaction rates are compared with oxidant maxima (WOGA reactivity classification) (*5*), reasonably good correlation is obtained with all three hydrocarbon classes (Figure 3). Only relatively unreactive ethane and very reactive 2,3-dimethyl-2-butene are significant outlyers.

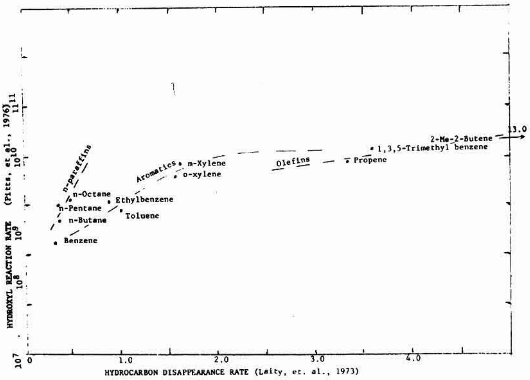

Figure 2. Hydroxyl reactivity vs. hydrocarbon disappearance

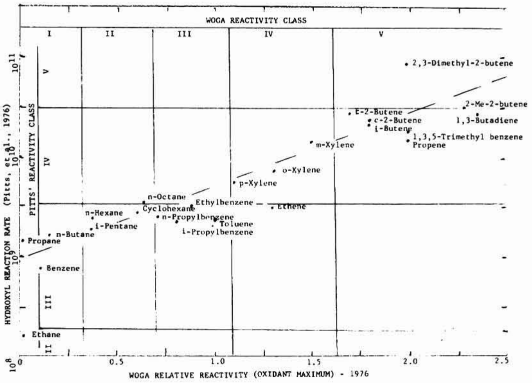

Figure 3. Hydroxyl reactivity vs. oxidant maximum

With methane as the only hydrocarbon in Class I, ethane and acetylene as the only hydrocarbons in Class II, and a few reactive olefins in Class V, the hydroxyl reactivity scale of Pitts and coworkers compresses nearly all hydrocarbons that have any practical use as solvents or liquid petroleum products into only two classes, namely, Class III and Class IV (Figure 3).

When the product of photochemical reactivity, namely, oxidant, is taken as the indicator of photochemical reactivity, the five-category WOGA classification results (*5*) as shown in Figure 4. The WOGA reactivity classes are also shown in Figure 3.

In both reactivity classifications there is a 100-fold range of reactivity from butane to 1,3-butadiene. For regulatory purposes, reactivity classifications should be designed to give the maximum practical usefulness in terms of optimization of control strategy trade-offs. Such trade-offs between consumer products (organic compounds) of widely varying reactivities could be used to reduce oxidant formation and thereby improve air quality. A subdivision of this 100-fold reactivity range into five classes as proposed by WOGA allows such flexibility in trade-offs and in substitution of one consumer product by another of lower reactivity, with resultant improvement in air quality.

Compression of this 100-fold range of reactivity into two classes, as in the Pitts classification, destroys much of the practical usefulness of a reactivity classification and severely limits flexibility of trade-offs between practical organic liquids of high and low photochemical reactivity. The Pitts classification could be made more useful by subdividing Classes III and IV, without changing its technical validity.

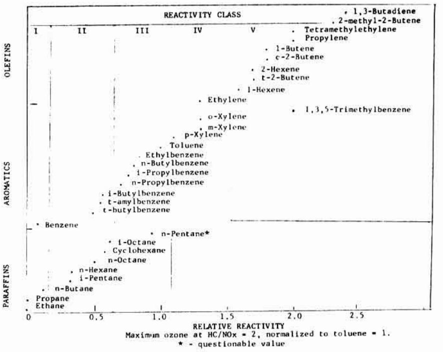

Figure 4. Relative reactivity of hydrocarbons

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SIR: We have been interested in relationships between "hydroxyl (OH) reactivity" and oxidant-forming potential since first proposing a hydrocarbon reactivity scale based on rate constants for the reaction of OH with organics (*1–3*). Thus, the correlation between OH rate constants and oxidant maxima shown in Figure 3 of the preceding letter by Farley is of interest with respect to its potential as a predictive indicator of oxidant-forming potential. There are, however, a number of issues raised in the preceding letter which we wish to clarify.

Regarding our published work on hydrocarbon reactivity and OH rate constant determinations, it should be pointed out that our reactivity classification (*3*) includes the available room temperature OH rate constants for organics determined not only by relative rate techniques, but also by absolute methods. In our relative rate studies, we have not *implied* a relationship between "hydroxyl reactivity" and hydrocarbon disappearance rate as stated by Farley, but have in fact *obtained* the OH rate constants from the measured hydrocarbon disappearance rates and the use of a reference compound whose absolute rate of reaction with OH had been measured previously. Thus, as pointed out in each of our reports of OH rate constant determinations (*4–9*), the assumption that, under our experimental conditions, hydrocarbon disappear-

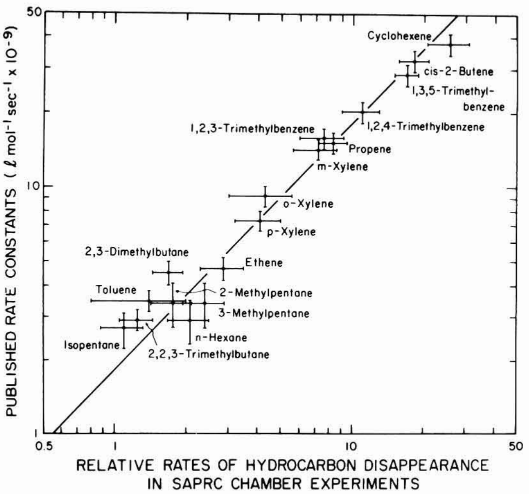

Figure 1. Comparison of relative rates of hydrocarbon disappearance determined in SAPRC all-glass environmental chamber (*4–9*) (relative to *n*-butane = 1) with published rate constants for reaction of hydrocarbons with OH radicals (line shown represents one-to-one correspondence and has slope of 1.8 × 10^9 L mol^{-1} s^{-1})

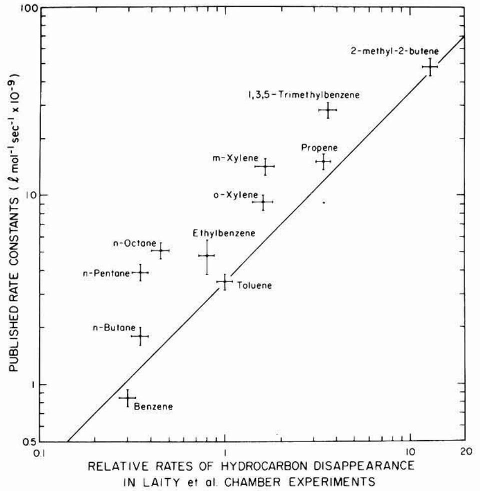

Figure 2. Comparison of relative rates of hydrocarbon disappearance determined in Shell environmental chamber by Laity et al. (*10*) (relative to toluene = 1) with published rate constants for reaction of hydrocarbons with OH radicals (line shown represents one-to-one correspondence and has slope of 3.6 × 10^9 L mol^{-1} s^{-1})

ance rate was directly proportional to rate of attack by OH was fundamental to our relative rate studies and not just an "implication". This assumption has been validated by the generally excellent agreement of our relative rate constants with those obtained by absolute methods (*4, 5, 8*).

Farley's conclusions (see Figures 1 and 2 in his letter) that correlations between hydrocarbon disappearance rates [from the earlier smog chamber studies of Laity et al. (*10*)] and either OH rate constants (i.e., "hydroxyl reactivity") or oxidant formation are a function of hydrocarbon class must be seriously questioned: (a) these conclusions are based on a very limited data set; (b) the experimental uncertainty in the hydrocarbon disappearance rate data is not discussed; (c) the extended extrapolation shown for the paraffins and the olefins does not appear justified on the basis of the very limited number of data points for these two classes of compounds. If one ignores the dashed lines and draws a best fit line through the data in Figures 1 and 2 of the preceding letter, there is a rough proportionality between hydrocarbon disappearance rate and either oxidant maxima or OH rate constants, with about the same scatter as in Farley's Figure 3.

For comparison with Farley's Figure 2, we present a plot of normalized hydrocarbon disappearance rates from our studies vs. published OH rate constants (Figure 1). There is good correlation independent of compound type with the greatest (but random) scatter associated with the relatively unreactive alkanes. In our studies the rates of disappearance of the hydrocarbons of interest were measured relative to that of a compound with a known absolute OH rate constant (internal standard) so that our results were independent of the actual OH radical concentration, both within an experiment and from experiment to experiment. In contrast, it is our understanding that Laity et al. (*10*) measured rates of disappearance of a single hydrocarbon (and the corresponding oxidant formation) in each experiment and that they interspersed toluene runs throughout their experimental program against which they could "normalize" their data.

Strictly speaking, one cannot justify plotting the disappearance rates vs. OH rate constants of Laity et al. unless the OH radical concentration was the same in each and every one of their experiments. However, we have (*7, 9*) used hydrocarbon disappearance rates reported by Laity et al. (*10*) to calculate OH rate constants and in several cases obtained values which appeared reasonable or were in rough agreement with our rate constants or those from other laboratories. This suggests that in their chamber the OH concentration may have been more dependent on wall effects and/or NO_x concentrations than on the compound under test.

On the other hand the extent to which (a) the OH radical concentration may *not* have been constant in a number of Laity et al. runs or (b) other experimental factors influenced their hydrocarbon disappearance rates is suggested by Figure 2 which shows their hydrocarbon disappearance data (*10*) (with their estimated uncertainty of ±10%) plotted against the literature OH rate constants. As seen from Figure 2, for the limited number of compounds where comparison was possible, the relative rates derived from the data of Laity et al. are generally low, sometimes very substantially so with respect to the published OH rate constants. One is forced to conclude that the use of periodic toluene experiments by Laity et al. to "normalize" their data with respect to dirty chamber effects and trends in chamber reactivity was not wholly successful.

The conclusion of Farley that different correlations between hydroxyl reaction rate constants and hydrocarbon disappearance rate occur for paraffinic, aromatic, and olefinic hydrocarbons is arguable from another point of view. Our understanding of the chemistry of smog formation has greatly increased during the past decade; in particular, the crucial role of the OH radical as the primary chain carrier in the atmosphere has been well characterized. Thus, both modeling and experimental (laboratory and chamber) studies have shown that in the case of alkanes and aromatics, OH is by far the dominant species responsible for consumption of these compounds. Even when concentration differences are taken into account, species such as O_3, HO_2, $O_2(^1\Delta)$, and $O(^3P)$ have rate constants that are too low for them to contribute significantly to the consumption of alkanes and aromatics. This generally also applies in the case of alkenes except that O_3 can, at ambient levels, compete approximately equally with OH in consuming olefinic compounds. Thus, Farley's suggestion that additional species contribute to the consumption of hydrocarbons (and different species for each class of hydrocarbons at that) is unwarranted based on the data he cites and is completely contrary to our present understanding of the chemical transformations in photochemical smog.

With regard to Farley's concern (in paragraphs 5, 7, and 8 of his letter) about the compression of most commercially important hydrocarbons into two classes in our five-class scale, he failed to note that a major point made in our papers (*1–3*) was the option of dividing our OH reactivity classification into as many classes as desired up to, in the extreme, a class for each compound. This was put forward as a significant advantage and is possible in our scale since it is based on OH rate constants of generally high accuracy (relative to measurements of secondary smog manifestations such as ozone maxima), and one can rank compounds with very good resolution (i.e., within the experimental uncertainty of the data). Thus, one need merely consult Table 3 in ref. *3* to obtain a completely subdivided (i.e., rank ordered) reactivity scale for 113 compounds. As we have made quite clear in our reports, the five-class scale published was only one possible subdivision that happened to correspond to the five orders of magnitude in rate constants of the compounds included in our scale.

Finally, Farley does not deal with the more substantive issue of the general validity of basing assessments of oxidant-forming potential on rates of reaction of organics with OH. Thus, while the rough correlation between oxidant maxima and OH reactivity evidenced in Farley's Figure 3 is encouraging, as we have pointed out previously (*1–3*), OH reactivity may or *may not* be a reliable indicator of oxidant-forming potential depending upon the specific chemical mechanism following OH attack on a given hydrocarbon. For example, in general, the OH scale would be expected to overpredict oxidant formation from higher alkanes since, as we have shown, these undergo radical isomerization that reduces the production of chain-carrying free radicals (*11*). Similar considerations undoubtedly apply to other classes of compounds.

Clearly, the ultimate utility of the OH reactivity scale to practical control strategy decisions will depend upon obtaining as complete an understanding as possible of the reaction pathways leading from initial OH attack to the formation of ozone for the various classes of organic compounds.

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Riverside, Calif. 92521

ES&T
INDUSTRY TRENDS

Peabody Air Resources Equipment Co. will engineer/install a 3-module electrostatic precipitator to handle 85 000 cfm of emissions at U.S. Steel's Texas works at Baytown.

American Ceca Corp. (Oak Brook, IL) has a turn-key contract for a 70 000-cfm solvent and heat recovery plant at World Color Press. Together with a 140 000 cfm facility Ceca previously built there, this plant will be one of the U.S. largest.

Envirex Inc., a Rexnord company, will manufacture/market a line of filter presses, under license agreement, for NGK Insulators, Ltd. (Nagoya, Japan), which Envirex considers to be "best available technology" in its field.

The National Association of Metal Finishers has moved from New Jersey to Chicago, IL.

General Electric (Schenectady, NY) has received a $5.98 million contract from the Dept. of Energy to develop and construct two experimental 4-passenger electric automobiles, together with Chrysler Corp.

Public Service Electric & Gas Co. (Newark, NJ) broke ground at Hillsborough Township, NJ for a national facility to test "futuristic" batteries for electric power systems that could cut consumer costs, and save up to 1 million bbl/d of oil.

Olin Corp. (Stamford, CT) announced that its "Solar-Bond" copper absorber plates collect the same solar heat with 12.5–33% less collector area, thanks to a new design.

Biospherics Inc. (Rockville, MD) has opened a special laboratory to provide pesticide analytical services to industry and government.

Stone & Webster Engineering Corp. has a $511 000 ERDA contract to study large subterranean salt domes at storage sites for commercial nuclear power plant wastes.

AG Brown, Boveri & Cie (Switzerland) is offering an electron irradiation process as a hygienization method to make sewage sludge usable for agriculture.

WAPORA, Inc. (Bethesda, MD) is acquiring Enviro Audits, Inc. (Roanoke, VA). The acquired firm specializes in regulatory services, environmental studies, and related activities.

Leeds & Northrup Co. has received a NIOSH contract to develop an automated fiber-counting instrument for analyzing worker exposure to fibrous aerosols, especially asbestos. Fibrous glass and mineral wool will also be analyzed.

Pope, Evans and Robbins (New York, NY) and Stone & Webster Engineering Corp. now have a jointly-owned subsidiary, AFB Combustion Associates, Inc., to market engineering, consulting, and construction services in atmospheric fluidized-bed combustion.

Autotrol Corp. (Milwaukee, WI) was successful bidder for the supply of secondary wastewater treatment equipment to the City of Guelph, Ontario, Canada.

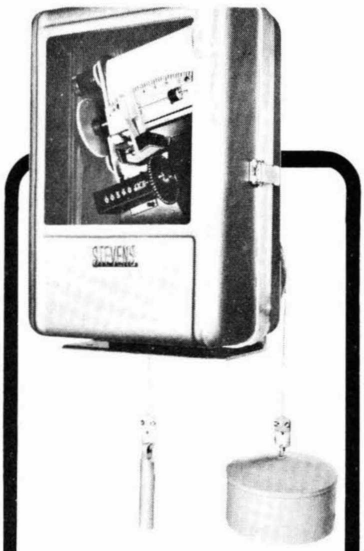
General Public Utilities Corp. (Parsippany, NJ) announced the dedication of an advanced coal cleaning plant at Homer City, PA (*ES&T*, December 1977, p 1148).

Stauffer Chemical Co. (Westport, CT) will build an environmental health center for environmental and biomedical studies of company products. The center, at Farmington, CT, is to be completed in spring, 1979.

American Air Filter Co., Inc. is supplying 7 "Roto-Clone" wet collectors to control lignite-handling dust from 560 tph at Texas Utility Co. System. Total air cleaning capacity could exceed 100 000 cfm.

Dorr-Oliver Inc. is providing disc filters to Raccoon-Elkhorn Coal Co. (Pikeville, KY) to recover fines that are normally lost in coal washing effluent.

Matthey Bishop, Inc. (Malvern, PA) says that per-pound costs for re-



claiming spent platinum catalysts have remained stable despite inflation.

Frost & Sullivan, Inc. estimates that pollution control over the next 8 years in South Africa will be a more than $700 million market.

Arthur Technology (Fond du Lac, WI) is the new name of Arthur Bros. Co., Inc., maker of highly technical wastewater treatment plant operation and control equipment.

ITT Rayonier Inc. has installed new "Aqua-Chem" systems in its pulp/paper mills at Hoquiam, WA, Jesup, GA, and Fernandina, FL. The systems recover chemical values that can be, and are marketed.

Varian Associates (Palo Alto, CA) has a $1 million order for an automatic chromium plating system for lightweight plastic. The system cuts plating cost by 50%, saves 30% of energy, and is non-polluting, according to Varian.

Enviro Development Co., Inc. (Mountain View, CA) will supply three Archimedean Screw Pumps for the Ina Road Water Pollution Control Facility of Pima County, AZ.

The Fluid Systems Division, UOP Inc., has more than $250 000 worth of contracts from Texas Instruments Inc., and Warren Petroleum Co., to expand their water purification systems.

Gilbert/Commonwealth (Jackson, MI) has a $102 000 contract from the Federal Insurance Administration to do an 18-mo flood elevation study for evaluation of flood hazard areas in several Michigan counties.

EG&G Inc. (Wellesley, MA) has a NASA contract to analyze radar altimeter data from the GEOS-3 satellite to evaluate the current state of the earth's polar ice cover.

Mitsubishi Heavy Industries, Ltd. and other Japanese firms have signed a contract to build Phase I of the al-Jubail Desalination Plant to make 136 400 tpd of water in Saudi Arabia.

WAPORA Inc. (Chevy Chase, MD) has opened a new branch office in Atlanta, GA, and a new analytical chemistry laboratory in its branch office at Cincinnati, OH.

The **Air Pollution Control Division of Wheelabrator-Frye Inc.** has an approximately $3.8 million order for a dust collection system (fabric filter) for Southwestern Public Service Co., at Amarillo, TX.

The Babcock & Wilcox Co. received a $35 million contract for a radiant boiler, precipitator, and flue gas scrubber from the Board of Municipal Utilities of Sikeston, MO. The units will handle 235 MW.

Reynolds Aluminum Recycling Co. said that it has paid the public more than $16.6 million for a record 98 million lb of aluminum recycled from last January through September. More than 50% of the aluminum cans Reynolds made during that period were recycled.

J. F. Pritchard and Co. (Kansas City, MO) will provide process design, detail engineering, and supply of certain equipment for NO_x abatement for a nitric acid plant of Fertilizantes de Centro America (Costa Rica) S.A.

Zurn Industries, Inc.'s Cooling Tower Division has received a Tennessee Valley Authority contract for $71.7 million—the largest ever let for cooling towers by TVA—for 6 natural-draft cooling towers for nuclear plants.

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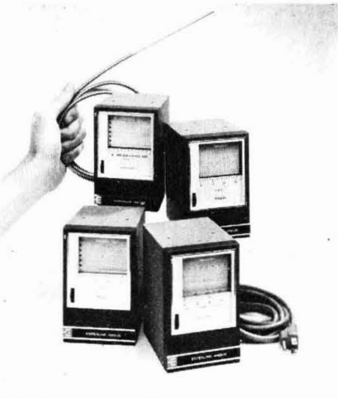
This bacteriologically based product biodegrades hydrocarbons in salt water. It can be used to clean up oil spills, tanker ballast and bleedwater without harming the environment, claims the manufacturer. Natural Hydrocarbon Elimination Co. **101**



Miniature recorders
Three recorders are available—an events, temperature and analog recorder. Each offers inkless recording and a choice of 70 chart speeds. Sensitivities as low as 10 microamps dc are possible. Esterline Angus Instrument Co. **102**

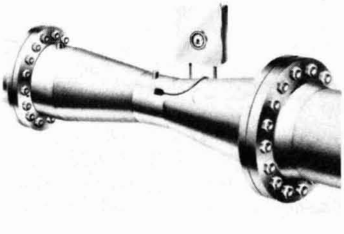
Ultrasonic liquid level switch
The switch features a crystal-activated sensing system that reacts to contact with liquids by tripping a relay switch. The sensor, available in any desired length, can be mounted in any type of vessel either horizontally or vertically. The sensor can be used at temperatures from −40 to 80 °C. The switch has a 10 amp rating at 110 or 220 V dc. Rexnord Instrument **103**

Water quality monitoring system
The system's main feature is a self-contained digital magnetic tape recorder. The instrument can be programmed to record up to 8 environmental parameters at time intervals from less than 2 s to up to one set per hour. InterOcean Systems **104**

In-stack particulate sampler
The sampler is a thimble holder with a built-in after filter. The holder and filter feature no-gasket tapered seat seals that eliminate the temperature constraints of older filter designs. GII Enterprises **105**

Fluorescence detector
This continuously variable wavelength detector is designed for liquid chromatography. The unique design feature, according to the manufacturer, is a 2π steradian cuvette design (5 μL) that enables light to be collected from weak fluorescing signals emitted from minute samples. Schoeffel Instruments **106**

Sludge solvents
The solvents, emulsifiers, dispersants and rust inhibitors are designed to clean and condition fuel oil tanks. Regular treatment of the tanks prevent formation of sludge. The Rolfite Co. **107**



Flow meter
The device for water and wastewater applications consists of a non-invasive, ultrasonic flowmeter combined with a standard venturi tube. A sensor or transducer is mounted on the outside of the venturi and connects via cable to the indicator/transmitter totalizer in a weatherproof enclosure. Tech Tube Corp. **110**

Auto sequencer system
The units provide automatic hardware control of the company's GC/MS instruments. The system directs the

measurement and injection of samples into the GC/MS system. Up to 60 samples can be run unattended. Finnigan Instruments **108**

Compactor for radioactive wastes
It is suitable for disposing of hazardous, low-level radioactive waste materials. The compaction chamber size permits compaction within 55-gal drums. The full drum can then be covered, sealed, weighted and disposed of. Total height is 10 ft and width in 39 in. S&G Enterprises **109**

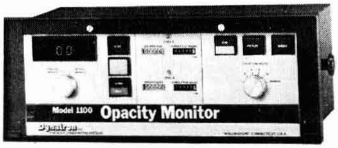
Aquatic weed harvester
The harvester consists of a harvesting module, a flat-decked pontoon boat and a propulsion unit. The harvester cuts a path 5-ft deep and 4-ft wide; the cut weeds are conveyed to the deck, and are not allowed to float free. It is adaptable to small lakes and waterways. Aquamarine Corp. **111**

Semicircular chart recorder
This recorder will monitor viscosity and records values on a 6-in. circular chart that rotates in two planes to conserve panel space. High and low alarms are features of the recorder. Norcross Corp. **112**

IR detector
The pyroelectric IR detector consists of a sensing element and an input current mode amplifier with an integrated high-megohm feedback resistor. The mode amplifier functions as a high gain current to voltage converter. The sensing element and electronics are electrically floating within the hermetically sealed detector housing. Eltec Instruments **114**

Turbidimeter
The unit is a direct reading, solid-state instrument that meets EPA requirements. Accuracy and reproducibility are ±2%, sensitivity is ±0.05% and response time is less than 5 s. Sargent-Welch Scientific **113**

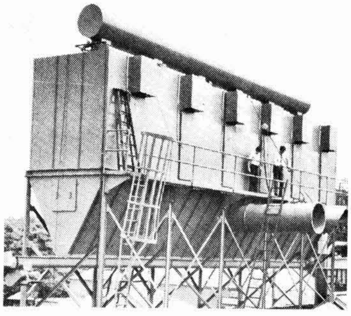
Data logger
The microprocessor-controlled loggers feature remote programming, expanded inputs and new alarms. John Fluke Manufacturing Co. **115**



Opacity monitor
The system meets EPA compliance requirements for a variety of industrial emission sources. The unit features a solid-state zero and span check system such that calibration is automatic and continuous. Data are in the form of opacity or optical density. Dynatron Inc. **116**

Submersible pump motor
The motor operates underwater next to the pump, not on the surface. These motors range in horsepower from 0.5–1000, and can be used in depths of 1000 ft or more. The smallest unit has a 3.5-in. diameter, and the largest, a 30-in. diameter. Melco Sales **117**

Sound level meter/microprocessor
The portable kit includes a sound level meter that measures and displays "A" weighted sound amplitude level over a 64 dB range. The microprocessor cal-

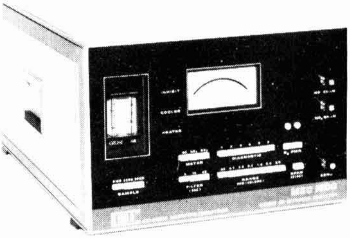


culates and displays L_{eq}, maximum sound level sampled and total test duration. Metrosonics **119**

Diaphragm pump
The high-pressure, high-volume pump is available in capacities up to 130 gph and pressures to 3500 psi. The capacity is adjustable by using the micrometer dial. Discharge and suction valves are removable for cleaning. Neptune Chemical Pump **120**

Heat recovery unit
The unit is a self-contained exhaust/make-up air system that incorporates a counterflow heat recovery cell that recycles up to 70% of the exhausted heat back to the building. Allied Air Products **121**

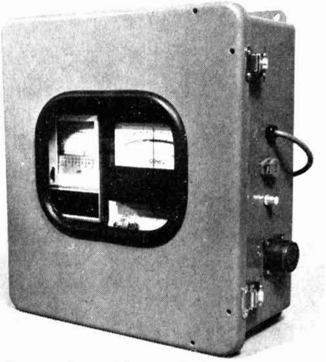
Combustible gas detector
The hand-held, battery-powered device detects the presence of a combustible gas and sounds an alarm. Sensor life exceeds 6000 h, according to the manufacturer. Anacon **122**



NO_x analyzer
The instrument measures ambient levels of $NO/NO_2/NO_x$ from 0–50 ppb to 0–5 ppm. According to the manufacturer, a novel feature is a high speed, pneumatically chopped NO/NO_x signal that permits accurate measurements of NO_2 in the presence of rapidly changing NO_x levels. McMillan Electronics **123**

Diversion barriers
These floating barriers, consisting of 6-in. or 18-in. flotation members, control the water flow in settling ponds/waste ponds and lagoons. The barriers are designed to resist a wide range of corrosive chemicals. Slickbar **124**

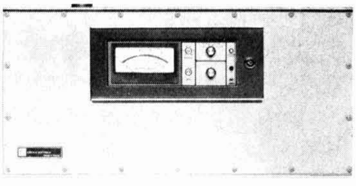
Digital-to-analog converters
The converters are available in 8- and 10-bit resolution versions with a choice of three output voltage ranges: 0–10 V (unipolar); 0 to ±5 V, and 0 to ±10 V (bipolar). Each model consists of a precision reference, a stable thin-film nichrome resistor network, output amplifier and switches. Hybrid Systems **125**



Process recorder/controller
This pH metering system is designed for monitoring pH whenever a permanent record and control function feature are required. The model is a combination automatic strip-chart recorder and line-operated indicating controller. Kernco Instruments Co. **126**

Filter bags
The Teflon fiber bags are resistant to chemicals across the entire pH range, are heat resistant up to 500 °F and are resistant to flex degradation. Because they have a low coefficient of friction, filter cake release is enhanced. P & S Textiles **128**

Cyclone preseparator
The model attaches to in-stack cascade impactors to collect particles larger than 5 μ in size. This miniature model, only 1⅝-in. in diameter, is constructed of stainless steel. Sierra Instruments **129**



Suspended solids monitor
Designed for process and waste treatment applications, the instrument automatically and continuously monitors suspended solids in a liquid stream. Measurement is linear and independent of the size distribution or color of the sample. Leeds & Northrup **127**

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ES&T
LITERATURE

SO_2 scrubber design. Publication RC 1205 discusses various types of scrubbing systems and their merits, and single-loop and multi-loop processes, sludge generated, and the like. Research-Cottrell **151**

Chrome recovery. Case history, "Recovers 80 Pct of Chromium Solution", tells how evaporative recovery helps to reclaim 80–85% of chromium plating chemicals (*ES&T,* August 1977, p 752). Corning **152**

Solar energy. Bulletins C-103, CP353, and CP-354 describe "teflon"/"tedlar" glazing for panel solar collectors, which improves efficiency. Chemplast, Inc. **153**

Oxygen transfer costs. Updated tables detail relationship of oxygen transfer efficiencies to wastewater treatment costs. Hinde Engineering Co. **157**

Drinking water test. Brochure, "The Complete Wateraction Set", describes field testing kit for potable water. Kit is self-contained and portable. Bausch & Lomb **154**

Filtration. Form No. 179-ADV describes upflow filtration system for removing suspended solids from water, wastewater, and other fluid streams. Flow 0.01–11 million gpd. Zurn Industries, Inc. **156**

Field and lab supplies. Winter catalog lists water test kits, pH meters, pumps, and many other items for environmental lab and field work. Horizon Ecology **158**

Sludge recycling. Booklet tells how to minimize sludge disposal through production of dry pellets, which are very compact. Much energy can be saved. Organic Recycling, Inc./UOP **159**

Leak detectors. Brochure, "Du Pont Leak Detection Systems," explains how sensitive equipment can detect/measure leaks. Leak analysis is fast. Du Pont **160**

Scrubber reagents. Dissertation RC 1204 discusses relative advantages of lime and limestone as flue gas desulfurization scrubber reagents. Costs can be compared. Research-Cottrell **161**

Gas analysis. Brochure describes company's "Dynacalibrator" line of gas analyzer calibration instruments. These different models are listed/described. Metronics Associates, Inc. **162**

Solvent recovery. Brochure is condensed catalog that lists equipment for solvent recovery, pilot units, lumpbreakers, self-cleaning feeders, and "cleanable" observation ports. Wyssmont Co., Inc. **163**

Nuclear gaseous waste. Brochure, "Dynamic Adsorbtion" (sic), offers practical solution to gaseous waste-management problems for various nuclear plant applications. CTI-Nuclear, Inc. 155

Screening/filtration. Brochure describes synthetic and metallic media for filtration and screening. Filter media, fabrics, screen cloth, and wet/dry applications are covered. Jelliff Corp. 164

Dredged material. Brochure, "Analysis of Dredged Material", talks about laboratory procedures for determining potential impacts of dumped sediment on the marine environment. United States Testing Co., Inc. 165

Sludge dewatering. Brochure highlights innovations in filter press technology which focuses on improved, energy-efficient, economical methods of sludge dewatering. Enviro Development Co., Inc. 166

Fabric filters. Brochure APC-11 examines company's expertise in dust collection, ductwork, hot gas handling and cooling for custom fabric filter systems. Working examples are given. Wheelabrator-Frye 167

Baghouse monitoring. Applications Note EID-3 describes baghouse monitoring by a method that detects particulates by surface ionization. Extranuclear Laboratories, Inc. 168

Solar energy. Brochure discusses solar energy engineering, research, and testing for heating/cooling and power generation. Wyle Laboratories 169

pH meter. Bulletin 1110-EC-10T describes multi-purpose instrument to measure pH, dissolved or gaseous oxygen, temperature, or conductivity. Environmental monitoring applications. Beckman Instruments 170

Applying pesticides. TART/TIGA Agricultural Applicator Brochure covers application and values of fungicides, insecticides, herbicides, and desiccants, and how to use on a very economical basis. Available in English, Spanish, Portuguese. Tifa Ltd. 171

Landfill operations. Bulletin 5388-Sept. 1977 describes Rex Trashmasters, specifically designed for landfill operations. Rexnord 172

Modeling. Brochure outlines uses of mathematical models in predicting air/water quality impact of new and existing facilities. Modeling results are discussed. TRC 173

Pesticide analysis. Newsletter, "Pesticide Notes", offers many guides to precise pesticide analysis and EPA compliance monitoring. Waters Associates 174

Ozone generation. Brochure DB 195 concisely, but completely provides an explanation of how ozone is generated in company's equipment. Infilco Degremont, Inc. 175

Double-alkali FGD. Bulletin 25300-A, "Boiler Emissions Control", tells about the company's double-alkali flue gas desulfurization (FGD) system, and its installation (250 MW) at a public utility. Sodium is a key to how it works. FMC Corp. 176

GC/MS "software". Technical papers 23-5952-5865 through 5867 describe gas chromatography/mass spectrometry (GC/MS) computer programming "software" for easy programming. A pollution library is included. Hewlett-Packard 177

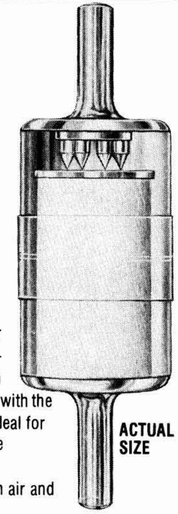
Water services. Booklet, "Municipal & Industrial Services", cover water/wastewater treatment and supply services and consulting offered. "Bio" sketches of key people are given. York Research Corp. 178

Rotary screen. Bulletin RS-1101 describes rotary screen for wastewater, food processing, pulp/paper, sludge dewatering, and other applications. It is self-cleaning. Hycor Corp. 179

Mist eliminators. Bulletin No. ETS-2 details uses of high-performance mist eliminator units for low-cost removal or recovery of condensates from gas streams. Removal of 99.9%, and of drop sizes to 1 μ, is possible. Munters Corp. 180

Fume scrubbers. Brochure describes fume scrubbers with sizes/capacities of 400–70 000 cfm. Packed-tower, water jet eductor venturi, and cross-flow is used for energy. Ajax Electric Co. 181

Benzene in gasoline. Publication, "Current Peaks", describes GC that



automatically measures benzene concentration in "gas". Toluene can also be singled out. Carle Instruments, Inc. **183**

Sewage treatment. Bulletin ST-A7 lists extended aeration-type packaged sewage treatment plants, 325–12 500 gpd, recently certified by the National Sanitation Foundation. Demco Inc. **184**

Sugar refinery effluent. Brochure describes unique wastewater treatment system that removes more than 98% of BOD from sugar refinery effluent, as well as suspended solids and ammonia. Activox Inc. **185**

OSHA inspection. Checklist helps laboratory personnel prepare for OSHA inspection. Lab Safety Supply Co. **186**

Ammonia filter. Bulletin pinpoints benefits that ammonia filter can confer on nitric acid operations. Submicron particle collection efficiency approaches 99.5%. Monsanto Enviro-Chem. **187**

Smoke suppression. Bulletin 352 describes automatic control system for complete combustion/smokeless flaring. Stack is monitored. National AirOil Burner Co., Inc. **188**

Process alarms. Technical Bulletin describes the "Pa-11 SOR", a process monitor that detects and warns of off-normal events to a resolution of 1 millisecond. Process Automation Co. **189**

Oceanography/limnology. New 1977 catalog lists more than 110 products for oceanographic/limnlogic work of many kinds. InterOcean Systems, Inc. **192**

Dust filter media. Brochure WWC-1 offers a problem-solving approach to dust collector filter media. There is a comprehensive guide to filter fabric and design. Wheelabrator-Frye **197**

Air pollution. Qualified requesters can receive aid for literature searches in air pollution. EPA Library (MD-35), Research Triangle Park, NC 27711 (write direct).

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.

Radioactive waste. The dilemma of its safe disposal. Report EMD-77-41. Comptroller General of the United States, Washington, DC 20548 (write direct).

Sludge disposal. Cost-effective sludge disposal is subject of a study, "Economics of Municipal Sludge Disposal". WWEMA, 7900 Westpark Drive, Suite 304, McLean, VA 22101 (write direct).

Oil spillages. Report covers cross-country pipeline oil spillages in Western Europe. Stichting CONCAWE, van Hogenhoucklaan 60, The Hague 2018, The Netherlands (write direct).

"Bottle bills". Publication tells how container legislation cuts waste. Single copies. National Wildlife Federation, 1412 16th St., N.W. Washington, DC 20036 (write direct).

Organics in water. Technical Paper No. 9 tells how they affect health. WHO International Reference Center for Community Water Supply, P.O. Box 140 2260 AC, Leidschendam, The Netherlands (write direct).

Solar engineering. "Solar Engineering Directory". First of its kind. American Consulting Engineers Council, 1155 15th St., N.W., Washington, DC 20005 (write direct).

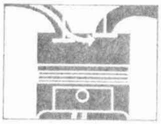
Labware. Catalog lists complete line of "Teflon" labware, pickling vats, high-pressure autoclaves, and digesters. Berghof/America, Inc., Bend, OR 97701 (write direct).

Environmental services. Publication fully describes company's services to local, state, federal, and foreign governments. "Our Services Make a World of Difference". Metcalf & Eddy, Inc., 50 Staniford St., Boston, MA 02114 (write direct)

Coal and health. September 1977 issue of *EPRI Journal* has article on how coal-fired power plants affect air and human health. Pat Streib, EPRI, P.O. Box 10412, Palo Alto, CA 94303 (write direct).

Asbestos analysis. New procedure defines analytical reference technique for asbestos, and can help to implement current and future regulations. Dr. Jack Wagman, EPA Environmental Sciences Research Laboratory, Research Triangle Park, NC 27711 (write direct).

Approaches to Automotive Emissions Control



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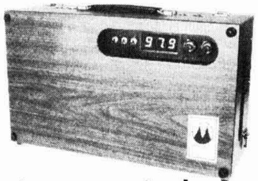

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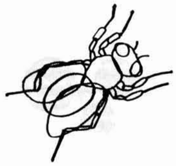
Mechanism of Pesticide Action



As a timely state of the art, this authoritative guide takes a rigorous look at the complex interactions between organism, host plant, environment, and improved pesticidal composition.

ACS Symposium Series No. 2

G. K. Kohn, *Editor*

A symposium sponsored by the Division of Pesticide Chemistry of the American Chemical Society.

Fourteen papers take a three-faceted approach in discussing current research on the mechanism and metabolism of broad groups of pesticides, activity relationships of specific pesticides, and analysis of cellular and model systems:

- cholinesterase inhibitors; metabolism in insects; herbicide-lipid interactions
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- insect sterilants; pyrethroids; chlorella as a model for herbicide study

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ES&T BOOKS

Environmental Policies in Developing Countries. Raymonde Gour-Tanguay, Ed. vii + 706 pages. Erich Schmidt Verlag, D-1000 Berlin 30, Genthiner Strasse 30 g, Berlin, German. 1977. DM 48 (about $21.15), paper.

What are environmental policies in Afghanistan? Zaïre? Ivory Coast? This book lists them with respect to air, water, noise, flora/fauna, and other such concerns. Many related topics are also covered.

Solar Heating Design. William A. Beckman, Sanford A. Klein, John D. Duffie. xv + 200 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1977. $14.95, hard cover.

This book looks at common types of solar heating systems designable by the "f-Chart" method. It also covers thermal performance, effects of collector orientation, estimating heating loads, and best use of fuel and system cost information. "f-Chart" design procedure is also discussed.

Origins of Pest, Parasite, Disease and Weed Problems. J. M. Cherrett and G. R. Sagar, Eds. x + 413 pages. Halsted Press, 605 Third Ave., New York, NY 10016. 1977. $35, hard cover.

This volume covers the origins of pest, parasite, plant disease, and weed problems, and explores ways in which future problems might arise. Not only origins of causative organisms, but also origins of problems themselves are discussed. New problems, and ways of preventing problems from arising are also examined.

Marine Natural Products Chemistry. D. J. Faulkner, W .H. Fenical, Eds. x + 433 pages. Plenum Publishing Corp., 227 West 17th St., New York, NY 10011. 1977. $42.50, hard cover.

So halogenated organics in the sea are the result of human activity at all times? Maybe not (*ES&T,* May 1977, p 442). Certain marine organisms create these compounds with no precursors of human origin, whatever; yet, they can be "pollutants." This book explains how these, and many other chemicals are formed in the sea, their behavior and fate, possible uses to man, and activity in the marine ecosystem.

Mathematics of Environmental Processes. Thomas D. Waite, Neil J. Freeman, xiv + 170 pages. D. C. Heath and Co., 125 Spring St., Lexington, MA 02173. 1977. $18.95, hard cover.

Not all environmental science is inexact; many aspects involve some very precise mathematics. This book offers the necessary mathematical information necessary to build a base of knowledge applicable to the construction of environmental models.

Microbiological Aspects of Pollution Control. R. K. Dart, R. J. Stretton. 215 pages. Elsevier Scientific Publishing Co., P.O. Box 211, Amsterdam, The Netherlands, or 52 Vanderbilt Ave., New York, NY 10017. 1977. $34.75, hard cover.

Microbiology plays an important role in public health and hygiene. This book discusses bacteria and fungi, how they act as pollutants, or produce chemical pollutants. Health hazards, countermeasures, eutrophication, sewage treatment, and oil pollution are among the many topics covered.

Nuclear Microanalysis. Vlado Valković. xii + 415 pages. Garland Publishing, Inc., 545 Madison Ave., New York, NY 10022. 1977. $27, hard cover.

Many nuclear materials and contaminants occur in trace quantities, yet, at times, they can present a real threat. This book presents an exhaustive treatment of the subject of how to analyze and determine these trace materials. It tells "how to do it."

Evaluation of Current Developments in Minicipal Waste Treatment. vi + 121 pages. National Technical Information Service, U.S. Department of Commerce, Springfield, VA 22161. 1977. $4.75 ($9.50 outside North American Continent), paper.

What can you do with sludge? You can irradiate it; you can compost it; you can recycle it in some cases. This book contains papers on the subject presented at The Johns Hopkins University last January. Information about legislation, as well as some cost figures are given.

Environmental Impact Analysis: A New Dimension in Decision Making. L. V. Urban et al. xi + 330 pages. Van Nostrand Reinhold Co., 450 West 33rd St., New York, NY 10001. 1977. $22.50, hard cover.

What if a project affects the environment (and most do)? Then the law may require an environmental impact statement (EIS). This book provides step-by-step guidance in preparing an EIS, looks into all EIS parameters, reviews major assessment methodologies, and offers other necessary help. An appendix gives the text of the National Environmental Policy Act.

Pollution Control for Agriculture. Raymond C. Loehr. xiii + 383 pages. Academic Press, Inc., 111 Fifth Ave., New York, NY 10003. 1977. $17, hard cover.

Agriculture and industries related to its products put out certain organic wastes. How can these be treated and disposed of? This book explains how, with coverage of aerobic and anaerobic treatment; ponds and lagoons; physical/chemical treatment; and land disposal. Nitrogen control, waste utilization with by-product development and methane generation, and water reclamation are also among topics discussed.

Energy/Pollution Illustrated Glossary. Esber I. Shaheen. 183 pages. Engineering Technology Inc., 503 East Main St., Mahomet, IL 61853. 1977. $8.35 (add 41¢ for postage), hard cover.

In the energy and environment fields, many terms are bandied about, sometimes too loosely. This book gives the precise definitions that eliminate any confusion, and provides illustration where needed.

Aquatic Toxicology and Hazard Evaluation—STP 634. 316 pages. ASTM, 1916 Race St., Philadelphia, PA 19103. 1977. $30.75 + 3% shipping charges for U.S., Canada, Mexico; 5% elsewhere.

This work provides a state-of-the-art for some research approaches, new applications of old methods, and new data on several pesticides and other chemicals. It covers testing equipment/methods; biological effects and evaluation; the rationale of hazard evaluation; and other pertinent topics.

Environmental Monitoring, Volume IV. xiii + 181 pages. Printing and Publications Office, National Academy of Sciences, 2101 Constitution Ave., N.W., Washington, DC 20418. 1977. $7.75 (must be prepaid), paper.

This report points up weaknesses in EPA's monitoring programs, as to scientific method, design, operation, and evaluation. It tells that monitoring for anticipation and discovery, as well as source control of pollution, is needed. Recommendations are made as to how to coordinate responsibilities for monitoring among local, state, regional, and federal agencies, as well as within EPA itself.

Environmental Toxicology: A Guide to Information Sources. Robert L. Rudd, Ed. xii + 266 pages. Gale Research Co., Book Tower, Detroit, MI 48226. 1977. $18.

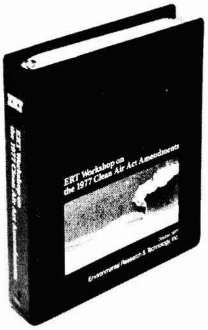
This book is Volume 7 in the Man and the Environment Information Guide Series. It looks at general sources on environmental toxicology; consequences of intentional, and of unintended environmental pollution, and other related and special topics.

Methods of Air Sampling and Analysis. 2nd ed. American Public Health Association, 1015 18th St., N.W., Washington, DC 20036. 1977. $45 + 50¢ for handling.

This work offers 130 reproducible methods, of high accuracy, for sampling/analysis of ambient and workplace air. It covers techniques, precautions, state-of-the-art, actual methods, and many techniques for specific substances.

BETZ Handbook of Industrial Water Conditioning. 7th ed. BETZ, Trevose, PA 19047. 1977. $15 + 50¢ postage, hard cover.

This work covers pretreatment, chlorination, wastewater reuse, scale/deposit control, fouling, and many other topics of importance to the industrial water user. Compliance and energy conservation are also discussed.



ES&T

MEETINGS

January 23–24 Atlanta, Ga.
Integrated Community Energy Systems Planning. Battelle Columbus Laboratories

Write: Amanda Hamilton, Suite 1038 North, 101 Park Ave., New York, N.Y. 10017

January 23–27 Albuquerque, N.Mex.
Second National Conference and Exhibition on Technology for Energy Conservation. American Petroleum Institute, and others

Write: Energy Conservation Conference, c/o Information Transfer Inc., Suite 202, 1160 Rockville Pike, Rockville, MD. 20852

January 24–25 Cambridge, Mass.
The Economics of Large-Scale Algae Biomass Systems as Energy Sources. MIT Marine Industry Collegium and others

Write: Norman Doelling, manager, Marine Industry Advisory Services, Room 1-215, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, Mass. 02139

January 26–29 Boca Raton, Fla.
51st Annual Industry Convention. The Soap and Detergent Association

Environmental issues will be discussed. *Write:* The Soap and Detergent Association, 475 Park Park Ave. South, New York, N.Y. 10016

January 30–February 1 Orlando, Fla.
Fifth National Conference on Sludge Management, Disposal and Utilization. Information Transfer Inc. and the Hazardous Materials Control Research Institute

Write: Information Transfer, Inc., 1160 Rockville Pike, Suite 202, Rockville, Md. 20852

January 30–February 2 Savannah, Ga.
58th American Meteorological Society Annual Meeting. American Meteorological Society

There will be a session on "Chemistry of Aerosols and their Sources in Polluted Atmospheres." *Write:* Evelyn Mazur, American Meteorological Society, 45 Beacon St., Boston, Mass. 02108

February 2–3 Phoenix, Ariz.
The Solar Energy Business: Opportunities and Outlook. The Energy Bureau, Inc.

Write: Robert W. Nash, executive director, The Energy Bureau, Inc., 101 Park Ave., New York, N.Y. 10017

February 7–9 San Diego, Calif.
CLEOS '78: IEEE/OSA Conference on Laser & Electro-optical Systems. IEEE and Optical Society of America

Environmental monitoring applications will be discussed. *Write:* CLEOS, c/o Optical Society of America, Suite 620, 2000 L St., N.W., Washington, D.C. 20036

February 12–17 Washington, D.C.
AAAS Annual Meeting. American Association for the Advancement of Science

Environmental and energy issues will be discussed. *Write:* AAAS Meetings Office, 1776 Massachusetts Ave., N.W., Washington, D.C. 20036

February 13–15 Champaign, Ill.
Third Annual Illinois Private Sewage Disposal Symposium. Illinois Dept. of Public Health and the Illinois Cooperative Extension Service

Write: Michael Neumann, Regional Engineer, Illinois Dept. of Public Health, 2125 South First St., Champaign, Ill. 61820

February 13–15 Atlanta, Ga.
Process Measurements for Environmental Assessments. U.S. EPA

Write: Eugene A. Burns, TRW DSSG, Building 01, Room 2020, Redondo Beach, Calif. 90278

February 15–16 Pittsburgh, Pa.
Symposium on Energy-Related Health Problems of the Future. Industrial Health Foundation

Write: Industrial Health Foundation, 5231 Centre Ave., Pittsburgh, Pa. 15232

February 20–22 Miami Beach, Fla.
Fifth Ocean Thermal Energy Conversion (OTEC) Conference. University of Miami/Clean Energy Research Institute

Write: Clean Energy Research Institute, School of Engineering & Environmental Design, University of Miami, P.O. Box 248294, Coral Gables, Fla. 33124

February 26–March 4 Washington, D.C.
1978 ACSM/ASP Convention. American Congress on Surveying and Mapping and the American Society of Photogrammetry

Write: Ron Brewer, chairman, publicity committee, 9206 Fairhaven Ave., Upper Marlboro, Md. 20870

February 27–March 1 Washington, D.C.
5th Energy Technology Conference & Exposition. EPRI, American Gas Association and the Dept. of Energy

Write: 5th Energy Technology Conference & Exposition, 4733 Bethesda Ave., N.W., Washington, D.C. 20014

Courses

January 19–20 West Palm Beach, Fla.
Fundamentals of Dispersion Modeling. Trinity Consultants

Fee: $280. *Write:* Richard H. Schulze, Trinity Consultants, P.O. Box 31481, Dallas, Tex. 75231

January 19–20 Boston, Mass.
Energy Conservation in Industrial Plants. New York University

Fee: $485. Write: Heidi E. Kaplan, Dept. 14NR, New York Management Center, 360 Lexington Ave., New York, N.Y. 10017

January 23–25 Albuquerque, N.Mex.
Workshop on Inhalation Toxicology. American Industrial Hygiene Association

Fee: $350. *Write:* American Industrial Hygiene Association, 66 South Miller Rd., Akron, Ohio 44313

January 23–25 Madison, Wis.
Advanced Sanitary Landfill Design, Course No. 368. University of Wisconsin-Extension

Fee: $185. *Write:* University of Wisconsin-Extension, Dept. of Engineering and Applied Science, 432 N. Lake St., Madison, Wis. 53706

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Recognition, Evaluation & Control of Occupational Hazards, Course No. 549. National Institute for Occupational Safety & Health and the Wichita State University

Fee: $350. *Write:* Wichita State University, CHCM, Box 36, Wichita, Kans. 67208

January 26–27 Washington, D.C.
Third Annual Energy Users Law Seminar. Government Institutes, Inc.

Fee: $295. *Write:* Government Institutes, Inc., 4733 Bethesda Ave., N.W., Washington, D.C. 20014

January 27–28 Berkeley, Calif.
Solar Energy for Buildings, Houses and Pools. University of California at Berkeley/College of Engineering and the UC Extension

Fee: $100. *Write:* Continuing Education in Engineering, University of California Extension, 2223 Fulton St., Berkeley, Calif. 94720

January 30–February 3 San Francisco, Calif.
Legal Aspects of the Occupational Safety & Health Act of 1970, Course No. 599 National Institute for Occupational Safety & Health

Fee: $250. *Write:* National Institute for Occupational Safety & Health, Division of Training & Manpower Development, 4676 Columbia Parkway, Cincinnati, Ohio 45226

January 30–February 3 Chicago, Ill.
Energy Conservation/Application Fundamentals. Institute of Gas Technology

Fee: $310 (member); $360 (nonmember). *Write:* Gerald G. Wilson, director, Industrial Education, Institute of Gas Technology, 3424 S. State St., Chicago, Ill. 60616

February 6–8 Chicago, Ill.
Solar Energy. New York University

Fee: $495. *Write:* Heidi E. Kaplan, Dept. 14NR, New York Management Center, 360 Lexington Ave., New York, N.Y. 10017

February 6–9 Cincinnati, Ohio
Occupational Respiratory Protection, Course No. 593. National Institute for Occupational Safety & Health

Fee: $250. *Write:* National Institute for Occupational Safety & Health, Division of Training & Manpower Development, 4676 Columbia Parkway, Cincinnati, Ohio 45226

February 6–10 Seattle, Wash.
Recognition of Occupational Health Hazards, Course No. 510. National Institute for Occupational Safety & Health and the American Industrial Hygiene Association

Fee: $250. *Write:* American Industrial Hygiene Association, 66 South Miller Rd., Akron, Ohio 44313

February 6–10 Philadelphia, Pa.
Introduction to Occupational Safety, Course No. 508. National Institute for Occupational Safety & Health and Temple University

Fee: $250. *Write:* Temple University, School of Pharmacy, 3307 N. Broad St., Philadelphia, Pa. 19140

February 6–10 Cincinnati, Ohio
Biological Treatment Technology, Course No. 162.2 Environmental Protection Agency

Fee: $110. *Write:* Instructional Resources Center, National Training and Operational Technology Center, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268

February 12–17 Blacksburg, Va.
Institute for Water and Wastewater Managers. American Water Works Association

Fee: $225 *Write:* John Kemper, American Water Works Association, P.O. Box 1080, Norfolk, Va. 23501

February 13–15 Madison, Wis.
On-Site Disposal of Small Wastewater Flows. University of Wisconsin–Extension

Fee: $200. *Write:* University of Wisconsin–Extension, Dept. of Engineering & Applied Science, 432 N. Lake St., Madison, Wis. 53706

February 13–16 Cincinnati, Ohio
Planning Monitoring Activities in Water Quality Management Programs, Course No. 161.2. Environmental Protection Agency

Fee: $88. *Write:* Instructional Resources Center, National Training and Operational Technology Center, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268

February 14–16 Athens, Ga.
Applied Ecology Seminar, Course No. 146. Environmental Protection Agency

Fee: $66. *Write:* Instructional Resources Center, National Training and Operational Technology Center, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268

February 22–24 Washington, D.C.
Air Pollution Control Equipment Operation and Maintenance, Course No. 489. George Washington University

Fee: $375. *Write:* Martha Augustin, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

February 22–24 Houston, Tex.
Environmental Health Management. International Safety Academy

Fee: $300. *Write:* International Safety Academy, 10575 Katy Freeway, P.O. Box 19600, Houston, Tex. 77024

International

January 30–February 10 Geneva, Switzerland
International Environmental Management Seminar. Center for Education in International Management

Write: The Admissions Secretary, CEI, 4 chemin de Conches, CH-1231, Conches-Geneva, Switzerland

March 6–7 Basle, Switzerland
First World Recycling Congress. The Royal Society, U.S. Bureau of Mines and others

Write: Michael E. Henstock, Dept. of Metallurgy and Materials Science, University of Nottingham, Nottingham, NG7 2RD, England

March 10–19 Rome, Italy
25th International Exhibition of Electronics, Nuclear Energy, Aerospace Technologies. Rassegna Internazionale Elettronica, Nucleare Ed Aerospaziale

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March 20–22 Oxford, United Kingdom
Resources Policy Conference 78: An International Conference on the Economics, Politics and Social Implications of Resource Use and Conservation. Resources Policy Journal

Write: IPC Science and Technology Press Ltd., 32 High St., Guildford, Surrey, England GU1 3EW

March 26–30 Riyadh, Saudi Arabia
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April 3–6 London, United Kingdom
April 11–14 Paris, France
Envirotrol 78: Pollution Control and Instrumentation Exhibit. U.S. Dept. of Commerce

Write: R. Connan, Office of International Marketing, U.S. Dept. of Commerce, Washington, D.C. 20230

April 5–7 Geneva, Switzerland
8th Annual Symposium on the Analytical Chemistry of Pollutants. Organized by scientists throughout the world

Write: Congress Secretariat, P.O. Box 182, CH-4013 Basle, Switzerland

April 20–26 Manila, Philippines
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Write: U-M Extension Service, Conference and Institutes, 412 Maynard St., Ann Arbor, Mich. 48109

April 26–27 Buckinghamshire, United Kingdom
Major Chemical Hazards. Harwell

Write: Ron Ely or Clive Fewins, Press Office, PR Group, Building 329, Harwell, Oxfordshire OX11 ORA, United Kingdom

April 30–May 6 Dubai, United Arab Emirates
Water Treatment and Environmental Pollution Control Exhibition. Dubai Chamber of Commerce & Industry

Write: Fairs & Exhibitions Ltd., 21 Park Square East, London NW1 4LH, United Kingdom

Call for Papers

February 1 deadline
Conference on Carbonaceous Particles in the Atmosphere. National Science Foundation/RANN and Lawrence Berkeley Laboratory

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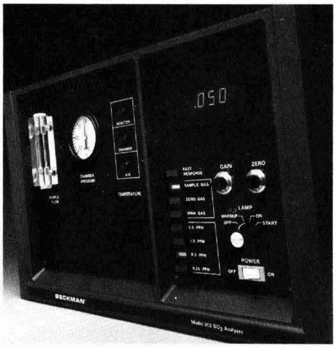

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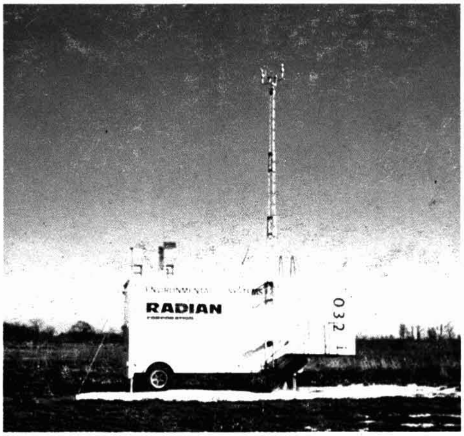
Fullerton, CA 92634.

BECKMAN®



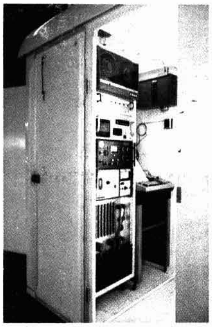
Environmental Monitoring Systems

The System I Mobile Monitoring Van With Computer-Controlled Data System

- Housed in a 26 ft. mobile van
- Large comfortable working space
- Exceptional strength for location in unusual environments
- Programmable digital computer-based control
- Continuous monitoring
- Automatic daily zero and span calibration
- Real time data processing
- Triple redundancy in data storage
- Hardcopy data reports generated on site
- Continuous system status check (on site or remote display)

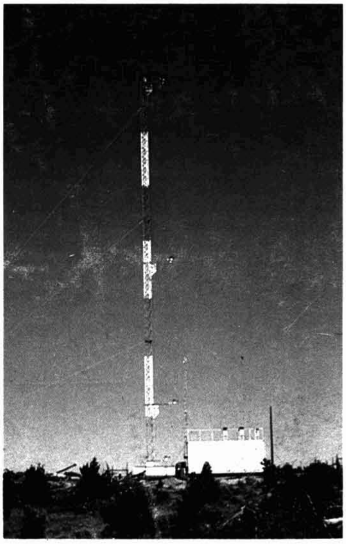
The System II Portable Monitoring Station

- Lightweight modular construction (4 modules)

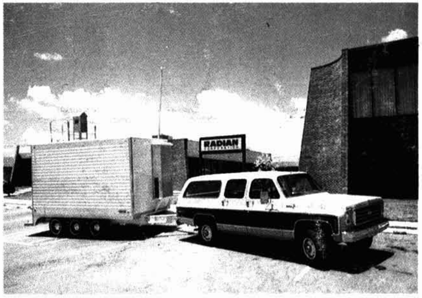


- Temperature-controlled instrument compartment

- Easy assembly/disassembly
- Easy transport in a standard pick-up truck
- Safety systems to prevent electrical shock
- Vandal resistant and weatherproof
- Automatic fire extinguisher system
- Separate compartment for bottle gas storage
- Easy access to instruments for repair and maintenance



The New System III Portable Monitoring Shelter Provides for On/Off Road Movement with Minimum Disturbance to Instruments



- Separate compartment for bottle gas storage
- Minimum setup time
- Complete environmentally-controlled instrument and work areas
- Ample work space for maintenance
- Maximum flexibility in interior layout

Additional custom design features for a variety of air quality and meteorological monitoring are available on all three Radian Corporation field monitoring systems. Sales or Lease (Long or Short term). All systems available including 10 and 60 meter meteorological towers.

Professional Technical Services in Energy and Environment

RADIAN CORPORATION

P.O. Box 9948 / Austin, Texas 78766 / (512) 454-4797

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