Environmental
Science & Technology

Incentives
for controls 250

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CONTENTS

CURRENT RESEARCH

* To whom correspondence should be addressed.

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

The Calgon Adsorption Service.^{SM}
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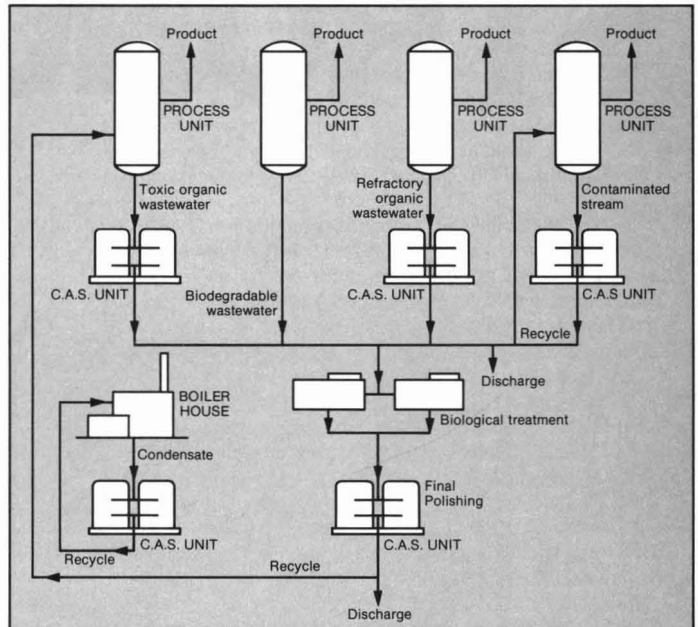
IMPROVED BIO SYSTEM OPERATION — By reducing the concentration of organic materials — some of which may be toxic to the biomass — in a waste stream before it goes to an existing biological treatment unit, a Calgon Adsorption Service system can increase efficiency greatly. The adsorption system also can be used to upgrade the effluent from a biological plant.

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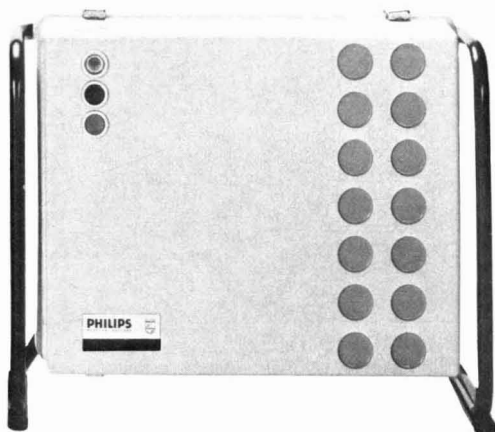
EDITORIAL

An invitation

If you are interested in the application of chemical technology to environmental improvement, consider participating in the activities of the Division of Environmental Chemistry. The proud history of this Division, which dates to 1915, reveals a consistent tendency to anticipate trends in chemical research and member interest. The record includes an extensive preprint publication series, symposia, the launching of this journal, and, up until recently, the organization of symposia in recognition of Monsanto award winners.

The current dynamic Chairman, Dr. Nina McClelland, is seeking ways to make the Division attractive to an expanded membership, and her efforts are worthy of support from each of us. Dr. McClelland is calling for an infusion of new spirit in Divisional activities, involvement with chemical engineering and health-related disciplines, and establishment of a patron program for partial financial support. She argues that the Division is not the exclusive domain of full-time environmental researchers, and should function as a forum for the exchange of professional views on all aspects of chemical hazards in the human and natural environments.

As chemists, we have a moral responsibility to consider whether the considerable benefits brought to mankind as a result of our profession outweigh the potential for harm. We cannot deny that the development of useful materials in chemistry has been beneficial, but it has also unwittingly sponsored a vast geophysical experiment with this planet through the discharge of wastes and the exposure of living systems to compounds of unknown effects. Through Dr. McClelland's and the Division's activities we have an opportunity to participate in this dialogue.

The program activities scheduled for New Orleans this month are particularly appropriate. Little more than two years ago the potential for human health impact from organic materials in drinking water dawned on the national conscience as a result of studies in the New Orleans–Jefferson Parish area. A two-and-a-half-day symposium on drinking-water quality enhancement is now scheduled for New Orleans, along with programs on wastewater technology, atmospheric sulfates, and the monitoring of gaseous pollutants.

In addition, you are invited to meet Dr. McClelland and the Divisional Executive Committee at their meeting in the Choctaw Room of the Royal Sonesta at 8 p.m. on Sunday, March 20. Your views, ideas, and participation will be welcomed.

R F Christman

ENVIRONMENTAL SCIENCE AND TECHNOLOGY 1977

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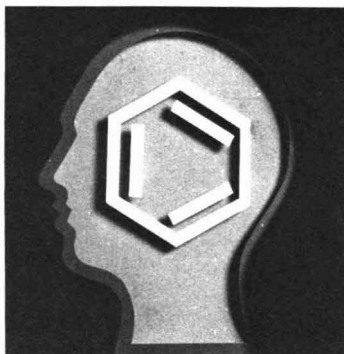
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OF THE
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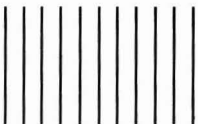
CURRENTS

INTERNATIONAL

In its 5-y environmental program (1977–81), the European Economic Community strives for improved quality of life without compromising economic growth. Among its eight objectives, the report cites improved integration of environmental protection and regional development. The majority of the program's budget is devoted to research to identify the problems and suggest appropriate solutions. An ecological map of Europe to assess the causes and effects of pollution is to be produced.

WASHINGTON

As one of his last official acts, former President Ford presented his final budget to Congress. EPA's share is $802 million for fiscal 1978; this represents an increase in the operating budget of $28 million. A major item in Ford's budget for EPA is $45 billion over a 10-y period beginning with $4.5 billion in fiscal 1978 for construction grants for new municipal sewage treatment plants. This $45 billion comes on top of the $18 billion in grants already authorized by Congress and which EPA must obligate by the end of this fiscal year, September 30. Under Ford's program, storm sewers and sewer rehabilitation projects would not be eligible for federal funds. The Carter administration did not alter Ford's budget for EPA, and the agency is now appealing. ERDA's share of Ford's budget is $2.8 billion for direct energy RD&D, fully 90% of Ford's budget in the energy field.

EPA has issued final standards that will limit industrial discharge to waterways of five toxic chemicals. The industrial discharges to be limited are benzidine, aldrin/dieldrin, DDT and related compounds, endrin and toxaphene. These standards are issued under P.L. 92-500, but do not cover indirect discharges through municipal sewage treatment plants. DDT, aldrin/dieldrin are banned completely; endrin discharges are limited to 1.5 ppb for existing plants; toxaphene is limited to 1.5 ppb and benzidine is limited to 10 ppb in existing plants. In a separate issuance, the EPA prohibited the discharge of PCBs into waterways; this standard was also issued under P.L. 92-500.

In a recent report "Problems and Progress in Regulating Ocean Dumping of Sewage Sludge and Industrial Wastes," the General Accounting Office recommended that EPA take the lead in locating sites where dumping can occur at rates safe to the marine environment and to navigation. Further, GAO asked EPA to consider the effects of alternatives to ocean dumping, since these alternatives may be more harmful than ocean disposal. To the Dept. of Transportation, specifically the Coast Guard, GAO recommended increasing the level of dumping surveillance, especially night dumping; and the development of new methods to better monitor compliance with ocean-dumping permits.

OSHA's ability to enforce workplace safety and health standards may be hampered if the Supreme Court upholds a recent U.S. District Court (Boise, Idaho) ruling. In the Idaho case, the District Court ruled that OSHA's inspection authority under the Occupational Safety and Health Act violates the Fourth Amendment search and seizure rights. OSHA sought to have the decision stayed, but its motion was denied in January. The agency has suspended all inspections in Idaho, but not in other states, while it seeks relief in the Supreme Court from the District Court's ruling. The ramifications are vast: should the District Court's ruling be upheld, warrantless inspections by other federal agencies and state and local fire and health departments may also be affected.

A Federal Power Commission (FPC) judge has recommended a trans-Canadian route for delivery of Alaskan natural gas to the energy-starved Midwest U.S. Natural gas would be transported 4175 mi in a pipeline traversing Canada and branching into western and upper midwestern states. The $8.5 billion proposal was submitted by a 16-company (U.S. and Canada) consortium, the Alaskan Arctic Gas Pipeline Co. Administrative Law Judge Nahum Litt recommended this proposal over those submitted by El Paso Alaska Co. and the Alcan Pipeline Co. Environmentalists favor the Alcan proposal. Competing companies claim that Canadian provinces could unreasonably tax the proposed Arctic

Alcan Pipeline Co.
El Paso Alaska Co.
Alaskan Arctic Gas Pipeline Co.

Prudhoe Bay

San Francisco

Chicago
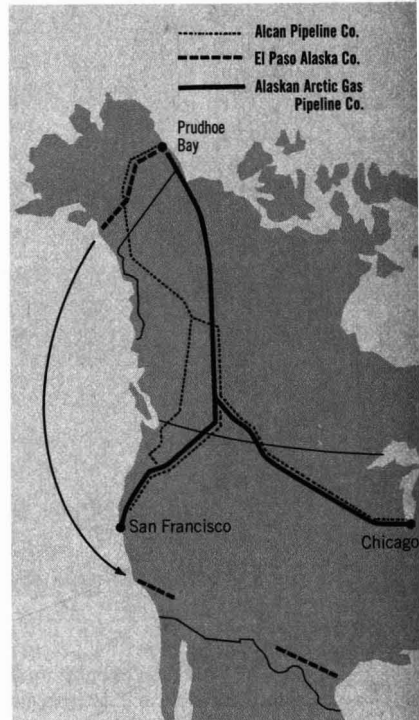
pipeline and thereby raise consumer prices in the U.S. A final recommendation must be made by the full FPC and delivered to President Carter by May 1. Carter must then make a decision by December 1.

EPA is now using the blacklist to persuade major industrial polluters to comply with air and water laws. Under never-before-used provisions of the Clean Air Act and the Federal Water Pollution Control Act Amendments of 1972, the EPA can list serious, continuing violators, making them ineligible for federal contracts, subcontracts, grants or loans. The first company to be blacklisted for polluting the air is Allied Chemical's coke plant in Ashland, Ky. Several months ago, EPA blacklisted Del Monte and Star-Kist for violating P.L. 92-500. EPA was prodded into using this method under pressure from the Natural Resources Defense Council. The agency refuses to estimate the number of companies eligible for blacklisting, and claims it will not use the list indiscriminately.
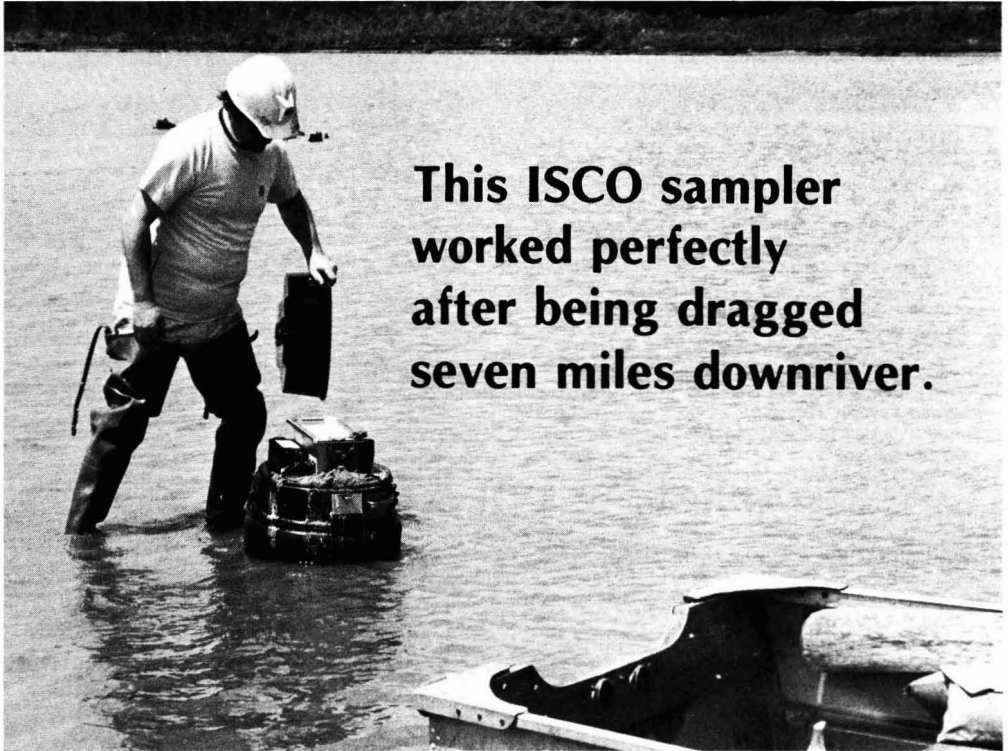
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STATES

Birmingham, Ala., is the first U.S. city to set up an Environmental Economics Department (EED) to assess the impact of proposed environmental activities on its economy. This new department, established by the Birmingham Area Chamber of Commerce and funded by the city's citizenry, will be managed by Alan Mason, a former banker.

Birmingham EED's Mason

According to the Chamber's executive vice president, Don A. Newton, the objective of this department is "promotion of environmental protection practices that are compatible with the preservation of our economy and the free enterprise system." The EED will supply Birmingham's citizens with the necessary information to make intelligent decisions.

How to handle the sewage sludge problem? The Los Angeles/Orange County Metropolitan Area Regional Wastewater Solids Management Program has entered its second phase. During this phase, 17 identified feasible alternative sludge management schemes will be evaluated. Each of the 17 systems is designed to recover, reclaim, or recycle at least one resource—be it energy, nutrients or metals—contained in sewage sludge. Muskegon County, Mich., is applying the products of treated wastewater—water and fertilizer—to land. In 1975, the county grew more than 250 000 bushels of corn on previously unproductive land. New York state recently promulgated rules and regulations governing the certification of pesticide applicators and the disposal and reuse of pesticide containers.

Progress in improving air quality around the country is mixed. Chicago claimed a 15% drop in peak hourly ozone levels since 1974; the city also recorded a significant decrease in particulate matter, sulfur oxide, carbon monoxide, nitrogen oxides and hydrocarbons. The latter reductions

were achieved by converting 239 schools heating plants from coal to gas fired, and from the success of citywide industrial air pollution programs. New York City claimed improved air quality for 1976. Citywide carbon monoxide levels were down by 13% over 1975 levels, and none of the city's monitoring stations reported violations of sulfur dioxide standards. On the other hand, the Lane Regional Air Pollution Authority (Oregon) reported slightly higher levels for suspended particulate matter and carbon monoxide in 1976.

New Mexico recently adopted statewide groundwater regulations, which are believed to be the first such detailed regulations in the nation. These regulations set numerical standards for groundwater quality and establish limits of contaminant concentrations in discharges to groundwater. Sources to be controlled are sewage and other wastewater disposal lagoons, injection wells, ore-leaching operations, tailings ponds and land applications of wastewater. Exempted from the regulations is the largest user of groundwater—irrigated agriculture. This exemption was based solely on inadequate information; agriculture's adverse impact on groundwater is considered serious. Those to whom the regulations apply must submit "discharge plans" to the Environmental Improvement Agency prior to discharge of contaminants.

New York City must enforce its transportation control plan as mandated by the Clean Air Act, the U.S. Court of Appeals for the Second Circuit ruled recently. The transportation plan calls for the imposition of bridge tolls, the prohibition of taxis from cruising on busy streets in midtown and the reduction of parking space in the central business district. Also to be studied is the ban on truck deliveries during peak hours of congestion. Robert Low, administrator of the city's Environmental Protection Agency, argued for the elimination of the bridge toll stipulation, and a modification of other provisions of the plan. He contended that the tolls would not discourage motorists from driving into the city and, therefore, would not help to improve air quality.

New Jersey, with the highest cancer rate in the U.S., is contemplating the banning of 16 industrial cancer-causing agents from the state. Among the chemicals that would be subjected to zero emissions standards are vinyl chloride and asbestos. Last November, the state's voters approved the "New Jersey Clean Waters Bond Act of 1976." This act authorizes the sale of $120 million in bonds to be used for the

planning, construction and maintenance of water pollution control and water supply facilities. The city of Camden, N.J., has received another reprieve in its long-standing battle to continue dumping its untreated sewage sludge in the Atlantic Ocean. Denied the right to dump its sewage 35-mi off the Maryland and Delaware coast, the city has received permission to continue dumping in the ocean 90 mi due east of Cape May, N.J.

TECHNOLOGY

SO$_2$ abatement could be enhanced by the simultaneous use of a slurry as a scrubbing agent and as an electrode in an electrochemical cell. According to Henri Maget, manager, business development of United Technologies' Chemical Systems Division (Sunnyvale, Calif.), SO$_2$ is adsorbed by a suspended, moving adsorbent, such as carbon. The next step is

Carbon slurry process
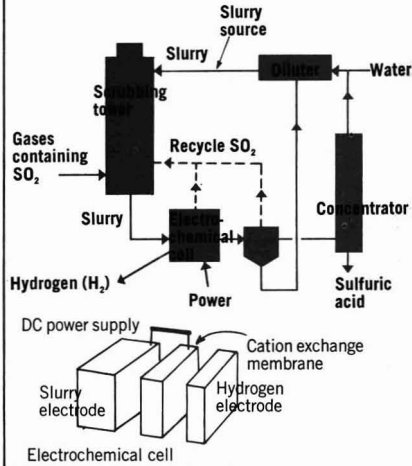
electrochemical oxidation of SO$_2$ into sulfuric acid. Adsorption efficiencies of 90–100% can be expected if the adsorbent, slurry concentration, and residence time are properly selected, Maget says. Oxidation is more efficient with slurry electrodes than with conventional electrodes. Slurry can be regenerated, and water recycled; and sulfuric acid, and hydrogen resulting from the electrochemical process, are marketable.

Flue gas desulfurization (FGD) systems can be made to work, but they will be expensive, and their perfection will take time. This was a "consensus" of government, utility, and research organization representatives at a meeting on FGD held recently at Battelle (Columbus, Ohio). What was not pinned down at the meeting was

Down the drain?

Process water isn't cheap any more. It's expensive to acquire. To use. Even to throw away. A sensible solution is to re-cycle it. Use it over and over again. But to do this you must control its quality. Especially its organic pollution load. Otherwise, forget it.

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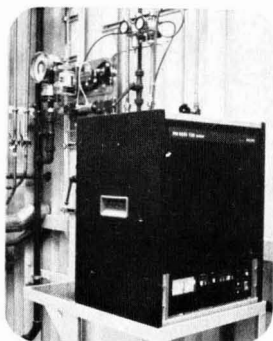
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what the expenses and perfection time necessary for FGD—involving mostly scrubbers—would be. While EPA took the position that FGD scrubbers are a viable option, an American Electric Power speaker said that they are uneconomical and unworkable. An Electric Power Research Institute (EPRI) assessment was that scrubbing is the only near-term alternative, but that EPRI is actively pursuing other technologies. Meanwhile, FGD costs are expected to be 15 mills/kWh by 1985.

Steel mill wastes are recycled in a novel way at Kawasaki Steel Corp. (Japan). Iron ore dust discharged from mill furnaces is recaptured and processed to make reduced iron ore pellets by use of a technique known as the Reduced Pellet method. Furnace dust is blended and reshaped into particles of 12–13 mm in diameter. These are preheated, reduced in a rotary kiln, and cooled. The reduced pellets have an average iron content exceeding 90%. Normally, such dust is an air pollutant that a 10 million-tpy steel mill can belch out to the tune of 360 000 tpy. This method abates that dust and recovers important ferrous values.

A solar energy concentrator can focus the sun's rays without the need for a tracking mechanism. It was invented by Katsunori Shimada of NASA, and patented by NASA; it uses a multi-faceted Fresnel lens system to magnify solar energy 10 times. The heat transfers to a suitable liquid released by a thermostatically controlled valve. NASA has licensed Owen Enterprises, Inc. (Wilmington, Calif.), an American Indian-owned firm, to produce the device. Meanwhile, governor Jerry Apodaca and the New Mexico Congressional delegation expressed enthusiasm about plans to add a solar receiver/mirror array to an existing gas-fired power plant near Albuquerque, under an idea presented to ERDA by Public Service Co. of New Mexico.

Ozone generators designed and built by Emery Industries, Inc. (Cincinnati, Ohio) will be used for upgrading and expanding an 8 mgd (peak 10 mgd) wastewater treatment plant for the City of Murfreesboro, Tenn. About 560 lbs/d of ozone, made from high-purity oxygen, will act as a disinfectant, along with an oxygen-activated sludge system and cryogenic oxygen generators. This installation is the second to use large-scale ozone disinfection systems developed by Emery; startup is expected late next year. The company sees advantages in shorter contact time, smaller doses, no harmful by-products, and better taste, odor, color, clarity, and virus kill. Emery is the

world's largest ozone producer and consumer, mainly for its normal chemical operations.

Free, unlimited energy, even with sun and wind absent? Herman Sheets, chairman of the ocean engineering department, University of Rhode Island, says yes, and that it is to be found in the oceans, especially in warmer climates. Sheets suggests using ocean temperature differences, by which cold water from about a 2000-ft depth condenses a gas, such as ammonia, freon, or propane. The condensed gas is pumped up to warmer ocean layers, boils, and runs a power-generating turbine. To be economical, the plant should generate at least 100 MW, which would require a 250 000-t platform in place for 25–40 years. Costs might be $2100–2600/kW—about the same as for nuclear plants—but the "fuel" is free, Sheets said.

INDUSTRY

Georgia-Pacific (Portland, Ore.) has announced a "first in the nation" paper recycling system that can change once unusable waste paper into high-quality printing stock, save energy and water, and reduce other environmental problems. The key is a new process which removes ink, varnish, lacquer, staples, binding tape, glue, thread, and even plastics. Recycled fibers are blended with "virgin" fibers to meet specifications for any printing needed. The $3 million-plus system can handle 33 000 tpy. It also uses 3000 gal of water/t of cleaned fiber; standard washing systems use about 14 000 gal. The water used is also 60 °F cooler, and is recycled. What heat the make-up water needs is reject heat from the paper machine.

W.R. Grace & Co. (New York, N.Y.) will help to take salt out of the Colorado River near Yuma, Ariz., at a 104-mgd desalination plant to be completed in 1981. The plant, under construction by the U.S. Dept. of the Interior, will use reverse osmosis (RO) and electrodialysis (ED) to reduce salinity of water draining from farmlands in the Wellton-Mohawk Valley, in keeping with a 1973 treaty with Mexico to improve river water

W. R. Grace's Triggiani

quality. Grace research division president Leonard Triggiani foresees that the use of RO/ED membrane technology could have a long-term impact on potable water availability, as well as energy use reduction. He also sees membrane technology as a major advance over present energy-intensive distillation methods of desalination.

"Power company executives are insensitive to environmental and social concerns"—this is a popular image. Is it correct? A University of Notre Dame study indicates that as individuals, they are not insensitive; but as industry representatives, they are. To evaluate these attitudes, Notre Dame researchers used some standard, and some specially devised tests. They consider their findings important—and "disturbing"—because the decisions these executives make at work can have extensive public impacts, while they involve value judgments seldom exposed to public scrutiny. Most of the value weaknesses the study found involved a lack of active concern for future generations and of sensitivity to considerations of equitable distribution; and a tendency to equate desire for electric power with need.

Resource recovery from solid waste got a boost when American Can Co. announced that its Americology project at Milwaukee, Wis., processed its first truckload of municipal refuse. By mid-April, the $18 million privately-funded facility goes into commercial operation. It will process all of the 250 000 tpy of waste collected within Milwaukee under a 15-year agreement between the city and the company. Recovery of up to 90% by bulk is anticipated, including ferrous metals, aluminum, newspaper, corrugated board, and glassy aggregate. Some 50–60% of the refuse will be combustible fuel to be used by Wisconsin Electric Power Co., to save 75 000 tpy of coal.

An improved construction growth period may have EPA's construction grants program to thank, according to Robert Sansom, who is studying the matter for the National Utility Contractors Association (NUCA, Washington, D.C.). The program granted $1.42 billion/y in 1975, and $2.25 billion last year. Sansom estimated outlays of $3.2 billion for this year. Sansom is a former EPA assistant administrator for air and water programs. NUCA president Bill Lee said that "tens of thousands of jobs are available if the program is regulated properly," but feared that if long-term funding and system improvement are not passed by Congress this year, these new jobs—almost 26 000 in New York alone—could be lost.

A way to lower NO$_x$ in utility boilers

The Exxon thermal deNO$_x$ process reduced emissions
50% and worked at full load on a refinery in Japan

When fossil fuel is burned within most combustion devices, nitric oxide (NO) is formed both by thermal fixation of atmospheric nitrogen and by oxidation of organic nitrogen compounds present in the fuel. The NO formed in these different modes is often referred to as thermal NO$_x$ and fuel NO$_x$, respectively. While the NO formed within the combustion device is discharged to the atmosphere largely as NO, it is thereafter slowly converted into NO$_2$, a key component of photochemical smog and by itself a highly poisonous substance. Accordingly, the emission of NO and NO$_2$ (NO$_x$) from mobile and stationary sources has been regulated in the U.S., Japan, and to a lesser extent in other countries.

The problem

The prospect in the U.S. is for increasingly severe regulation of stationary sources in those regions where the ambient air quality is a problem. The reason for this is twofold: First, regions with air quality problems tend to be regions with high industrial growth rates. Thus, if the total contribution of all stationary sources

to the air quality burden is to be held constant, the amount each source may emit must be reduced in proportion to the growth.

Second, there is a growing body of opinion to the effect that it is more cost effective to control stationary sources than to control mobile sources. To regulate mobile sources one must regulate all mobile sources nationwide, whereas one can selectively regulate only those stationary sources within air quality critical regions. Further, since one large stationary source has NO$_x$ emissions equivalent to those of many automobiles, there is an obvious economy of scale to regulating the former. In direct conflict with this trend toward more severe regulation, there is a concurrent trend toward the use of fuels with higher nitrogen contents, especially coal and, in the not too distant future, shale oil.

The technology now used in the U.S. to meet NO$_x$ emissions standards is combustion modification, chiefly the two-stage combustion and flue-gas recirculation processes. The former involves burning the fuel with insufficient air, followed by

adding more air to complete the combustion. The latter involves diluting the combustion air with recirculated flue gas, thereby decreasing the peak flame temperature.

While both processes can provide substantial reductions of thermal NO$_x$, two-stage combustion has a very limited effectiveness against fuel NO$_x$, and flue gas recirculation is totally ineffective. Thus it seems probable that many areas in the U.S. will have more severe NO$_x$ emission standards that can be met with combustion modification technologies. In Japan, such severe standards are already law.

One control option

To meet this challenge, Exxon Research and Engineering Company (ERE, Linden, N.J.) has developed a new process based on the selective homogeneous gas-phase reduction of NO by NH$_3$ (ammonia). Practically, what this means is that no catalyst is required. One simply contacts the flue gas with NH$_3$ at the correct temperature. A rapid reaction occurs in the gas phase, and NO is reduced to N$_2$ and H$_2$O. Because this is a selective reaction, the amount of NH$_3$ needed is comparable to the amount of NO reduced.

Thus, the Exxon process is extraordinarily simple. One finds the location within a boiler/furnace at which the temperature of the flue gas is optimum for the process and, the internal configuration of the boiler/furnace permitting, installs the ammonia injection hardware in that location. However, use of the correct temperature is critical because the chemistry of the selective reduction of NO by NH$_3$ is highly temperature sensitive.

Laboratory data, obtained by ERE's Corporate Research Laboratory, illustrate this sensitivity. When the temperature is too low, NH$_3$ and NO tend to remain unreacted; when the temperature is too high the NH$_3$ tends to be consumed inefficiently, with relatively little net reduction of the NO. Thus, it is possible to achieve

Data. *Richard K. Lyon of the Corporate Research Labs of the Exxon Research and Engineering Company checks the temperature distribution within the boiler with changing load*

Reduction of NO$_x$ up to 70% are possible...

...50% reduction was achieved under full load

Percent DE NO$_x$

NH$_3$/NO$_x$ RATIO-MOLE/MOLES

- ■ Boiler
- ▲ Furnace
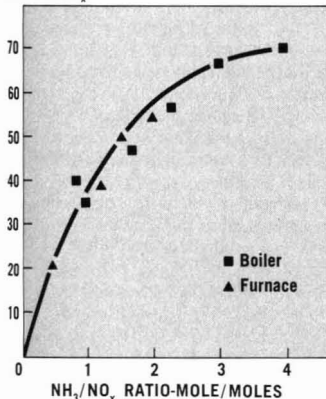
Selective reduction is highly temperature sensitive...

NH$_3$ ppm

H$_2$ = OFF
O$_2$ = 2%

NO ppm

TEMP - °C
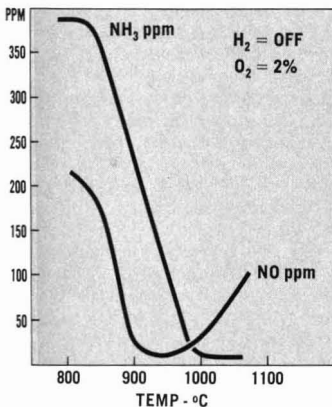
.but addition of hydrogen controls temperature for optimum results

NH$_3$ ppm

NO ppm

H$_2$ = ON
O$_2$ = 2%

TEMP. - °C
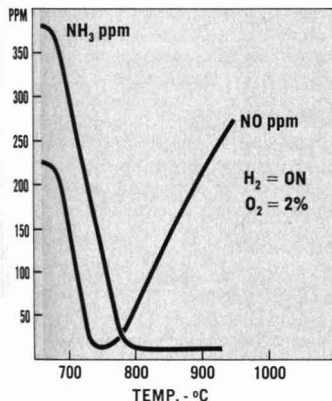
Source: Exxon Research & Engineering

Exxon thermal denox process, how it works[a]

[a] Larger units involve multiple injection points
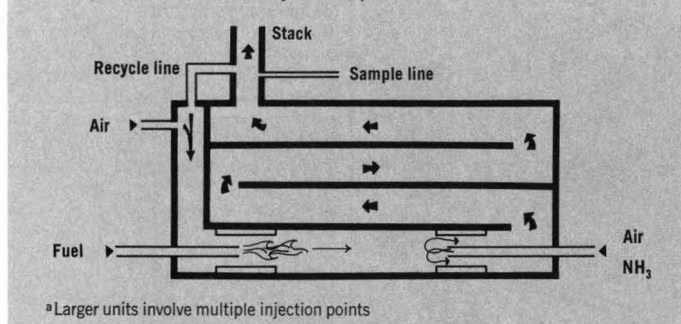
an efficient reduction of NO with little NH$_3$ remaining, but only within a narrow temperature range.

For furnaces and boilers that operate at varying loads, this would appear to pose a severe problem since the temperature distribution within the furnace/boiler varies with changing loads. However, the addition of a small amount of hydrogen (H$_2$) markedly decreases the temperature at which optimum results are achieved. The extent by which the temperature for optimum results is reduced depends on the amount of H$_2$ added; thus, by adding the correct amount of H$_2$, one may control the temperature for optimum results to match the variation of the temperature of the injection point caused by changing load. Laboratory data illustrated ERE's solution to this problem.

Field evaluation

Obviously, conditions cannot be as accurately controlled in practical combustion equipment as in laboratory apparatus. Consequently, the nearly quantative NO reductions achieved in laboratory experiments cannot be obtained in real furnaces and boiler.

This demonstration of the Exxon process on a real furnace and boiler was done at the Kawasaki refinery of Exxon's Japanese affiliate, and was an entirely retrofit operation: both the boiler and furnace were taken as found and the process installed within them without modification of any operating component of either unit. Reductions of NO$_x$ of up to 70% were achieved by the Exxon Thermal Denox Process during its commercial demonstration (August 1974).

The installation was done by the regular operating staff of the refinery, and with no interruption or interference with normal refinery operation. The demonstration boiler is oil-fired, and operates at up to

140 million Btus per hour. It's a swing boiler, used when one of the other boilers is out of service. The furnace is gas-fired, operated at 500 million Btu/h, and is in continuous service.

Since this commercial demonstration the process has been installed in other units in the Kawasaki refinery with similarly good results. Further, one Japanese firm not associated with Exxon has taken a license for use of the process and installed it in a boiler. Although the internal configuration of the boiler was not entirely suited to the process, reductions of NO of 50% at full load were achieved.

Costs

While costs of the Thermal Denox Process are sensitive to the user's particular circumstances, for normal retrofit ERE estimates the range to be 7–15¢/10^6 Btus fired.

Naturally, considerable savings are possible if, when new equipment is designed, provision is made to accommodate the process. This is a consideration of importance to those now planning new boilers/furnaces for operation in regions where the ambient NO$_x$ level is now considered marginally acceptable. In such areas, the standards for NO$_x$ emissions may be made more stringent during the normal lifetime of combustion equipment. If provision is now made within the boiler/furnace design for the Thermal Denox Process, it will later be possible to install the process at reduced cost in the event that more severe standards are promulgated.

Secondary effects

There have been a number of cases, recently publicized, of pollution control processes which, despite their initial promise, were later found to solve one pollution problem only at the expense of

Calibrate your gas analyzer...

objectively.

creating a new and equally serious one. Recognizing the danger of other undesirable secondary effects, ERE has implemented an extended program of laboratory and field testing.

Special attention was given to the question of whether or not such substances as N_2O, CO, HCN, SO_3, and NH_4HSO_4 might be produced within the Thermal Denox Process and constitute new pollution problems.

Although the main products of the reduction of NO by NH_3 are N_2 and H_2O, N_2O (nitrous oxide) is also formed in trace amounts, about 1 or 2 moles of N_2O for every 100 moles of NO reduced. This amount of N_2O proved too small to be detected by gas chromatography but was readily measurable by long-path infrared spectroscopy.

This production of N_2O would not appear to represent a significant disadvantage to the Thermal Denox process, since N_2O is generally accepted as a harmless substance, and, harmless or not, it is naturally present in the environment at a worldwide ambient concentration of about 0.3 ppm. Thus, since N_2O is present in nature in massive amounts, its ambient concentration is not readily subject to change by human activity, and the production of traces of N_2O by the Thermal Denox process does not represent a problem.

Tests for CO (carbon monoxide) emissions show that the Thermal Denox reaction does not reduce CO_2 to CO. Thus, the reaction does not per se generate CO; however, it was also found that NH_3 does inhibit the oxidation of CO to CO_2. Thus, if any CO is left unburnt at the point where the flue gas reaches the NH_3 contactor, that CO may be left in the flue gas when it is discharged to the atmosphere. For normally operating gas- and oil-fired units, this is not a problem. In these units CO oxidation is complete long before the combustion gases reach the ammonia injection point. At present, not enough information is available to determine whether or not incomplete CO oxidation will be a problem in coal-fired units.

It was found that HCN (hydrogen cyanide) can be formed if and only if hydrocarbons are present in the region in which the Thermal Denox reaction occurs. For a normally operating boiler, gaseous hydrocarbons will be present only if one injects them along with the NH_3. However, if one injects NH_3 with H_2 added for temperature compensation, HCN cannot be formed. If one injects NH_3 with CH_4 (methane) for temperature compensation, then a few ppm of HCN can be formed—less HCN than is found in automobile exhaust.

Whenever one burns a sulfur-containing fuel, the sulfur appears in the combustion gases chiefly as SO_2, but there are also traces of SO_3 (sulfur trioxide), normally 1–2% of the total sulfur. This small amount of SO_3 is a significant concern because at lower temperatures, SO_3 tends to form sulfuric acid mists that can cause corrosion problems at the back end of the boiler. Also, if the flue gas is not properly dispersed, the formation of sulfuric acid mist can be a severe local problem, although there is controversy about this in the technical literature. It appears that some of the SO_3 comes directly out of the flame, and some is produced by oxidation of SO_2 on the heat exchange tubes; that is, some SO_3 is produced by a homogeneous oxidation and some by a heterogeneous oxidation. Detailed laboratory experiments have been completed and the Thermal Denox process was found to cause neither additional homogeneous nor additional heterogeneous oxidation of SO_2 to SO_3.

However, although there is no change in the amount of SO_3, there is an effect. The thermal reduction of NO leaves some NH_3 unreacted, and downstream of the Denox reaction zone the combustion gases are cool enough for the ammonia to react with SO_3 and H_2O to form ammonium sulfates. Whether or not these sulfates should be considered as an added source of particulate emission is a question of definition. Both SO_2 and SO_3, when discharged to the atmosphere, can form sulfate particulates. The effect of using the Thermal Denox process is that a small fraction of the total sulfur oxides are discharged as a particulate rather than forming a particulate at a later time.

While this change does not appear to be of environmental concern, it is of concern with respect to boiler/furnace operation. It is normal practice to avoid corrosion by sulfuric acid mist by running the back end of the furnace/boiler at a temperature above the acid dew point, generally around 180 °F. In contrast, ammonium bisulfate is a corrosive liquid in the temperature range 400–500 °F. Thus, one might fear that ammonium bisulfate formation might result in a new corrosion problem.

Prior to the first commercial demonstration, a laboratory simulation of a boiler was set up and the corrosion rate of steel in flue gas was measured in the presence and absence of NH_3. No change in this corrosion rate was observed up to the highest NH_3 concentration tested, 45 ppm. Moreover, short-term commercial demonstration has not disclosed difficulties with corrosion or fouling. Long-term experience is being accumulated.

Patent licenses

The Exxon Thermal Denox Process is covered by U.S. Patent 3,900,554. Those interested in purchasing licenses under this patent and technical assistance in using the process may contact Mr. S. Stahl, Patents, Licenses, and Technology Sales Division, Exxon Research and Engineering Co., 1600 Linden Ave., Linden, N.J. 07036.

Don't let winter salt spoil your summer green!
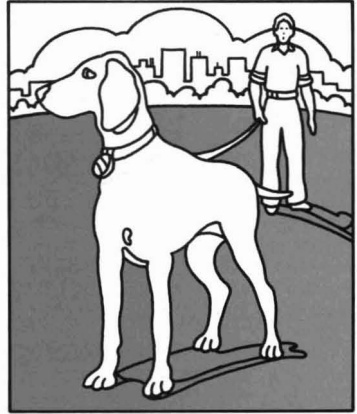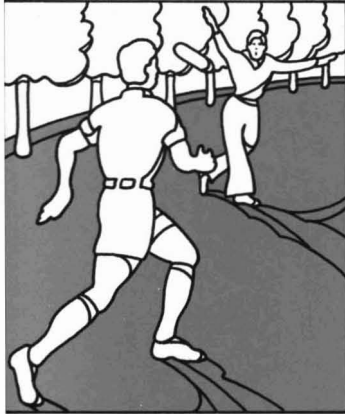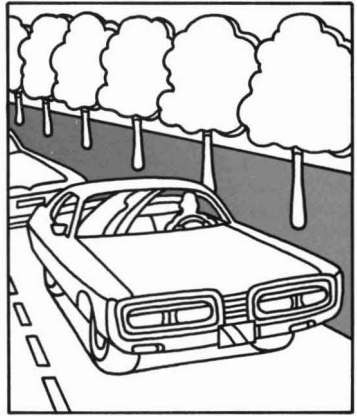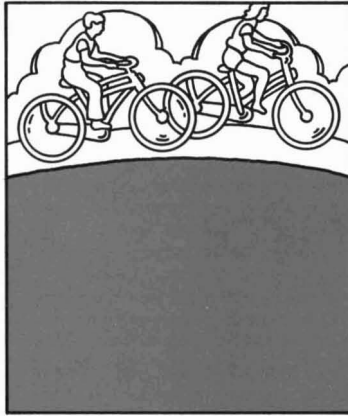
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OUTLOOK
Garbage is a waste is a hazard is a resource
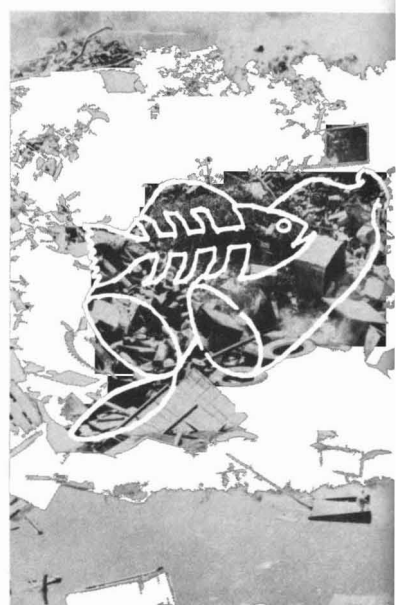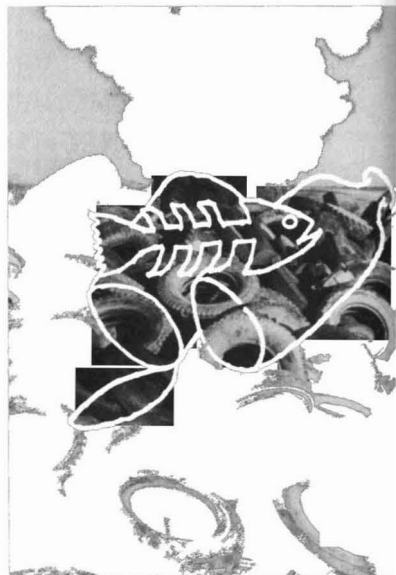
We Americans are so inventive and so intrigued by new products wrapped in ever-so-clever packaging that we flit from one new gadget to another, discarding the old for the new. This throw-away mentality results in mounting piles of refuse and severe headaches for the states and municipalities charged with the ultimate disposal of this solid waste.

Ironically, adding to the disposal burden are the industries who fulfill the public's whims. These industries must comply with air and water laws now on the books, and so they take pollution control measures to prevent pollutants from escaping to the media. But these very control measures generate enormous quantities of solid waste in the form of sludges and other residues.

The usual and, until recently, cheapest disposal method—land disposal—has generally gone unregulated and uncontrolled. Dumped onto open land, into pits, ponds or lagoons, the sometimes hazardous waste leaches from the original disposal site to contaminate ground and surface waters.

But help is on the way! Lost in the wake of the enactment of the Toxic Substances Control Act, another piece of major environmental legislation was passed by the 94th Congress and signed by former President Ford last October. This new law, the Resource Conservation and Recovery Act of 1976 (P.L. 94-580), regulates those wastes destined for land disposal and is designed to recover valuable materials and energy, whenever possible.

Of proportions large

The dimensions of the disposal problem are clearly delineated by the enormous volumes of solid waste generated in the U.S. According to EPA's latest figures (1974) in millions of wet metric tons per year, industry generates 344, municipal wastes amount to 122, and sewage

wastes total 33. Of the total industrial wastes, about 40 million tons/year are estimated to be hazardous. The energy potentially recoverable (1973 figures) from municipal and commercial waste is also tremendous: 899 trillion Btu's or 154 million bbl/y of oil equivalent.

These numbers are expected to rise as the effluent limitation guidelines of P.L. 92-500 go into effect in 1977 and 1983, and as industry begins to meet the requirements of the Clean Air Act. The potentially hazardous portion of solid waste alone is expected to increase by about 3% a year. The generation of all waste has been nearly 8% per year.

According to the advocacy group Environmental Action (EA), municipal waste totaled 150 million tons in 1976, a staggering 1400 lb (4-lb/day) of resource-containing garbage per person. This group estimates that recycling this trash would save the U.S. the equivalent of 400 000 bbl/day of oil, 7% of its iron, 8% of its aluminum and 14% of its paper. Industry's contribution to the waste burden in 1976 according to EA was 380 million wet tons, most of which was destined for disposal in unregulated landfills, open dumps and lagoons.

But America is rapidly running out of land, at least in high-density areas, to dispose of its mounting heaps of solid waste. As Sheldon Myers, deputy assistant administrator of EPA's newly created (mandated by P.L. 94-580) Office of Solid Waste, so aptly stated: "The sink of last resort is going to disappear as an inexpensive option for hiding our mistakes and in its place environmentally sound procedures for dealing with wastes will emerge."

To this aim, P.L. 94-580 was enacted "to promote the protection of health and the environment and to conserve valuable material and energy resources . . ." P.L. 94-580 is the evolutionary product of two

previous laws, the Solid Waste Disposal Act of 1965 and the Resource Recovery Act of 1970; this new law provides for continued and stronger federal involvement in solid waste matters. It significantly extends the federal involvement and, in turn, state involvement, in solid waste management with special emphasis on hazardous waste management, resource recovery and resource conservation.

The act mandates

The major provisions of the law are those pertaining to hazardous waste management; the closing or upgrading of existing open dumps and the prohibition on the establishment of new dumps; and the promotion of resource recovery technology and markets for recovered materials. The latter responsibility is entrusted to the Department of Commerce.

The act clearly spells out an "up front" state and regional presence in the management of solid waste, and spokesmen for the EPA have repeatedly called for major state and local involvement. The act, however, does not set up a program

similar to the construction grant program of the Federal Water Pollution Control Act Amendments of 1972, although it does authorize substantial funds for specific purposes. Total authorizations including general authorizations for fiscal 1978 are $179.7 million, and for fiscal 1979, $158.5 million.

Specifically, the new solid waste law requires that EPA develop guidelines for solid waste management by October 1977. Included in these guidelines are minimum criteria to be used by the states in defining those activities that constitute open dumping. The EPA is also to provide technical assistance on solid waste management, resource recovery, and resource conservation to state and local governments requesting such aid. The EPA will provide this assistance in teams termed "Resource Conservation and Recovery Panels."

By April 1978, the EPA must develop and promulgate criteria and regulations for identifying hazardous waste. By this date, the agency must also list particular materials as hazardous wastes. One of the most troublesome problems for EPA is the

definition of hazardous waste, which is truly the cornerstone of the foundation for managing these materials.

Current agency thinking on the definition's parameters, according to John Lehman, director of EPA's Hazardous Wastes Management Division, calls first for separation of these wastes into acute and chronic hazardous materials. Acute materials would display the characteristics of explosivity, corrosivity, flammability, acute toxicity and infectivity (etiological agents such as viruses and bacteria capable of inducing disease). Chronic characteristics under consideration include chronic toxicity, carcinogenicity, mutagenicity, teratogenicity, persistency and bioaccumulation. Lehman cautions that all these parameters may not appear in the final definition and, at present, the criteria levels have not been set. EPA published an advance notice of proposed rulemaking on the criteria for defining hazardous wastes last month.

More provisions

The agency also must promulgate, by April 1978, regulations and standards covering the total life of hazardous waste from its generation to ultimate disposal. These regulations and performance standards will affect generators, transporters and owners/operators of treatment, storage or disposal facilities.

The hazardous waste will be tracked at each step of its life through the use of a manifest system. This system will identify the quality, composition, origin, routing and destination of hazardous waste and assure that all generated hazardous waste is destined for a facility holding a permit signifying that it can properly handle these dangerous substances in an environmentally sound manner. Regulations governing permits are to be promulgated by the agency by April 1978.

To assist the states in the development of hazardous waste management programs, the EPA is to develop guidelines by April 1978. States will be authorized to manage their own programs if, upon compliance with EPA's guidelines, they receive the agency's authorization. The law authorizes $25 million for each of fiscal 1978 and 1979 to assist the states in the development and implementation of hazardous waste programs.

To foster environmentally sound state or regional waste disposal programs, to encourage the maximum use of valuable resources, and to stimulate resource conservation, the new law authorizes funds totaling $30 million in fiscal 1978 and $40 million in fiscal 1979. An additional $15 million is specified for each of these years for grants to implement specific programs of approved plans.

(Continued)

Operational resource recovery systems [a]

Location	Process	Output	Status
Ames, Iowa	Baling; screening; other mechanical separation plus [b]	RDF [c] for use by utility; baled paper; [d]; and other non-magnetic metals	Operational
Baltimore, Md.	Landgard® process: shredding, pyrolysis, water quenching, magnetic separation	Steam; magnetic metals; glassy aggregate	Shakedown stage—city only; Monsanto pulled out
Baltimore County, Md.	[b]	RDF; glass for secondary products; [d]	Partially operational; fully operational by spring 1977
Brockton, Mass.	[b] plus other mechanical separation	Eco-Fuel II® for industrial boiler; magnetic metals	Fuel is being made; presently testing
Chicago, Ill.	[b]	RDF for use by utility; magnetic metals	Operational
Franklin, Ohio	Hydrasposal™/Fibreclaim™ proprietary processes using wet pulping and magnetic separation; heavy media; jigging; electrostatic precipitation; optical sorting	Paper fibers; colorsorted glass; [d]	Operating since 1971
Milwaukee, Wis.	[b] plus other mechanical separation	RDF for use by utility; bundled paper and corrugated; glass concentrate; [d]	Shakedown phase; fully operational spring 1977
Nashville, Tenn.	Incineration	Steam for urban heating and cooling	Operational
New Orleans, La.	[b] plus other mechanical separation; hand-picking (paper)	Paper; [d]; non-magnetic metals; glass	Operational May 1977
San Diego County, Calif.	[b] plus other mechanical separation; froth flotation; pyrolysis	Pyrolytic oil; magnetic, non-magnetic metals; glass	Beginning shakedown mid-May 1977
Saugus, Mass.	Water-well incineration; magnetic separation	Steam for industrial use; magnetic metals	Operational
South Charleston, W. Va.	Purox™ oxygen converter (pyrolysis); shredding	Fuel gas	Operational demonstration plant

Source: National Center for Resource Recovery

[a] As of January 1977 [b] Shredding; air classification; magnetic separation [c] Refuse-derived fuel [d] Magnetic metals, aluminum

State plans must meet certain minimum requirements to be eligible for such funds. Among these requirements are:
- the prohibition of new open dumps
- a plan to close or upgrade all existing open dumps
- the disposal of discarded materials at a resource recovery facility, in an approved sanitary landfill or in an environmentally sound manner
- the establishment of regulatory powers within the state to carry out the solid waste management plan.

By October 1977, the EPA must publish criteria that can be used by states to distinguish open dumps from sanitary landfills. The agency is now wrestling with the problem of whether pits, ponds and lagoons used for the disposal of industrial wastes are to be considered open dumps. One year later, October 1978, the EPA must publish an inventory of all open dumps in the U.S. By 1983 all open dumps must be closed or upgraded to sanitary landfills.

The new law provides for authorizations of $25 million for fiscal 1978 and 1979 to assist rural communities in managing their solid waste problems. The new law also authorizes $45 million in fiscal 1978 for special studies, RD&D, training and information activities.

The lawmakers have also been generous in their authorizations for the general administration of the new law: $35 million in fiscal 1977, $38 million in fiscal 1978 and $42 million in fiscal 1979. At least 30% of these funds must be used to implement the hazardous waste program, and another 20% must be used for the Resource Conservation and Recovery Panels.

Roles are defined

The act gives the Department of Commerce the responsibility for developing standards for the substitution of recovered materials for virgin materials. Commerce must also stimulate the development of markets for recovered materials and, in general, promote resource recovery technology. At present, however, the line separating a commodity (recycled material) from a waste is hazy.

The law also requires that the federal government institute a policy of procuring recycled materials in lieu of virgin materials when the former meet certain specifications and can be purchased at reasonable prices.

This new legislation makes very clear the preeminent role to be assumed by the states in the administration and enforcement of solid and hazardous waste management programs. But, the act does not require that the states "play the game." Should states fail to act, the EPA would have to do the job; it clearly has the power to step in.

Efforts under way

In the face of burgeoning mounts of solid waste, steps are being taken to decrease the amount destined for land disposal, and to recover both valuable materials and energy.

A 10-year-old European innovation has recently been transported to American shores. The industrial waste exchange, which acts as a mediator between buyer and seller, makes one company's wastes another's feedstock. Such an exchange has been flourishing for one year in St. Louis, Mo. This exchange has made 13 deals during the year involving baghouse dust, waste oils, lime slurry and spent sulfuric acid, among other items. Other regions are beginning to pick up on this clearinghouse idea.

The Iowa Industrial Waste Information Exchange, which is supplying information on items for exchange to businesses in that state, went into operation in April 1976. In October of last year the Houston Chamber of Commerce began an information program on recycling chemicals.

These waste exchanges act merely as conduits of information; they take no part in negotiating transactions or in setting prices. But they serve a very beneficial purpose, both to industry and to the protection of America's environment.

Communities or, in some cases, states prodded by scarcity of land, spoilage of potable water sources, economic incentives, the need for recovered materials and energy, and the technical wherewithal to initiate resource recovery facilities, have begun the search for more environmentally acceptable ways of getting rid of their discards.

Several systems have emerged, from the simple but labor-intensive source-separation programs to the more technical materials and energy recovery facilities. The National Center for Resource Recovery (Washington, D.C.) keeps a close watch on these emerging systems. Their latest tabulation shows that almost 31 facilities for materials and/or energy recovery were in operation (9); in the shakedown stage (3); being planned, designed or constructed (6); being contracted for or at the bid stage (3); or had requests for proposals issued (10). Two additional projects are under way to recover methane gas from sanitary landfills. America's throwaway mentality is slowly being whittled away.

Solid waste by any other name—trash, garbage, refuse, discards, rubbish, sludge, hazardous waste—is still waste requiring disposal. The Resource Conservation and Recovery Act of 1976, and the recent spate of state and local efforts, go a long way in assuring that all solid waste, including the most hazardous variety, will be disposed of in an environmentally sound manner.   LRE
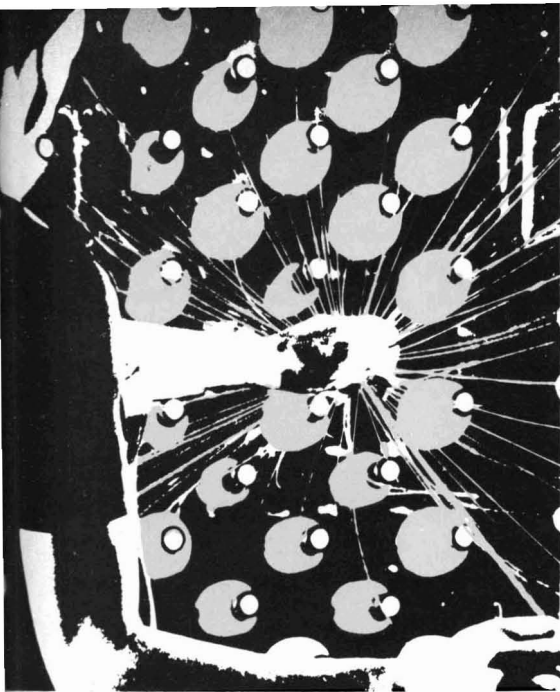
Textile plants are processing cleaner wastewater discharges

The American Association of Textile Chemists and Colorists discuss the best technology for meeting pressing practicable deadlines

There is nothing like a colorful environment, particularly if one thinks of the myriad colors of nature. However, nature did not intend that the colors in the environment come from dyes, dye wastes, and related chemical compounds. Such colors come under the heading of pollution, especially in the water. Accordingly, to address this problem, the American Association of Textile Chemists and Colorists (AATCC, Research Triangle Park, N.C.) organized its Committee RA 58, Environmental Science Technology.

It started in 1952

The stimulus for the organization of what is now Committee RA 58 was the passage, in 1951, of the North Carolina Stream Sanitation Law—that state was then rapidly becoming a major world textile manufacturing center. Thus, in 1952, the AATCC formed RA 58's predecessor, the National Committee on Stream Pollution. That committee had certain objectives as regards pollution:

• to be concerned primarily with textile industrial wastewater
• to promote technical investigations on specific problems in this field
• to study new methods for the examination and treatment of textile wastes
• to study BOD determinations as a measure of pollution in textile wastes
• to study specific textile chemicals as related to pollution
• to publish case histories.

Currently, the Committee's scope is to provide a forum for the dissemination and exchange of knowledge on problems concerned with air and water conservation and pollution abatement. Another function is to encourage research on textile waste disposal.

Then and now

One of the first accomplishments of the National Committee on Stream Pollution was the compilation and publication of a Bibliography on Textile Waste. This happened in 1955, and in that year, and the succeeding ones, the committee publicized pollution control research work of some of its member mills. The principal effort was to show how highly alkaline textile waste could be biologically treated without addition of acid, in a cost-effective manner. Also, during those years, cooperatively with the U.S. Department of Health, Education, and Welfare, the committee put out the industrial guides to wool-processing wastes, cotton-processing wastes, and laundry wastes.

During the 1960's, the committee's research began to pay dividends. Based on what was learned, textile companies began installing aeration-type activated sludge systems to treat textile wastes, and create a forerunner for "best practicable." Also there was a move to use low- or no-BOD chemicals, development of environmentally "cleaner" detergents, and publication of a waste guide for synthetic textile fiber processors.

From 1969 to now, the committee launched a series of symposia concerning textile industry pollution control, and started exchanging technological know-how with other industries—especially paper and leather. By 1971, the RA 58 Committee was constituted in its present form, and branched out to cover air, as well as water pollution. In 1972–1973, it cooperated in an EPA study concerning radiation as a means of treatment. Since then, the committee has also become concerned with OSHA matters. Its fourth symposium was covered in *ES&T* (August 1975, p 706).

Meeting in Atlanta

Would you like to hear, for example, how ozone and chlorine compare in textile-chemical waste treatment? Might chlorine become *passé*? Allison Maggiolo of Bennett College, Greensboro, N.C. (*ES&T*, January 1977, p 27) will explain what he found out, at the AATCC RA 58 Committee's Fifth Environmental Symposium, to be held at the Omni International Hotel in Atlanta, Ga., on March 29–30. Other papers will cover toxic chemicals, water reuse, monitoring, bioassays, and numerous other practical topics discussed by speakers from academia, government, and industry.

Hope to see you in Atlanta!   JJ

AATCC committee chairman Lesslie
Committee organized in 1952
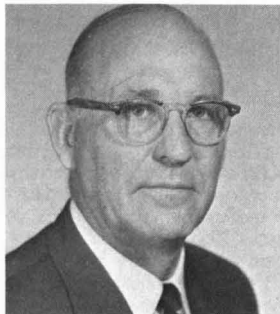
Looking for ways to take the economic pain out of compliance, and maybe come up with some new items to sell? Then consider this approach . . .

. . . Don't control pollution; prevent it!

"This is a noteworthy occasion—when the makers and enforcers of environmental rules and those who must comply with them meet harmoniously on common ground." With these opening words, Lewis Lehr, president of U.S. operations for the 3M Co. (St. Paul, Minn.), keynoted the conference, "Beyond Environmental Regulations: Industry Takes the Initiative." The conference, held at Chicago, Ill., in January, and attended by almost 400 people, about 98% of whom were from industry, also heard Lehr note that the cooperation of government and industry in organizing the conference may be "a sign of mutual maturity." It was sponsored by EPA Region V, the Department of Commerce, chambers of commerce, and industrial firms.

To Lehr, the conference presented two significant points:
- the need for government and industry alike to look beyond more pollution removal to protect the environment
- recognition of industry for taking direction—"a refreshing change from being castigated as Ogre of the Eco-System." The initiative Lehr meant is the effort to prevent pollution at the source, where possible, rather than control it at the end of the pipe. This effort is essentially energy and resource conservation/reuse oriented, and is being increasingly exerted by a number of companies. However, its broadest and most thorough application is presently found at 3M, where it is called, "Pollution Prevention Program", or "3P".

A recession baby

In a sense, the 3P program was born of the 1974–1975 recession, during which many companies sought ways to cut expenditures. Accordingly, in late 1974, at a top management meeting of 3M, chairman Raymond Herzog asked where outlays could be reduced. When Herzog turned to Joseph Ling, 3M's vice president for environmental engineering and pollution control, Ling said that there was no way that pollution control (pc) costs could be cut. At the time, Ling foresaw that environmental regulations would grow ever more restrictive, and that the EPA, other agencies, and Congress would most likely not ease up on their cleanup achievement and maintenance goals, even if the U.S. economy was "hurting".

Thus, Ling suggested to 3M's management that rather than control pollution, prevent it. Then, there would be little or nothing to control, and even a possible solution to the problem of meeting 1985 zero discharge goals. By contrast, an end-of-pipe pc "black box" would use up 90–95% of company environmental capital. Then, because regulations become stiffer, the black box must become more expensively elaborate, and costlier to operate and maintain. Moreover, Ling pointed out that trained personnel are needed to run these black boxes, and these people do not come cheaply.

Ling also noted at these management meetings that once a capital investment in a black box is made, the company "is stuck with it forever. Also, the device could produce bad 'gunk' one may have to dispose of, and that could add much to one's problems," Ling reasoned at the time.

So chairman Herzog asked Ling, "Joe, can you come up with a money-saving program incorporating your concept?" Ling answered, "Yes, but not with a handful of people. But if the 4000 technical people we have at 3M could help, we can do it." Herzog gave his consent, the 3P program started in 1975, and the conference—an outgrowth of the program—learned from Ling that 3M had, by late 1976, launched 19 pollution prevention projects. These projects have eliminated 73 000 tons of air pollutants and 500 million gal of polluted wastewater. They also saved $11 million in actual or deferred pc equipment and operation, energy, and raw materials costs, as well as product sales over the next few years, according to 3M.

How 3P works at 3M

In order to be considered by 3M, a proposed project must first meet two criteria:
- It must reduce or eliminate a pollutant that is, or could become a problem.
- It must carry monetary benefits through reduced or deferred pollution control or manufacturing costs; increased sales of an existing or new product; or other reduction in capital or operating expenses.

There are secondary guidelines, as well. The project should reduce energy consumption, and improve efficiency in

3M vice president Ling
"End-of-pipe controls cost too much"

Rep. Florio
Wants to help innovators

materials and resource utilization. It should also involve a technical accomplishment, innovative approach, or unique design. The pollution prevented must occur at the source, not through addition of pc equipment. The pollution prevented must also stem from generally accepted practice, and be "first generation". Moreover, the individuals working on a 3P project should have made concrete efforts to reach the accomplishments, as well as put forth the idea.

If a 3P proposal meets the criteria that 3M set forth, it becomes a "recognized" project. Employees who launch such a recognized project receive a certificate signed by chairman Herzog, vice presi-

dent Ling, and their division vice president or general manager.

Legislative impact

Rep. James Florio (D, N.J.), whose district takes in Camden, told the conference that the pollution prevention approach might well have a legislative impact, especially because it entails an energy and resource conservation aspect. He said that Congress recognizes that a company has a very hard time trying to comply with existing and forthcoming regulations, and developing innovative approaches at the same time. Thus, he noted that, for example, in the Clean Air Act Amendments, if they pass (they died in the last Congress), he hopes to see a provision granting a company a 5-year compliance extension. The company would have to demonstrate that it is innovating, particularly if costs could be cut, and resources and energy could be conserved. However, some compliance schedule would be mandated, so that "no one gets a free ride," Rep. Florio explained.

Rep. Florio acknowledged that present environmental legislation and rules, as well as tax regulations and incentives, emphasize the end-of-pipe pc approach. However, he predicted that Congress would take a much closer look at process changes and other prevention concepts, especially as more information becomes available from meetings such as the Chicago conference, and other sources. Still, he warned the meeting that Congress would not move automatically—"Like it or not," he said, "laws will be put together

by politicians. If you feel that certain provisions or changes are necessary, come in, get involved in the legislative process, give your expertise, so that we will have the necessary information with which to make sound judgments."

3M's Ling added that he foresees that legislators, regulators, and businessmen *can* work together. He also predicted that legislation will take increasing cognizance of the prevention/conservation approach, and observed that "technology itself is not the problem; those who apply it sometimes are."

How about self-regulation?

In 1972, Carl Gerstacker, then chairman of Dow Chemical Co. (Midland, Mich.), said that his company would meet its own guidelines, or those of government, "whichever are tougher." Still, meeting such guidelines had to be done in a way that would enhance the profit picture, for, as in any company, profits affect the jobs, pay, dividends, and futures of employees, management, and stockholders. Earle Barnes, executive vice president of Dow, mentioned a number of steps that Dow took toward meeting tough guidelines.

For example, in the drier climates of the southwestern U.S., Dow's Western Division has converted everything to solar evaporation. This, of course, saves energy, and allows for virtually zero discharge. At another plant, Dow recovered hydrocarbons worth about $100 000/y, representing a 3% return on the investment in a certain process.

In the light of Dow's strict approach,

Barnes recommended that industry be given a chance at environmental self-regulation, such as ERDA is allowing Dow for 2 years on the Equal Employment Opportunity (EEO) program. Barnes predicted that Dow's, and other companies' in-house administrators would be much tougher and more thorough, just as they are on the EEO program. And Barnes has a precedent. In the securities industry, for example, the National Association of Securities Dealers (Washington, D.C.) is one of the strictest, most thorough-going industry self-policing organizations that one could imagine. An environmental self-policing organization could be just as tough, or more so.

A systematic approach

Perhaps a clear idea of a systematic approach to conversion, where possible, of pollution control to prevention was offered to the conference by Richard Sawinski of Hydroscience, Inc. (ES&T, January 1975, p 22). He recommended a thorough look at process modification, involving all phases of chemistry, equipment, operation, waste segregation/reduction, and recycling. The specific steps he advocated were baseline evaluation, problem definition, process definition, process design, and waste characterization aimed at developing a logical work plan with economic incentives for preventing pollution at the source.

Thus, for one client, Hydroscience found a way to recover SO_2 from spent pulping liquor, rather than sewering the waste. The result was saved sewer fees and other money, and led to smoother process operations because of "debottlenecked" evaporators, and recycled wastewater. Another client reduced emissions toxic to plants by 90%, and increased saleable product yield by 10% through process change, Sawinski said.

The prevention approach, however, will not become instant reality. It will take considerable development time, as well as interdisciplinary cooperation within a company or industry, and between industry and government. But it is an idea whose time has not only come, but is overdue; perhaps better late than never. The prevention/conservation concept, however, might be a key to taking much economic pain out of pollution abatement, and, perhaps, generating profits from otherwise lost by-products. It is an idea that 3M's Ling worked with for a long time, and if he had one complaint about the conference—in large measure brought about through his efforts—it was that the meeting did not take place at least 15 years ago! JJ

Making pollution prevention pay:

technical people came up with some answers

Project	Estimated benefit	Type of benefit	Pollution eliminated	Amount eliminated
100% solids coating	$3 million	Pollution control eliminated	Hydrocarbons	35 000 tpy
High-conversion polymer	$1 million	Pollution control eliminated	Odor	80% reduction
Cooling water recycle	$200 000	Pollution control eliminated	Water	1.5 mgd
Modified polymer coating	$800 000	Operating cost savings	Hydrocarbons	4.5 million lbs/y
Product reuse	$500 000	Operating cost savings	Incinerated scrap	100 tpy
Incinerator improvement	$175 000	Operating cost savings	SO_2 and particulate	21 tpy
Resin reformulation	$330 000	Sales retained	Mercury	5000 g/y

Source: 3M Co.

the second incineration venture of the *Matthias III,* stack monitors for carbon dioxide, carbon monoxide, oxygen, and organic chloride apparatus were supplied by Drägerwerk, AG (Lübeck, W. Germany). These monitors were installed and operated by David J. Davies, a Drägerwerk employee.

No significant effects on the ocean were found below the plume of either ship. There were no significant changes in the pH or in the organic chloride content of the ocean in either case. Even when ocean samples were subjected to gas chromatographic separation and concentration, followed by mass spectrophotometric analysis, the level of organic material lies below or at the level of sensitivity of the analytical system.

Ocean incineration anew

Further trials chart the way of this technology for chemical wastes disposal

What is new with ocean incineration of waste chemicals? Shell Chemical Company (Houston, Tex.), the first user of the technique in the country (*ES&T,* May 1975, p 412), last month began burning organochlorine chemical wastes once again on an incineration ship in the Gulf of Mexico.

Now, under an EPA special permit the Shell Chemical Co. has been granted a 2.5 year permit to burn at sea as much as 50 000 metric tons of chemical waste by-products. This burn (February–March 1977) will destroy about 16 000 metric tons. The Shell liquid wastes are by-products—organochlorine materials from five process waste streams—generated in the manufacture of epichlorohydrin, epoxy resins, glycerine, and vinyl chloride; all streams result from purification processes.

Previously, Shell Chemical, as environmental watchers attest, was granted two research permits and an interim permit (see box) to burn similar wastes in the Gulf of Mexico. The data from these incinerations showed that the incineration of the Shell wastes were compatible with provisions of the Marine Protection, Research and Sanctuaries Act (P.L. 92-532).

During October 1974–January 1975 similar wastes from Shell Chemical Co. were incinerated on board the incinerator ship, *Vulcanus,* in the Gulf of Mexico. Extensive monitoring conducted in the early research incinerations qualified the *Vulcanus* to burn these wastes under an interim permit and now under the provisions of a special permit. One difference in the two permits is that the research permit requires elaborate monitoring and analysis of combustion products. Qualification tests for the incinerator ship

Matthias III were conducted last fall in the North Sea.

Operations

As stated, these wastes are being incinerated in a special area in the Gulf of Mexico, some 190 nautical miles south of Cameron, Louisiana, and 170 nautical miles south southeast of Galveston, Tex. For purposes of the environmental impact statement, this site in the Gulf of Mexico is good for five years. EPA filed its impact statement in July 1976.

Although the Shell permit leaves open the option for the selection of incineration ships, the only incinerator ships listed in the Shell special permit are the *Vulcanus* and the *Matthias III.* Qualification test burns aboard the *Matthias III* occurred August 29–September 3 in the Dutch incineration area of the North Sea off the coast of the Netherlands. Based on this burn, EPA contract representative Howard J. Fisher, who witnessed the operation on the *Matthias III* said that the two ships—*Vulcanus* and *Matthias III*—appear to be equivalent, based on performance criteria established by the U.S. EPA.

Ideally, the complete incineration of a chloroorganic material yields water, carbon dioxide, hydrogen chloride, and nitrogen. Because of its high chloride content, the ocean is peculiarly adapted to receive large amounts of hydrogen chloride without serious imbalance of chloride content. Furthermore, because of its built-in carbonate-bicarbonate buffering system, the ocean is also able to deal with the acidity produced by the HCl in order to maintain its normal pH of approximately 8.

To date, the monitoring and sampling of both the air and water were pursued in the incineration areas. For example, on

Earlier, on the *Vulcanus* burns in the Gulf of Mexico, it was noted that the stack sampling operation suffered from problems of inadequate reach of the sampling probe, resulting in the inability of either probe to draw samples of gases from all parts of the stack exit.

The *Vulcanus* is being sampled with a probe designed by TRW (Redondo Beach, Calif.) under contract to the U.S. EPA. When *Matthias III* is tested an even longer probe will be required because of the reach, owing to the large diameter (15 m), of the furnace on this ship. The French scientists of the French Atomic Energy Commission (CEA) used similar equipment during a previous *Matthias III* burn (June 1976).

The French scientists also looked at an optical method for measuring temperature and identifying components of stack gases by IR emission spectroscopy. They concluded that the system held promise but that it was still in the research stage.

Analyses

The chemical waste materials are analyzed for:
- calorific value (kcal/kg or Btu/lb)
- chlorine content in wt %
- pH
- trace elements such as heavy metals
- presence of multiorganic compounds
- bioassay of wastes.

The first three parameters point out combustion details; the latter three serve as environmental indicators. In actual practice the throughput of the *Vulcanus* in the Gulf of Mexico was 25 tons/h. The throughput on the second voyage of *Matthias III* was 28 tons/h.

The regulations

The *Vulcanus,* a 4770 dwt chemical tanker of Ocean Combustion Service, a subsidiary of the Hansa Line, and the *Matthias III,* a 19 300 dwt chemical tanker, of the SBB (Stahl- und Blech-Bau GmbH) are double-hulled vessels that meet all applicable requirements of the IMCO concerning transport of dangerous cargoes by tankers. The IMCO, the Intergovernmental Maritime Consultative Organization, a specialized agency of the United Nations, has under study the regulations and safety of such ships.

It may make economic sense to have a burn lane across the ocean. The economics of operation could favor a sea lane for burning across the Atlantic; these problems will be addressed by the IMCO safety and regulations committee.

On the international scene, The Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter was negotiated in London in November 1972. This convention became effective on August 30, 1975, when 15 countries ratified it. The IMCO organization was designed to implement the convention and held a first meeting on the subject September 14–20, 1976.

Incineration at sea is one of the agenda items of this convention; it will be discussed further at a second meeting in London this September. Some items for discussion include:

- identification of incinerator ships
- safety considerations
- sea route for incineration ships
- special provisions for the prevention of marine pollution from incineration.

The burners

The *Vulcanus* has two incinerators with three nozzles in each, whereas the *Matthias III* has only one incinerator and 20 burners around the base of the furnace. An additional feature of the *Matthias III* is the coincineration of solid wastes and wastes stored in drums with the liquid waste.

On each incineration ship the burners are a liquid/air type with air and liquid being fed through a firing nozzle through concentric tubes. The 20 liquid waste burners on *Matthias III* are arranged symmetrically and evenly spaced around the base of the incinerator. The burner flame, which can be seen through the burner mounting ports, was observed to be bright yellow to white, free of dark areas, and to be stable and non-sputtering.

Storage facilities for the chemical wastes are below decks in tanks that are contained inside the double hull. On *Matthias III,* liquid wastes are carried in nine inner tanks inside a double hull to eliminate the danger of ocean pollution in the event of a collision. One emergency shut off system goes into effect when the incineration temperature goes below 1200 °C, although this system was not in effect during the August 29–September 3 burn.

Flame temperature was measured by an optical pyrometer and wall temperatures were measured by several thermocouples. A minimum average flame temperature of 1200 °C was maintained. Calculated residence time for *Matthias III* is of the order of 2.6 s at 1200 °C; for

Vulcanus it is of the order of 1 s at 1200 °C.

On the *Vulcanus,* with two combustion chambers, three burners are located roughly symmetrically around the bottom of each furnace. The *Vulcanus* has rotating cup-fuel injection that provides vortex turbulence and distribution of feed throughout the entire chamber.

The following environmental items must be resolved:

- criteria for designating incineration zones
- special provisions for controlling the operation of incinerating systems.

The following safety considerations must be resolved:

- appropriate identification signals for ships engaged in incineration at sea. For example, without these signals another ship might regard the "burning" ship as one in distress and come into the plume
- safety measures including the possible need for specifying a suitable route for incinerator vessels on a trans-Atlantic voyage. Here, the need for international controls are recognized.

Federal view

EPA regional administrator John C. White for Region VI said, "We have been encouraged by the prospect that ocean incineration is an acceptable, if not desirable, alternative to the disposal of these chemical wastes." He concluded, "We have been helped a great deal in this effort by several state, county, and local agencies, as well as other federal agencies, and we want to express our thanks to them for helping us evaluate this promising program."   SSM

Burns to date

Where	When	What	Ship
Gulf of Mexico	Feb 1977 EPA special permit	Shell Chemical wastes	*Vulcanus*
In the North Sea	August 9–September 3, 1976	—	*Matthias III,* 2nd burn
In the North Sea off the Dutch Coast	1st week June 1976	French chemical waste	*Matthias III,* initial operation
Gulf of Mexico	October 1974–January 1975 2 EPA research permits 1 EPA interim permit	Shell Chemical wastes	*Vulcanus*
In the North Sea off the Dutch Coast	For approximately 6 yrs	—	—
The competition	*Vulcanus* 4770 dwt tanker		*Matthias III* 19 300 dwt tanker
Combustion units			
Waste carrying capacity	4200 metric tons		15 000 metric tons
Burntime for capacity	168–210 h[a] 7–9 days		375–600 h[a] 16–25 days
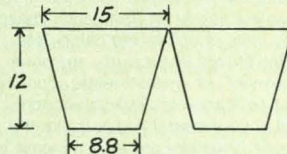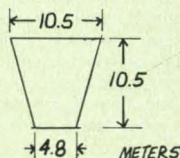
[a] Based on rates of 25–40 metric tons/h.

FEATURE

Siting power plants

Environmental and economic costs vary as a function of
site parameters and plant-design technology options;
estimating these costs is difficult at best

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Estimating economic and environmental costs for proposed power plant sites is a difficult art, which becomes even more difficult when a utility or a state wants to systematically screen an entire service area or region. Looking at a large region inevitably involves generalizing about environmental impacts ("costs") as well as the usual engineering and financial costs. Such problems are being faced more often in the early site reviews performed by the Nuclear Regulatory Commission (NRC) for nuclear stations, and in the site-banking programs of some utilities and states—Maryland, for example.

Certain methods are described that have been inspired, in part, by the ongoing efforts of the Maryland Power Plant Siting Program to acquire alternative sites to ensure backup sites for future energy needs. Illustrative costs of the type that could be used in such a program are also given.

Prices and quantities

In Maryland, one agency is responsible for the total cost-benefit analysis of a siting decision in a more comprehensive way than federal agencies are; for example, in the cost-benefit analyses done under the National Environmental Protection Act. The Maryland program has to invest tax-generated funds for future use in the acquisition of sites. The financial costs associated with power generation are expressed in dollars, and the screening process often involves elaborate numerical computations that compare total financial and environmental costs. In one way or another, the size of total costs are compared, so it would be rather artificial to insist on not expressing environmental costs in dollars. Also, expressing nonmarket costs such as habitat impacts in dollars tends to prevent one from hiding ill-considered value choices under the blanket of unfamiliar valuation units, such as "natural resource units" or "compatibility rankings."

Therefore, let us consider the problem of expressing both ordinary economic and environmental impacts in terms of dollars. Since units of dollars are being used, it is convenient to separate the impact into quantity and price.

The "quantity" of environmental goods is analogous to the quantity of ordinary marketplace economic goods, while the "price" of environmental goods is like the price of the usual market goods. Therefore, the environmental impacts of a power plant can be fitted neatly into the same kind of scheme that one applies to building a new railroad spur into the plant site. In this example, the quantity of "railroad" could be given in terms of new miles of track needed, and the price could be the total dollars needed for systems expenditures corresponding to each track mile. Similarly, the quantity of a particular kind of envi-

ronmental good could be specified as the area of habitat corresponding to a particular species that may be destroyed or degraded by the siting, while the price could represent the dollar value one attaches to the loss or degradation of habitat.

Such prices and quantities may take on rather extreme values. If one accepts that certain standards for water quality mandated by law, for instance, must be achieved, then the quantity of environmental goods (or "bads") associated with changes in water quality could be associated with a price of zero dollars for water quality values below the limits of the standard and infinite dollar prices for values over the standard. Zero prices and infinite prices correspond here, of course, to a yes or no decision on the prospective siting area.

Methods of valuation

Prices and quantities for the usual kind of financial or engineering factors—such as railroad spurs and protective levees—can be readily determined, at least in principle, in a cost-benefit analysis. In practice, of course, the art of cost estimating is a difficult one. Cost estimating is complicated here by the need to estimate average costs of factors over fairly large geographical segments.

Estimating environmental costs, of course, is even more difficult, in that one often does not know how to assign the costs even in principle. Some "environmental costs" are really losses of economic production, such as the conversion of farmland to a cooling lake for a power plant. In principle, this kind of substitution can be treated by standard types of economic analysis. Other environmental costs can be evaluated by correlation with the costs of abatement measures, even if those measures are not actually taken. Such abatement costs, however, can only supply a minimum value for environmental impact costs, but a lower bound is often far better than nothing.

Environmental costs may also be detected indirectly in the form of certain "transaction costs." The siting of all nuclear power plants and of many fossil power plants is regulated by state or federal agencies. The regulatory process incurs many transaction costs: costs of environmental report preparation; costs of hearings and public meetings; and especially the cost of extra delays resulting from unresolved environmental (or safety) issues. These are all real money costs to the utilities and are passed along to either the ratepayer or taxpayer. Experience in regulation of power plants is not yet sufficient to determine the exact value of expected transaction costs for a particular kind of siting. However, existing experience is adequate to provide some approximate estimate for many otherwise intractable environmental cost problems.
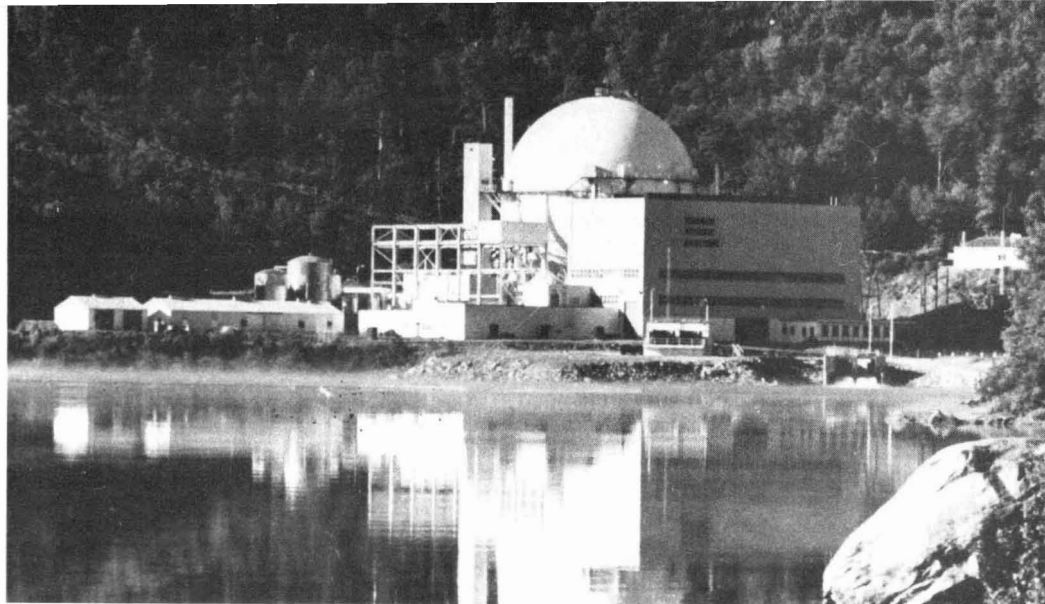
Another approach is to observe choices of different design alternatives that previous planners have made. Here, one presumes that those choices were made to avoid uncertainty about either state or federal regulatory approval or to shorten the regulatory process. For example, it is relatively easy to find examples of a utility's choosing a cooling tower instead of once-through cooling, especially in estuarine areas where effects on nursery grounds of important aquatic species are feared, but the probable extent of such impacts may be uncertain. Since the biological as well as the economic or economic-environmental impacts are so obscure in such cases, a direct measurement of cost would be difficult.

However, the fact that in certain cases the more expensive cooling tower option was chosen could serve as an indirect indication of the minimum value of the environmental costs involved. In some cases, one may also have several alternative closed-cycle cooling system options, and one may be able to imply differential environmental costs by observing the actual environmental equivalents of the economic costs chosen in substituting cooling ponds for cooling towers or vice versa. One might denote this type of reasoning—really a hypothetical abatement calculation—as a costing by a "balancing out of alternatives."

In general, the costs per unit impact are not independent of the quantities of impact involved. But often it is difficult enough to determine even a "price" for any one "quantity" of environmental impact, much less a complete environmental impact supply curve. On the other hand, data or even intuition may suggest that some total environmental cost curves can be relatively well approximated by linear forms (constant price per unit of impact) while other costs—of the standards type—can only take on values of either zero or infinity, depending on quantity of impact.

Where information is lacking, but linear or zero-infinity approximations seem inappropriate, a logarithmic extrapolation may be useful when the environmental price obviously becomes very large for large impacts. For the assumed logarithmic functions, "intermediate" impact values are then needed to specify the shape of the curve (see table). Naturally, the use of such extrapolation formulas or, alternately, of zero-infinity formulations, remains a matter of judgment.

Design options, siting costs

Environmental and economic costs vary as a function of site parameters and plant design technology options. Design technologies that can be considered are of several kinds. First of all, one can consider fuel type: nuclear, coal or other fossil fuel. Then there are cooling-type categories: once-through, cooling towers (natural draft, mechanical, dry), and cooling ponds. Also relevant are such subsidiary design features as height of smokestack for fossil plants and special "esthetic screening" designs for power plants located near natural areas.

The goal of the analysis is to identify relative siting feasibility for different geographical grid points (on a 9-acre scale) for each reasonable permutation of a set of specific design technologies. Some examples: nuclear with cooling pond or coal with once-through cooling and 400-foot smokestack. Then the impacts and their cost on the total environmental and economic picture of the region for the design technologies specified are determined. These impacts are divided into several categories: geology, seismology, meteorology, population, hydrology, ecosystems, land use, transportation, and transmission lines. This particular breakdown is found in a *Regulatory Guide* issued in 1975 by the Office of Standards Development, NRC.

Geology. An obvious possibility for specifying a quantitative geological criterion for large-scale site screening is slope. Land-use data are often available for slopes in several categories (1–5%, 5–10%, 10–20%, 20–30%, and over 30%). Extra construction costs per cubic yard of material to be excavated can be roughly estimated for each of such slopes.

The average one-gigawatt station has been taken here as having an area of 130 acres, and the amount of extra material to be moved has been taken as the volume of a uniform wedge having a square base and an altitude equal to the average slope of the land. The costs of moving the material obviously depends on the nature of the material (soil or rock) but for a very rough average, Federal Highway Administration figures for average earth-moving costs on highways have been used. This price apparently supposes that hauling of cut and fill material will be only over short distances, so it may represent a minimum price for many configurations. The conversion-factor cost, as given in the table, is $2.5/kWe/percent slope or $25 000 000 for a one-gigawatt plant on a uniform 10% slope. It can probably be assumed here that for the plant sizes of interest, the relationship is linear in kilowatts of capacity.

Other geologic parameters could also be costed. For example, areas having a liquefaction potential greater than a given figure could, at least in principle, be evaluated as incurring an extra cost per square foot of construction area, and a cost then assigned analogous to that for slopes.

Seismology. As far as the safety of the nuclear power plants is concerned, NRC guidelines for seismic investigations may be taken as an indication of possible health costs that might be risked by the public in the event of earthquakes. Since the

guidelines deal with borderline cases involving a distance of five miles from a "surface capable fault" greater than 1000 feet in length, such a fault could be used as a basis for mapping relative risks of locating plants at different grid points on a map.

To convert such risks into a dollar value is difficult, but a "balance of alternatives" technique could be used. For example, the NRC requires that applicants for nuclear power plants design against certain "safe shutdown earthquakes" and such earthquakes are defined in terms of expected ground accelerations (measured in units of g) at the site. Admittedly, there has been only limited experience in determining the extra costs of designing against particular safe shutdown earthquakes. However, construction of a nuclear plant might be inadvisable at very high g's, so a logarithmic form is suggested in the table, going to infinite cost at 0.5 g while giving moderate curvilinear changes at lower g's. Alternatively, a more conservative course would be to treat this as a zero-infinity criterion, with the cost jumping to infinity at 0.5 g. The rather arbitrary choice of parameters shown gives $10/kWe per 0.1 g in the interval close to 0.2 g.

Meteorology. For nuclear plants, meteorological criteria do not generally affect site suitability. Plant design can be changed or the configuration of exclusion zones can be modified to make acceptable the possible release of radioactivity under expected meteorological conditions.

Nuclear plants are also required to design against probable hurricanes or tornadoes, and in hurricane- or tornado-prone areas such design criteria may be quantified in the same way as the seismology criterion mentioned above.

The situation for air quality standards for fossil fuel plants is different. EPA or state air quality standards for emissions and for ambient air quality must be met for SO_2, particulate matter, and so on. For each possible design technology—scrubber, fuel type, smokestack height—emission standards will be met or not met at given geographical points for a particular plant. Therefore, within the simplified framework assumed here, one can consider this an on-off phenomenon, that is, the cost for a fixed technology is zero for meeting the standards and infinite for not meeting the standards. Alternately, one might introduce design flexibility (improved scrubbers) as a changing cost factor, depending on geographical grid points.

Fogging and icing from cooling towers or ponds and canals is somewhat more complicated. In environmental impact statements it is customary to estimate the number of extra hours produced by the facility over hours of natural fogging or icing. Taking this as a measure of impact, one might specify a rough cost by supposing that a doubling of natural fogging of a major highway or airport would be clearly unacceptable. Also, theoretically, it should be possible to move the highway away from the foggy area by a "thought experiment" and so to develop a cost calibration by such a radical but conceivable method of "abatement." Such a calibration has not, however, been attempted here.

TABLE I. Costs for environmental and economic impacts

Category[a]	Typical design options[b]	X: Impact variable	Extrapolation[c] formula, type	Extrapolation parameters[d]	Remarks
Geology	All	Slope, percentage	Linear	$y'_c = \$2.5/\text{kWe/percent}$ slope	Uses cost of earth-moving for average highways
Seismology	Nuclear	"g's" for safe shutdown earthquake	Logarithmic	$X(1) = 0.15$ g, $X(\infty) = 0.5$ g, $y(1) = \$10/\text{kWe}$	Rough estimate
Meteorology	Fossil	$\mu g/m^3$ or other concentration variables for pollutants	Step function	$X(\infty) = $ standards value	Use state and federal standards
Population: Population centers	Nuclear	Inverse distance, mile^{-1}	Logarithmic	$X(1) = 0.25$ mile^{-1}, $X(\infty) = 0.4$ mile^{-1}, $y(1) = \$2/\text{kWe}$	2 months delay, @ 10^6/month, used as surrogate measure
Population density	Nuclear	Persons/mile^2	Logarithmic	$X(1) = 500$ mile^{-2}, $X(\infty) = 1000$ mile^{-2}, $y(1) = \$2/\text{kWe}$	2 months delay, @ 10^6/month, used as surrogate measure
Hydrology: Floods	Nuclear	Depth below MPF level in feet (plus 1 foot)	Quadratic[d]	$y'_c(X) = \$0.015(1 + 0.25X)/\text{kWe}$	Cost of levee building
Quality	All	Concentrations of pollutants	Step function	$X(\infty) = $ standards value	Use state and federal standards
Supply cost	All	Distance, height	(No formula; use graphic solution)	Use New York PSC curves	See additional reading, N.Y. State Public Service Commission
Ecosystems: Impingement and entrapment	Once-through	Percentage of new water used	Logarithmic	$X(1) = 20$, $X(\infty) = 30$, $y(1) = \$70/\text{kWe}$	Hypothetical cooling tower costs used as surrogate.
Migratory species	Once-through	Percentage of waterway impacted	Logarithmic	$X(1) = 67$, $X(\infty) = 80$, $y(1) = \$70/\text{kWe}$	Hypothetical cooling tower costs used as surrogate
Habitats	All	Percentage of habitat impacted	Logarithmic	World: $X(\infty) = 1$, $X(1) = 0.5$ Nation: $X(\infty) = 5$, $X(1) = 2.5$ State: $X(\infty) = 10$, $X(1) = 5$ $y(1) = \$70/\text{kWe}$ (aquatic) $y(1) = \$70/\text{kWe} - p \cdot A$ (terrestrial)	Cooling tower costs less cooling lake costs where applicable

Population (radiological impact). Quantification of the economic costs of population-dose risks from radiation is controversial; however, it is possible to use reactor licensing experience, especially NRC regulations and those rules of thumb used by NRC staff for examining reactor license applications. According to NRC Regulatory Guide 4.7, the limit on population center distance for nuclear plants can, on a rule of thumb basis, be taken as four miles. Population centers much closer than this could well lead to difficult licensing problems. Therefore, the effective cost might be taken as infinite at, say, two and one half miles. The problem of assigning a cost to intermediate values is difficult. As a substitute for a correct safety or health calculation, however, a cost of licensing delay, set at $1 000 000 a month ($1/kWe) could conceivably be used, and a more-or-less arbitrary figure of two months' delay could be assigned to the critical or "intermediate" distance of four miles.

A similar heroic approximation might be used for population density. Recent licensing experience at the NRC (as expressed in "Standard Review Plans") implies that serious investigations involving some delay might come in at 500 people/mi², and so a $2 000 000 penalty ($2/kWe) is shown at this distance in the table, representing a (nominal) two-month delay. The figure of 1000 persons/mi² is taken to be the point where, assuming licensing is not allowable, effective licensing costs, at least in the context of this type of survey, can be taken as infinite.

Hydrology. As far as the maintenance of water quality is concerned, the approach is the same as for state and federal meteorology standards. It is assumed that groundwater quality problems can be handled at a fairly modest cost, while quality compromises made under Section 316(a) of P.L. 92-500 are treated below under "Ecosystems."

As far as floods are concerned, the relevant parameter for nuclear plants, and probably a reasonable enough one for fossil plants, is the depth of the site terrain below the level of the maximum probable flood (MPF) level (plus one foot) measured in feet. The relevant design to avoid this danger could well be in the form of a levee. For purposes of a rough screening, a levee 800 yd² (consistent with the standard 130-acre station discussed above) is assumed. According to informal Army Corps of Engineer staff estimates, a reasonably-sized levee might be made 10 ft wide at the top, with a 2.5 to 1 ratio for the slopes, assuming average soil material. Assuming a construction cost of $4/yd³, the total cost then is $4 × 3200 yd circumference × (3.3 + 2.5 H) × H, where H is measured in yards. This formula (converted from yards to feet) is given in the table in terms of capacity in kilowatts electric.

For consumptive use of water, the situation varies so much from place to place that individual regional water allocations or local prices for water must be consulted.

For water flow costs, that is, the expense of actually securing

Category[a]	Typical design options[b]	X: Impact variable	Extrapolation[c] formula, type	Extrapolation parameters[d]	Remarks
Land Use:					
Special public areas,[e] direct	All	Co-location or conversion	Step function	$X(\infty) = 0$	No conversion allowed
Special public areas,[e] indirect	Cooling towers	Visual angle subtended, steradians	Logarithmic	$X(I) = 0.5$ steradian $X(\infty) = 1$ steradian $y(I) = p \cdot A^e/-\$70$ kWe	Hypothetical replacement of tower by lake
Specialty cropland	Cooling lakes	Percentage of total specialty cropland	Logarithmic	World: $X(\infty) = 1$, $X(I) = 0.5$ Nation: $X(\infty) = 5$, $X(I) = 2.5$ State: $X(\infty) = 10$, $X(I) = 5$ $y(I) =$ value of lost crop	Use revenue lost as approximation to disbenefit
Transport:					
Airports (safety)	Nuclear	Air movements/year divided by distance cubed	Logarithmic	$X(I) - 50$ AM/d³, $X(\infty) = 100$ AM/d³, $y(I) = \$10$/kWe	Use seismic design estimates above as a cost correction for hardening
Road cost	All	Miles distant	Linear	$y'_c = (\$0.2M + 1.2\,p)/$ mile	Construction cost plus land price
Railroads	Coal	Miles distant	Linear	$y'_c = (\$0.35M + 1.2\,p)/$ mile	Construction cost plus land price
Transmission lines	All	Miles distant	Linear	$y'_c = (\$0.2 + 1.8\,p)/$ kWe-mile	Construction cost plus land price, scaled for capacity
Other					
Land cost	All	Price	Linear	$y'_c = p \cdot A$	Acreage A can be estimated from additional reading, Ramsay and Reed[f]

[a]Only those factors are shown that were approximately quantified or that represent legal standards. [b]Design options will in general have more overlap than shown: a study of typical plant performance characteristics may be necessary. [c]Formulas are given below in note d for the total cost y. Note extrapolation for many factors is tentative and could be replaced by other types of functions. [d]Extrapolation formulas and parameters are: Linear (or quadratic, for which $y'_c = y'_c(X)$): $y = y'_c \cdot X$; Logarithmic: $y = y\,(I)\,\log\,(1 - (\infty))/\log\,(1 - X(I)/X(\infty))$; Step function: $y = 0$ for $X \leqslant (\infty)$, $y \quad \infty$ for $X > X(\infty)$. [e]p is the price of land, adjusted for construction costs where applicable. A is the acreage involved (for a hypothetical or real cooling lake, plant, etc., as applicable). [f]See Regulatory Guide 4.7 (NRC, 1975) for definitions of special public areas.

Cooling tower. *Natural draft tower of the Trojan nuclear plant in Oregon tradeoffs water quality for atmospheric modification*
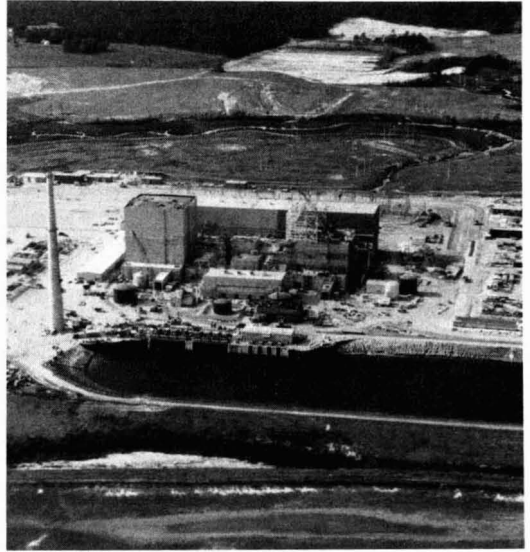
Intake canal. *In the foreground is the intake structure and canal of the Brunswick nuclear plant at Southport, N.C.*

the requisite amount of water for cooling, there are tradeoffs between piping water from a stream and locating close to a stream, and also tradeoffs between once-through and closed-cycle cooling. For these purposes, the table suggests the use of the curves developed by the State of New York in its siting investigations showing average costs as a function of distance from the water body and height of pumping needed.

Ecosystems. For the problem of impingement and entrainment, the suggestions in the Regulatory Guide 4.7 Appendix are followed, and a criterion based on the percentage of the water taken from the stream is used. Since 10–20% was defined as being an acceptable range, a logarithmic formula is used and the cost becomes infinite at 30%. The cost at 20%, the approximate upper limit indicated in the Guide, has been equated here to the costs of a possible partial abatement procedure: installing a cooling tower instead of once-through cooling. From the New York State reference, a very approximate figure of $70/kWe for this surrogate procedure can be obtained.

For migratory species, one-fourth to two-thirds of the waterway impacted (zone of passage blocked) is the limit recommended in the Regulatory Guide 4.7 Appendix. An impact of 67% is assigned a surrogate cost that corresponds to the cost for substituting an "average" cooling tower as a means of abating the impact. Costs are assumed infinite at 80%.

For impacts on habitats, a percentage of the allowable amount of habitat impacted can be considered. In these rough estimates for site screening, probably only gross acres of land and water by land-use type need be treated. In the first place, the extent and detailed nature of the habitats of most species are not yet well known. Moreover, much habitat analysis must be treated on the basis of a detailed site investigation. Therefore, recognizing different interests at different political levels, a triple standard—for state, national, and world ranges—is proposed here as a rough estimate. The percentages of habitat seriously degraded at which the impact cost becomes infinite are proposed rather arbitrarily at 10% (state), 5% (national), and 1% (world). The corresponding intermediate percentages for logarithmic functions are chosen to be 5, 2.5, and 0.5. For aquatic habitats, a cooling tower substitution could be taken as a possible abatement measure, and the figure of $70/kWe is again used for costs at the intermediate impact percentage value.

For terrestrial habitats, the major siting problem is apt to be

for cooling lakes that take up a considerable amount of land. Therefore, cooling tower costs could again be chosen as a possible surrogate costing factor. However, in the terrestrial case, the net cost of the hypothetical changeover should be reduced by the financial cost of the cooling lake, which may be approximated by the price per acre of the land times the acreage of the land (plus the construction costs for cooling lake dams and embankments, prorated by acreage, and included in the land price in the table).

Land use. As shown in the table, locating a site on special public use lands, such as those specified in Regulatory Guide 4.7, is counted as an infinite cost; the same would hold true for historical sites if the construction of the station would be certain to destroy or severely impact the site itself.

For indirect esthetic impacts on such critical areas, the angle subtended by plant structures (in steradians) is taken as the measure of the impact. Based on very fragmentary evidence, the intermediate point in a logarithmic extrapolation is taken at one-half steradian, which appears to be approximately the boundary between the "middle field" and the "far field" in one study (Burnham et al.), which investigated the esthetic preceptions of a planned cooling tower. The point at which the impact becomes infinite is put at one steradian. A surrogate value for the impact cost parameter can be estimated by noting that this case is the reverse of the terrestrial habitats case. Here, the esthetic impact is apt to be caused by a lake. Therefore, the equivalent impact cost is the same cost option as for the terrestrial ecology case, but reversed (that is, the cost of substitution of a lake for a tower).

In the category of specialty-crop agricultural land, the quantitative measure of impact is the number of areas converted. The limits of impact should be determined by an economic calculation, but in default of such, the same kind of percentages used for terrestrial ecology is proposed here: 10% of state, 5% of national, and 1% of world cropland devoted to the particular specialty crop constitute an unacceptable impact, while cost impact values of half these percentage acreage values are taken to be roughly measured by the dollar value of the crop impacted. Naturally, this total revenue dollar value is not all returned to the land factor. However, corrections to such a value (farm subsidies, open-space amenities) can go either way, so total revenue is taken as a very approximate estimate of benefits foregone.

Transportation, transmission lines, other costs. For airports, the Regulatory Guide 4.7 Appendix guidelines limits for aircraft hazards are used as an intermediate impact value, with twice that amount taken as infinite cost (see table). For the intermediate cost value, hardening costs are taken to be roughly those corresponding to the special seismic design costs used above.

For building railroads, the cost shown per mile for track and land costs are adopted; namely, $350 000/mi plus the price of land per acre (p) $\times$ 1.2 acres of land/mi. Equipment costs are not considered since they are relatively independent of geographical grid point.

For roads, estimates are used for "average terrain." The cost is taken to be $250 000/mi plus the cost of 1.2 acres of land per mile for right-of-way.

Costs for transmission lines vary greatly. However, very approximate average costs are given in the table: 20¢/kWe plus the cost of 1.8 acres of land, both per mile of right-of-way.

Other costs may need to be included but are not calculated here. One analytically accessible category is land acquisition cost (Table), which must be determined locally. Also, there are difficult social costs that seem impractical to quantify at present. For example, socioeconomic costs such as impacts on local government services and tax structures can undoubtedly be mitigated by clever siting procedures; this problem area deserves more investigation. Patterns of land ownership may also be of crucial importance to the state or the utility; but it is difficult to know how to treat such patterns, e.g., ownership of the land by government agencies such as the Defense Department may be a hindrance to land acquisition. On the other hand, if deactivation of a military base were to become a possible option, then such land may be very desirable for siting.

Summing up

Quantitative power-plant-site-screening analysis requires some numerical estimate of environmental impacts. Estimating these impacts in terms of real or hypothetical money costs is no worse than other methods, and the conventional cost method may, in fact, help the analyst detect very high-cost anomalies that might be obscured in other rating methods. Transaction costs such as licensing delays and the costs of alternative plant systems, including abatement devices, may be of use in assigning environmental costs in otherwise obscure situations by means of a "balance-of-alternatives" approach.

Additional reading

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Coordinated by LRE

Coal burns cleaner in a fluid bed...

... But it's always a good idea to look at what pollutants may remain. Here are a number of possibilities

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Fluidized-bed combustion systems operate at significantly lower temperature than conventional systems (about 1650 °F vs. 2700 °F, respectively). The solids are supported on a grid at the bottom of the boiler through which combustion air is passed at high velocities, typically 2 to 5 feet per second. The solids are held in suspension by the upward flow of the air and a quasi-fluid is created that contains many properties of a liquid. The most important liquid-like property to the boiler designer is the fact that the bed material is exceptionally well mixed and flows throughout the system without mechanical agitation.

Fluidized-bed combustion systems for the production of steam and/or electricity have several advantages over conventional combustion systems. These include:

- High heat transfer coefficients and volumetric heat release rates will reduce the boiler size by one-half to two-thirds or more compared to a conventional unit.
- Capital costs will be reduced because of the size reduction and the potential for shop fabrication instead of field construction.
- The use of limestone as bed material provides a means for in situ SO_2 removal.
- The high heat transfer coefficients permit lower operating temperatures (1550–1750 °F), which can potentially decrease NO_x emissions.

Questions have been raised concerning the emissions that could result at these lower operating temperatures. As a first step in answering these questions, one can conduct a "preliminary environmental assessment." In performing a preliminary environmental assessment, one's major role in a sense is to serve as a devil's advocate with respect to pollutant generation. The air is to focus attention on potential environmental problems as early in the development cycle as possible. This provides maximum lead time to gather the technical data on which decisions regarding control technology or process modifications (should they be needed) can be based.

It is widely known that fluidized-bed combustion (FBC) of coal results in low SO_2 and NO_x emissions. The idea in this feature article is to focus attention on the so-called "other" pollutants. These pollutants are divided into three generic classes: trace elements, organic compounds, and particulates. There are some limited experimental data available on trace elements in FBC; also, investigations of particulate size distribution and their chemical composition are just underway. Unfortunately, no data available on organic compounds that could be produced in coal-fired fluidized-bed combustion are yet available.

Numerous compounds can be included in an initial list of conceivable pollutants. Developing a list of conceivable pollutants is not necessarily a technically sophisticated task, but is an important effort. It establishes the scope of the environmental assessment; the more comprehensive the list, the less chance there is for unexpected pollutants to escape discovery.

Organic and other pollutants

Potential organic pollutants are those compounds that could form from the incomplete combustion of coal. One can simplistically view it as a sequential process. The particle vaporizes or volatilizes; the volatile compounds can react among themselves in a chemically reducing atmosphere. Next, they react with oxygen within the system in a diffusion flame. After devolatilization is completed, the char continues to burn. To specify the potential organic compounds that could form, the basic question is, what types of chemical species are produced during coal pyrolysis and to what extent will they survive in the reactive environment of a fluidized-bed combustor?

Only two classes of hydrocarbons should be of any significance in coal combustion: small hydrocarbons (less than about three carbon atoms) and polynuclear aromatic hydrocarbons. Both could form and survive within the bed at temperatures on the order of 1500 °F.

The chemical structure of coal can be viewed as a network of interconnected aromatic hydrocarbon compounds. Small hydrocarbons can form directly from cleavage of substituted alkyl groups. Polynuclear aromatic hydrocarbons can also form directly via bond cleavages in the structural network, or they can form through condensation reactions of various hydrocarbon decomposition products. Even though generally endothermic, at FBC temperatures of 1500 °F, these condensation reactions probably proceed at a significant rate. This belief is based on the fact that branched or cyclic hydrocarbons are seldom found as products of coal pyrolysis at similar temperatures.

Similar arguments apply to the generation of organic nitrogen and sulfur compounds. Species such as pyridine decompose at temperatures on the order of 1000 °F to form hydrogen cyanide (HCN) and small hydrocarbons. Thiophenes and mercaptans can also decompose to form small hydrocarbons and hydrogen sulfide (H_2S).

Concentration estimates

For a rough estimate of the concentrations at which some of the small hydrocarbons and reduced sulfur and nitrogen compounds might exist, one can use equilibrium calculations based on free energy minimization. An upper limit can be obtained from calculations performed in conjunction with coal gasification experiments where highly reducing, fuel-rich conditions exist. For example, even with only 60% stoichiometric oxygen present, concentrations of HCN, carbonyl sulfide (COS), carbon disulfide (CS_2), and the like, are less than 10 parts per million (ppm). Extrapolation of the calculations to typical operating conditions such as 20% excess air, in which case SO_2 and NO_x become the predominant sulfur and nitrogen compounds, indicates that compounds such as H_2S, HCN, COS, and cyanogen $((CN)_2)$ should be present in concentrations less than 1 ppm.

Free energy minimization calculations for the more complicated polynuclear aromatic hydrocarbons are impractical.

However, to estimate the concentrations at which these types of compounds might exist in the FBC flue gas, one can use empirical correlations between a compound such as benzo[α]-pyrene and methane (CH_4) concentrations from measurements in conventional coal-fired combustion systems.

Under normal operating conditions, about 3% O_2 in the flue gas (20% excess air), the concentration of hydrocarbons (as CH_4) is about 100 ppm (volume/volume or V/V). Although emissions can often vary between different fluidized-bed systems, 100 ppm provides a convenient average value. Previous measurements with conventional coal-fired systems indicate that the concentration of compounds such as benzo[α]pyrene is typically 10^{-5} times less than the concentration of total hydrocarbons as CH_4.

Thus, using a reference value of 100 ppm CH_4, one can infer that in a fluidized-bed system, polynuclear aromatic hydrocarbons (PAH) could exist in the flue gas at concentrations (V/V) on the order of 1 part ber billion (ppb). However, since flue gases are eventually diluted by roughly a factor of a thousand when they are emitted from the stack, ambient concentrations of PAH near FBC facilities would more likely be on the order of 1 part per trillion. This corresponds to about 0.6 ng/m^3, which is roughly comparable to the natural background concentration ranges found in rural areas. Accordingly, it seems that polynuclear aromatic hydrocarbon concentrations should not be high enough to cause problems.

Recently, some coal-fired flue gases have been tested for the presence of polychlorinated biphenyls (PCB) and trace concentrations have been reported. Experience in coal combustion

Assessment of trace element emissions from coal-fired fluidized-bed combustion

Elements of concern because they could be emitted in toxic concentrations (based on "worst case analyses.")	Be, As, U, Pb, Cr, V, Cl
Elements of concern because of possible enrichment on fine particles (<2 μm)	Pb, Cr, Se, Br, Hg

and coal pyrolysis indicates that at temperatures similar to that in coal-fired FBC, chlorine (when present) exists predominantly as hydrogen chloride (HCl). Accordingly, one would not expect significant concentrations of PCB's in coal-fired FBC. If present at all, they should be in concentrations less than those of the unsubstituted polynuclear aromatic hydrocarbons (1 ppb (V/

Trace elements

Trace elements and their compounds are of concern because some of these materials can vaporize and exit with the flue gas. Because they are in the gas phase, they are not captured by particle collection devices.

There is also concern about the enrichment of trace elements on fine particles in combustion processes. Studies have indicated that certain elements can concentrate in selected size ranges of particulates. For some elements, such as lead and cadmium, these sizes tend to be less than a few microns in diameter. Such small particles are of special environmental concern because they are difficult to remove from the flue gas, and once emitted, they can be readily embedded in the lung through normal breathing.

An atmospheric pressure fluidized-bed combustion system, including selected air and solid waste emission points
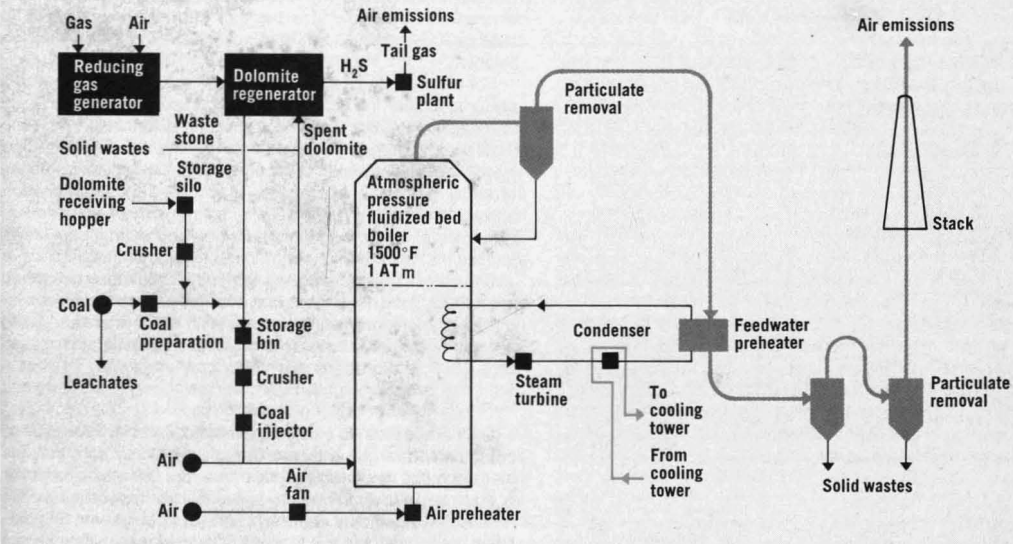
To assess the importance of trace element emissions in coal-fired fluidized-bed combustion, a "worst case analysis" approach was used. For both bituminous and lignite coals, ranges for the heat content and the concentration of trace elements were obtained. Under the assumption that all of the elemental material would exit with the flue gas as either a vapor or a particulate, a "worst case" emission factor was calculated (lbs/10^6 Btu), using the lowest heating value and highest trace element content of the coals. Based on this emission factor, stack gas concentrations were calculated and diluted by a factor of 10^3 to account for dispersion in the atmosphere. These "ambient" concentrations were then compared to industrial hygiene threshold limiting values (TLV).

Although industrial hygiene TLV's cannot be used to assess the absolute environmental impact of pollutants, they do provide a useful framework in which pollutants can be rank-ordered according to their toxicity. Any element whose predicted ambient concentration was within a factor of 100 of the industrial TLV was considered to be potentially harmful. This scaling factor of 100 was arbitrarily chosen to account conservatively for the effects of long-term exposure (industrial hygiene limits are usually based on exposures to healthy adults over an 8-hour period).

Table 1 lists those elements that could be of concern, based on the above "worst case analysis." It is important to emphasize that these worst case analyses are based on 100% emission of the various trace elements, which is most unlikely. Much of the trace element material will either be retained in the bed or be captured in particulate-control devices. Studies to determine trace element balances in FBC systems are currently underway, and preliminary results indicate that, in fact, significant advantages may result in controlling trace element emissions in fluidized-bed combustion. Compared with conventional com-

Schedule for development of selected fluidized-bed combustion units

Unit size	Contractor and/or location	Approximate starting dates [a]		
		Design	Construction	Operation
0.5 MW [b]	Pope, Evans, & Robbins Alexandria, Va.	—	—	In operation
0.63 MW [c]	Exxon Research and Engineering Linden, N.J.	—	—	In operation
1.0 MW [c]	Combustion Power Co. Menlo Park, Calif.	—	—	In operation
3.0 MW [c]	Argonne National Lab. Argonne, Ill.	Mid '76	Mid '77	Late '78
6.0 MW [c]	International Energy Agency Grimesthorpe, U.K.	Late '76	Mid '77	Late '79
6.0 MW [b]	Morgantown Energy Research Center Morgantown, W. Va.	Late '76	Late '77	Late '79
13.0 MW [c]	Curtiss-Wright Woodridge, N.J.	Late '76	Late '77	Late '79
30.0 MW [b]	Pope, Evans, & Robbins Rivesville, W.Va.	—	In progress	Sept. 76
Industrial and institutional applications	Various	Late '76 [d]	Late '77 [d]	Late '79 [d]

[a] Approximate schedule as of May 1976; [b] Atmospheric pressure; [c] Pressurized combustor; [d] Earliest starting date of any projects.

TABLE 2.

Estimated concentration ranges of potential pollutants from coal-fired fluidized-bed combustion

Gas phase

One hundred parts/million:	CH_4, CO, HCl, SO_2, NO
Ten parts per million:	SO_3, C_2H_4, C_2H_6
One part per million:	HF, HCN, NH_3, $(CN)_2$, COS, H_2S, H_2SO_4, HNO_3, F, Na
One part per billion:	Diolefins, aromatic hydrocarbons, phenols, azoarenes, As, Pb, Hg, Br, Cr, Ni, Se, Cd, U, Be
One-tenth (0.1) part per billion:	Carboxylic acids, sulfonic acids, polychlorinated biphenyls, alkynes, cyclic hydrocarbons, amines, pyridines, pyroles, furans, ethers, esters, epoxides, alcohols, ozone, aldehydes, ketones, thiophenes, mercaptans

Solids

One part per million:	Al, Ca, Fe, K, Mg, Si, Ti, Cu, Zn, Ni, U, V
One part per billion:	Ba, Co, Mn, Rb, Sc, Sr, Cd, Sb, Se, Ca
One-tenth (0.1) part per billion:	Eu, Hf, La, Sn, Ta, Th

bustion, fluidized-bed systems operate at lower temperatures and tend to reduce trace element vaporization.

Elements that could be enriched on fine particles are also listed in Table 1. The chemical composition of particulates as a function of particle size has not yet been investigated in fluidized-bed combustion. This investigation should receive high priority.

For the most accurate environmental assessment, one would prefer to identify the actual chemical compounds in which these trace elements exist. This is an extremely difficult task, because the concentrations of the elements are usually so low that the identification of specific compounds is beyond the capabilities of existing analytical technique. At present, the identification of trace element compounds is based primarily on speculation. Examples of exotic but highly toxic compounds that could form include nickel carbonyl, cobalt carbonyl and arsine.

By use of "worst case analyses" similar to those described previously, it can be shown that contributions to the trace element emissions from the limestone in an FBC system should be negligible compared to those of the coal. This estimate is based on a Ca/S ratio of 2 and coal sulfur content of 3%.

Particulate emissions

Only crude data on particulate emissions from fluidized-bed combustion are currently available. Preliminary data indicate that the mass median diameter of the flue gas particles (50% of the mass of the particles are above that size) is about 7 μ. This means that significant concentrations of troublesome fine particles could exist, but this is also the case in many conventional

FLUIDIZED BED COMBUSTION SYSTEMS *

	INDUSTRIAL	UTILITY		
1 USER	INDUSTRIAL	UTILITY		
2 PURPOSE	STEAM GENERATION	ELECTRIC GENERATION		
3 PROBABLE TYPICAL SIZE, 10⁶ Btu/hr FUEL INPUT	500	5000		
4 OPERATING PRESSURE	ATMOSPHERIC	ATMOSPHERIC	PRESSURIZED (10 ATM)	
5 EXCESS AIR, PERCENT	15-25	15-25	15-25	300 (ADIABATIC)
6 CYCLE TYPE	PROCESS STEAM	STEAM TURBINE	STEAM TURBINE (80%) AND GAS TURBINE (20%)	GAS TURBINE (80%) AND WASTE HEAT BOILER-STEAM TURBINE (20%)
7 FUEL-TO-ELECTRICITY EFFICIENCY	N.A.	36-38	36-38	31-38
8 REGENERATION	NO YES	YES	YES	YES
9 REGENERATION PROCESS	1-STEP	1-STEP	1-STEP 2-STEP PRESSURIZED	
10 FINAL S REMOVAL	S RECOVERY H_2SO_4 RECOVERY SO_2 SCRUBBING	S RECOVERY	H_2SO_4 RECOVERY	

* PROBABLE Co:S MOLE RATIO IN FEED TO COMBUSTION IS 2:1. COAL SULFUR CONTENT MAY BE 4 PERCENT IN INITIAL SYSTEMS. PROBABLE OPERATING TEMPERATURE OF THE MAIN COMBUSTOR IS 850-950° C.

combustion systems. With suitable central devices, the problem can be ameliorated. Further experiments on particle size distributions and chemical composition as a function of particle size should receive high priority.

Table 2 summarizes concentration estimates for potential pollutants from coal-fired fluidized-bed combustion. These estimates are often based on limited data and simple assumptions; hence, they are probably good only to within an order of magnitude. The term "gas phase" includes gases, vapors, and very fine particulates ($<2\ \mu$); the term "solid phase" includes the agglomerated bed material and coarse particulates ($>2\ \mu$), which should be collected by conventional particle control devices.

Pollution control technology

The two areas of fluidized-bed coal combustion that will probably require pollution control are flue gas emissions and spent sorbent stone disposal. In FBC flue emissions, particulates will probably pose the most significant problem. Their presence will require add-on control devices; possible options include electrostatic precipitators, wet scrubbers and fabric filters. Fabric filters look especially promising, in view of the lower gas temperatures and SO_2 levels encountered in FBC flue gases.

For pressurized operations, gas purity for turbine requirements may be stricter than environmental regulations; hence, pollution control *per se* may be unnecessary. Moreover, high temperature (1500 °F) particle cleaning devices, for the most part, are unproven and not yet commercially available. Gravel bed filters and special cyclones are options under consideration.

Gaseous pollutants that may require control are CO, hydrocarbons and in some cases, perhaps HCl. CO and hydrocarbons can be controlled by increased excess air or the addition of secondary air in the freeboard zone. HCl can be removed via alkaline scrubbers in conjunction with particulate removal, if necessary.

Large amounts of solid waste consisting of spent stone and coal ash will be produced by FBC systems. The amount of solid waste related to sulfur removal could be greatly reduced by regeneration and recycling. Proper landfill site selection and management can minimize the potential for groundwater pollution. Besides disposal other options are also available for spent stone utilization, including use in agriculture, bricks, wallboard, and fill material for roads and concrete. However, utilization as a gypsum substitute (wallboard and other products) may be very limited because of transportation costs and a plentiful natural gypsum supply. Uses in products in which coal ash is utilized will also be limited, as evidenced by the fact that only 13% of coal ash is utilized. Control of pollutants from coal storage, cooling, and water treatment can be accomplished by practices currently in use at conventional power plants.

Although there is virtually no experimental information available concerning potential organic pollutants that could form in coal-fired fluidized-bed combustion systems, simple thermodynamic considerations, chemical experience and empirical correlations with conventional combustion systems indicate that no special problems should occur. Experimental verification, however, should receive high priority.

In comparison with conventional coal-fired systems, fluidized-bed combustion seems to offer significant potential for reducing trace element emissions. However, data are lacking in several areas, particularly with regard to the elements arsenic, beryllium, chlorine, chromium, lead, mercury, selenium, uranium, and vanadium, and their compounds. Nevertheless, experimental data indicate that particulate loadings should pose no special problems, provided conventional control devices such as cyclones, electrostatic precipitators, or fabric filters are used.

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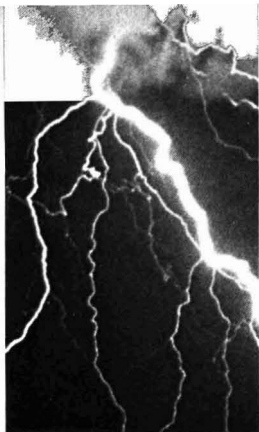
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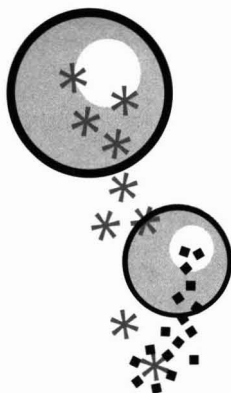
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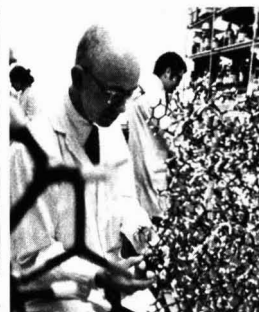
Choices Through Chemistry

Incentives for managing the environment

Once identified, these inducements
can enhance the functioning of
quality improvement programs

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A question increasingly being raised at all levels of government in the U.S. is, "How can environmental quality management programs be implemented more effectively, efficiently and equitably?" For example, the Senate Government Operations Committee recently held hearings on regulatory reform that included discussions on the implementation of environmental regulations. The report of the House of Representatives' Committee on Interstate and Foreign Commerce on the proposed Clean Air Act Amendments of 1976 cites the limited nature of enforcement options, the implicit incentives to polluters to delay compliance, and other problems of implementation under current legislation.

Even within EPA, burdened with National Pollutant Discharge Elimination System permits and State Implementation plan (SIP) air emissions limitations, some rethinking of alternative implementation strategies is taking place. In recent remarks to the National Conference on Regulatory Reform, the EPA Administrator stated that, ". . . the only alternative, or effective supplement, to such regulation would be a system of effluent and emission charges . . ."

Requirements of both the Clean Air Act Amendments of 1970 and the Federal Water Pollution Control Act Amendments of 1972 require the development of *enforceable* programs to implement state and regional environmental quality management plans, such as Air Quality Maintenance and Areawide Waste Treatment Management ("208") plans. The Resource Conservation and Recovery Act of 1976 calls for new efforts in planning and implementing state and local solid-waste management programs. These federally required programs are significant departures from previous legislation, which has tended to ignore considerations of implementation.

Background

The objective of this brief article is to raise some basic issues of identifying and selecting incentives, both positive and negative, as integral components of environmental quality management plans. In the article, the term "residual" is used to replace the terms pollutant and waste. A residual is a nonproduct material or energy output, the value of which is less than the costs of collecting, processing, and transporting it for use. This economic definition should be distinguished from its more narrow one in Section 208(b)(2)(J) of P.L. 92-500, which refers to "residual waste" as the sludge from wastewater treatment plants.

Some additional introductory remarks are required. First, producing and maintaining improved environmental quality, as measured by some set of indicators, involves functions of many public and private sectors. These include planning; research; legislation; translation of legislation into guidelines and procedures; design, construction, operation and maintenance of facilities; monitoring of ambient conditions, and the performance of activities; and enforcement and feedback of information. *All* these activities are essential to achieve the desired objective of improved environmental quality.

Second, the real world in which environmental quality management must be performed is dynamic and random in nature. The dynamic character is reflected in the continual changes that occur in an urbanized, industrial society in technology, qualities of raw materials, product specifications, prices, and social tastes. The random nature of the world is evident in aquatic, atmospheric, and terrestrial ecosystems—all of which have assimilative capacities that vary over time. Similarly, residuals generation by households, industrial plants, and agricultural operations varies within the day, from day to day, and seasonally, even under "normal" operating conditions. Upsets, spills, breakdowns, and clean-up operations also add to the variability of residuals generation and discharge.

Third, physical, technological and economic interrelationships exist among the various forms of residuals—liquid, gaseous, solid, energy—and among the three environmental media—air, land, water. Measures to reduce the discharge of one type of residual may increase the quality of other residuals generated, which in turn must be disposed of in some manner. For example, gaseous discharges can affect water quality via washout, as in the case of acid rain. Solid residuals can become airborne residuals when incinerated.

The management issues

Given the foregoing background, what are implementation incentives in relation to environmental quality management? Incentives can be positive or negative, but their objective is to induce action.

Broadly speaking, the desired action is reduction in the day-to-day use of the environment or maintenance of the use within some specified limits in order to achieve and maintain desired levels of ambient environmental quality. More narrowly, the actions desired are:

- the installation of some physical method or technological option

FIGURE 1

Alternative locations for the imposition of incentives

Key
I = Raw material/energy inputs
R_G = Residuals generated
R_D = Residuals discharged
M/E = Materials and/or energy
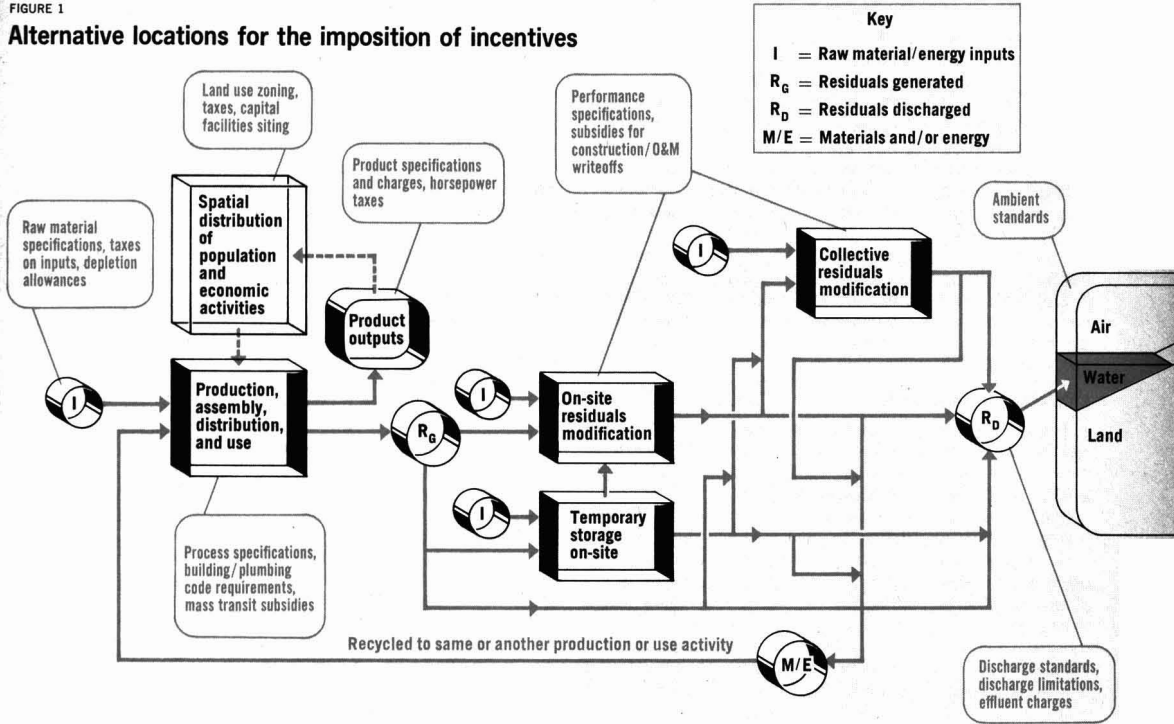
• the continuous operation of these physical methods at design levels over time. Most of the effort to date by government agencies involved in environmental quality management has been focused on installation without a corresponding concern with operation and maintenance. One exception is EPA's recognition of the problems of maintaining the performance of vehicle emissions-control devices over time.

Given the complexity of the task of achieving and maintaining specified levels of environmental quality, the incentives problem can be characterized by a set of questions (see box). These questions comprise the essence of the incentives problem. The problem in turn is most usefully addressed in the context of environmental quality-management strategies.

Incentives as components of strategies

An environmental quality management strategy consists of three interrelated components: a set of physical methods; implementation incentives; and an institutional arrangement.

The physical methods are those *actions* by households, institutions, industrial, commercial, or agricultural operations, or municipalities that reduce or modify the discharge of residuals to the environment and/or directly make better use of the assimilative capacity of the environment. Incentives are the positive and negative inducements that stimulate the installation and continued operation and maintenance of the physical methods. The institutional arrangements impose the incentives and complete other management functions. These three elements must be considered simultaneously, if the desired improvement in environmental quality is to be produced. In addition, the incentives and institutional arrangements must be considered simultaneously at all levels of government to ensure that an in-

centive adopted at one level is consistent with an incentive adopted at another.

Table 1 presents a classification of physical methods. The examples are illustrative, not exhaustive. In connection with physical methods, a great deal of confusion has arisen over the use of the terms "structural" and "non-structural." Structural measures have generally been defined as technological options, such as sewage treatment plants, emission control equipment on stacks, or emission control devices on automobiles. Zoning ordinances, performance standards, permits, and effluent charges have been defined as non-structural measures. The connotation has clearly been that the choice is either/or, that is, non-structural measures are alternatives to structural measures.

In reality, the objective in environmental quality management is to achieve some change in the behavior of the relevant sectors. Therefore, we prefer the terms "physical methods" and "implementation incentives." The adoption of a particular physical method can often be induced by more than one type of incentive. For example, if a sewage treatment plant is selected as the physical method for modifying discharges, a federal or state grant to help finance capital costs exemplifies an implementation incentive to induce construction. But construction of the plant could also be stimulated by an effluent charge. The point is that the methods and incentives are not independent of one another, but must be identified jointly and their costs and effectiveness evaluated in combination.

Implementation incentives induce action. They can be positive or negative, direct or indirect, or prescriptive or proscriptive. Figure 1 illustrates the locations in the physical system where incentives can be imposed. The figure indicates the flows of

materials and energy into, through, and from the physical system that generates and discharges residuals. These flows can be modified in quantity, quality, timing and location by the use of alternative physical methods. The adoption of a particular physical method is influenced by the incentives imposed. In a given regional context, the prevailing institutional arrangement has a set of incentives from which it can choose; each activity, in turn, has a set of physical methods from which to choose in responding to the implementation incentives imposed upon it. Finally, alternative institutional arrangements are possible.

Table 2 lists some implementation incentives. Each incentive has its strengths and weaknesses, so that the incentive chosen in a particular management context must be matched to that particular situation. No one implementation incentive is likely to provide optimal environmental quality management at any one geographical scale.

Characterizing incentives

Although the categories and examples in Table 2 are mostly self-evident, some further discussion is merited. First, some of the implementation incentives can be imposed at more than one level of government. For example, an upper limit on the sulfur content of fuel has been specified by local and state governments. Similarly, restrictions on non-returnable beverage containers have been imposed at both local and state levels. On the other hand, some incentives are more, or exclusively, relevant to one particular level of government. Requiring householders to keep used newspapers separate from other solid residuals is relevant at the local level; requiring automobiles produced in the U.S. to meet a minimum fuel/distance standard is relevant only at the federal level. Some incentives can be imposed incrementally at more than one level of government, such as a national effluent charge on suspended solids discharge into water courses combined with an additional state effluent charge on such discharges.

Second, mixes of implementation incentives can be applied to the same activity. An effluent standard in terms of mean daily kilograms of BOD_5 discharge can be coupled with an effluent charge (¢/kg) on all BOD_5 discharges or on all discharge above a specified limit.

Third, incentives imposed on one residual can have positive and/or negative impacts on other residuals and/or environmental media. An ordinance specifying limits on concentration of particulate discharges from building incinerators may force many of these incinerators to shut down with a consequent increase in solid residuals for disposal.

Fourth, many of the incentives are not under the jurisdiction of environmental quality management agencies. Probably the clearest examples are tax policies such as depletion allowances, capital gains, severance, accelerated depreciation, and real estate.

Fifth, "administrative" implementation incentives reflect internal responses to external stimuli. That is, a public or private manager reacting to external stimuli may adopt an administrative incentive *internally* within the scope of his jurisdiction. The stimulus may be economic, as when the costs of disposing of solid residuals increase to a level that recycling used paper merits consideration. It may be a public relations move, with or without external pressure from a public interest group. It may be in response to the possibility of a class-action court suit. It may be to set an example for other governmental agencies.

Problems associated with incentives

Consideration of implementation incentives begins with what now should be a universally accepted principle, namely, that environmental services, in terms of the capacity of environmental media to assimilate residuals, are no longer free. There is no "right" to the free use of such services, there is no "right to pollute." Given that principle, there are at least three problems common to all incentives.

TABLE 1

Classification of physical methods for improving environmental quality

Category of method	Subcategory	Examples
Reduce residuals generation	Increase longevity of consumer goods	Longer-lived appliances
	Change type of raw material inputs	High to low-sulfur-fuel oil
	Change production process, including mode of transport	Individual vehicles to mass transit
	Change final demand	
	Change product mix	Reduce number of grades or styles of product
	Change product specifications	High-octane to low-octane gas
Modify residuals after generation, in on-site and/or collective facilities	Materials recovery (direct recycle)	Chemical and fiber recovery in paper production
	By-product production (indirect recycle)	
	To final products	Peach pits into charcoal briquettes
	To intermediate products	Obsolete vehicles into steel scrap/steel
	Modification of residuals stream	Combustion of solid residuals to generate energy
	Effluent reuse	
	Direct	Recirculate water from washing to toilets
	Indirect	Groundwater recharge
Make better use of the assimilative capacity of the natural environment	Change the spatial distribution of existing and/or new activities	Establish "auto-free" areas
	Change the temporal distribution of existing and/or new activities	Phase the location of new activities until adequate public services are available
	Change the spatial distribution of the discharge of residuals	Pipe residuals to areas of higher assimilative capacity
	Change the temporal distribution of the discharge of residuals	Withhold residuals discharge during periods of low assimilative capacity
Increase the assimilative capacity of the natural environment		Low flow augmentation, artificial mixing or aeration
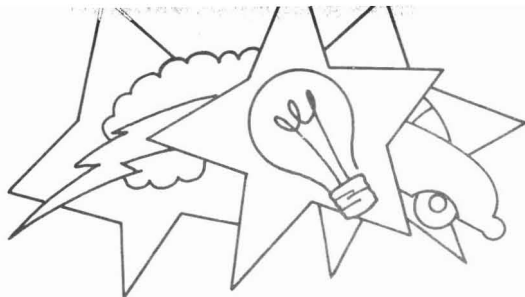
Some materials are so toxic that their discharge to the environment should simply be prohibited. However, it is no easy task to determine just what materials in what quantities under what conditions are toxic to what species, homo sapiens included. A particular concentration of a material in a body of water may have no adverse effect on some fish species under low or normal temperature conditions, but very adverse effects under high temperatures, or in the presence of some other material, or when dissolved oxygen is low. In some cases, other contributing or intervening variables may affect the response, such as the state of health of the target species. Finally, toxicity is both a short-run and a long-run problem. Concentrations that result in immediate fish kills are obvious; those that result in a build up in tissues and/or organs over time, with long-term effects on reproduction and viability, are not so obvious.

A related problem is the lack or incomplete knowledge of both the effects of the discharge of a residual on environmental quality and the damages (effects) to various species from this change in environmental quality. Again, both short-run and long-run time frames are involved. The impact of discharges of fluorochlorohydrocarbons on ozone content of the stratosphere is an example. The long-run impact of particulate matter and CO_2 discharges on the atmosphere is another.

The impact of the incentive on technological change is important. The relevant question is, "Does the implementation incentive bias the selection toward a particular discharge reduction technology, or does it stimulate the investigation of the entire range of alternative methods, in relation to residuals handling technology and in relation to altering factor inputs, product output specifications, and production technology?"

Evaluating strategies

Because any environmental quality problem can be managed by a variety of alternative strategies, criteria for the selection of a best strategy for any given situation must be developed. Suggested criteria for evaluating strategies follow.

• *Physical effects,* or the degree that the physical method will: reduce the discharge of a residual from a specific source category; reduce a specific total discharge of the residual in the environmental quality management area; and change the relevant indicator(s) of environmental quality, which in turn may result in other physical effects such as decreased mortality or morbidity, decreased deterioration of materials, or increased fish biomass.

• *Economic effects,* including: direct benefits, or the translation of the changes in physical effects into monetary value, where possible, such as reduced medical costs, reduced costs of cleaning and maintenance, or increased value of fish catch; the direct costs to the residuals discharger—industrial plant, municipality, feedlot—of implementing the physical method in terms of capital, operating and maintenance costs, or to the environmental quality management agency for implementing physical methods to reduce discharges or which directly affect assimilative capacity; administrative costs, both public and private, in terms of accounting and reporting, monitoring, analysis of samples, and supervision of operating personnel; and indirect economic effects in terms of employment effects, changes in income tax, changes in property taxes, increased cost of user goods and dislocation of people.

A most important consideration with respect to both physical and economic effects is their distribution. Who benefits from improved environmental quality, and who pays and in what forms for the improvement? Distributional effects should be determined in relation to political jurisdictions and socioeconomic groups within the environmental quality management area; and the division between direct costs incurred within the area and those incurred external to the area; for example, the proportion of costs to be forthcoming from federal or state treasuries.

• *Flexibility in administration,* or the administrative ease with which a strategy may be applied or removed, and the degree to

TABLE 2

Classification of implementation incentives

Regulatory—by law, or ordinance, permit

Specification of a physical method
Specify characteristics(s) of raw material input, e.g., no more than 1% sulfur fuel
Specify "production process," e.g., amounts of thermal insulation in buildings
Specify residuals modification and/or handling process, e.g., require householders to separate used newspapers from other solid residuals
Specify product output characteristics, e.g., amount of lead in gasoline

Specification of a result or performance
Specify discharge per unit of product or raw material processed ≤ some specified amount, e.g., ≤ X kilograms of suspended solids per ton of steel
Specify total quantity of a residual discharged per unit of time ≤ some specified amount, e.g., Y pounds of BOD_5 per day
Specify concentration of residuals in discharge ≤ some specified magnitude, e.g., ≤30 mg/L of SS
Specify environmental quality to meet or exceed certain levels for specified periods of time, e.g., mean annual concentration of sulfur dioxide ≤75 mg/m^3
Specify performance, e.g., automobile must achieve at least 40 km per liter of fuel in city driving

Specification of limitations on location of activity, e.g., prohibition of development where utility capacity—water, sewer, electricity—is insufficient

Specification of extent, timing, type of activity, e.g., prohibition of trucks on particular routes during particular times

Specification of procedure, e.g., requirement that environmental impact statement for each project be prepared according to guidelines

Economic
Applied directly to residuals, e.g., charge on each unit of residual discharged in ¢/kg
Applied to inputs or product outputs, e.g., charge on packaging
Applied to activities, e.g., reduced parking fees for car pools
Applied to residuals modification, e.g., federal and state grants for construction and operation/maintenance of municipal sewage treatment facilities
Direct public investment in other than residuals modification facilities, e.g., open space, mass transit

Administrative—by order *within* governmental agencies or private organizations
Applied directly to residuals, e.g., separate various types of paper residuals in offices for recycling
Applied to products used, e.g., specify energy limits not to be exceeded in new buildings
Applied to activities, e.g., specification of limits on thermostat settings for heating and air conditioning

Judicial
Court and/or administrative law review and action, or threat thereof, to compel compliance; civil and/or criminal suits

Educational/informational
Programs can be mounted to inform groups of the implications of their activities with respect to residuals generation and adverse impacts on ambient quality, and alternative behavior patterns that would reduce such impacts, e.g., litter campaigns, appliance labeling

Characterizing the incentives problem

- *What stimulates a state government to implement its responsibilities for environmental quality management? Is it the provision of planning funds? Is it the designation of particular types of planning areas or planning agencies? Is it the requirement of obtaining approval of plans and designs by EPA? The provision of planning funds clearly has resulted in the generation of planning documents. But, to what extent has these plans been implemented and the desired improvement in environmental quality actually achieved?*
- *What induces a state, in turn, to stimulate the sectors within the state—municipalities, industrial operations, state facilities—to act? Is it the provision of grants for construction of sewage treatment plants (or other facilities)? Is it the provision of grants for operation and maintenance? How can the states be induced to do a more adequate job of monitoring the activities of dischargers, and of enforcing whatever constraints are imposed on them? How can the federal government measure the performance of the states, and the states, in turn, measure the performance of lower levels of government?*
- *What implementation incentives are most appropriate for what types of residuals generated by what specific activities? Even if total suspended solid (TSS) residuals had the same environmental impacts, regardless of the source, the generation phenomena are not the same for industrial activities, mining activities, municipalities, urban-storm runoff, or agricultural activities. Assessing an effluent charge on TSS discharges from agricultural operations would be more difficult than assessing such a charge on an industrial discharge, but not impossible.*
- *Even if the installation of methods to reduce discharges can be induced, what incentives are there to induce operation and maintenance of these methods over time? Operating facilities involves costs; any reduction in O&M for any activity—industrial, municipal, or agricultural—reduces costs to that activity. Because there is no net gain to the activity from reducing the discharge of its residuals, particularly if the beneficiaries are downstream, there is no internal incentive to operate facilities efficiently.*
- *Considerable variation exists in residuals generation over time in most activities, even under normal conditions. What are the most efficient implementation incentives to reduce the variability and the mean discharges of residuals?*

which it remains effective under changed conditions. Consideration should be given to whether it can only be applied intermittently or continuously, as well as whether or not the strategy can be applied to selected activities—either within a category or among categories—or can only be applied to all activities generating the residual.

- *Simplicity in administration,* or the procedural ease with which an incentive can be implemented. A major criticism of permit systems, for example, is the multiplicity and duplication of applications and approvals that must be obtained before an activity can operate.
- *Timing considerations* relate to the fact that strategies vary with respect to both the time required to put the physical method in place and into operation and the time required after it is in operation before the effect on environmental quality occurs. Timing is particularly important where adverse ambient conditions exist that need to be ameliorated as soon as possible. Timing is affected also by legal considerations. If new legislation must be enacted, implementation may take longer than if legal authority already exists. Public receptivity also affects timing. A strategy new to the public may require more time to implement than one that is not.
- *Political considerations* would include at least six components. The first would be the policymaker's sense of his constituency's perception of the particular problem in relation to other environmental quality problems; for example, improved air quality vis-a-vis improved water quality. The second would be his constituency's perception of environmental quality management problems in relation to other social problems in the area, such as housing, transportation, and employment. A third would be the impact on inter-governmental relations, which should be considered vis-a-vis the strategy's effect on the normal way of doing the government's business. A fourth component refers to the degree to which an implementation incentive im-

posed at one level of government is consistent with those imposed at other levels of government. A fifth component would be public acceptance. Finally, the sixth component would relate to the degree of difficulty in obtaining legal authority for the institutional arrangement to impose the incentive. This includes such questions as: Does adequate authority to implement the strategy exist? Would existing legislation have to be changed to enable implementation, or would entirely new legislation have to be passed? Are questions of preemption, due process, or takings involved?

- *Intermedia effects* should also be explicitly considered with regard to the quantities of other residuals generated and discharged into any of the environmental media. Three primary resource-use effects to be evaluated would include net energy required, net land required, and net consumptive use of water. An environmental quality management strategy may be energy intensive, or it may actually reduce total energy use in the area. The land required by a strategy to dispose of mixed solid residuals and sludge, for example, may be an important consideration in a densely urbanized area. The use of ponds, lagoons, and spray irrigation to reduce discharges may increase the net consumptive use of water in an area.

After evaluating each strategy according to the indicated criteria, the final step in evaluating strategies is to combine the ratings on the individual criteria. This process involves assigning relative weights to the individual criterion, which is the responsibility of decision-makers, not analysts. Those in positions of accountability in any society are likely to have judgments concerning which criteria are more important than others.

Concluding comment

A wide range of physical methods for improving environmental quality exists, many of which, however, are never identified or evaluated in the planning phase. At the same time, a wide range of implementation incentives also exists, particularly in the category of economic incentives, which are rarely considered. Actions at all levels of government, as well as the private sector, affect environmental quality and these must be considered explicitly, particularly with respect to consistency among the incentives at various levels.

No single management strategy will be best for all situations. Only through a systematic evaluation of the many alternative strategies available for any given problem and an explicit trade-off of the many conflicting effects of any chosen strategy, is desired environmental quality likely to be achieved in an effective, efficient, and equitable manner.

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CURRENT RESEARCH

Biological Regeneration of Ammonium-Saturated Clinoptilolite
I. Initial Observations

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■ In the search for a more economical regeneration technique for ammonium removal from secondary effluents by use of selective ion exchange, tests were made to determine whether nitrifying bacteria can regenerate ammonium-saturated clinoptilolite. Small-scale batch regeneration tests were conducted in which known weights of ammonium-saturated clinoptilolite were contacted with varying concentrations of nitrifying sludge of known activity. Following contact under carefully controlled conditions for a measured time period, the extent of regeneration was determined by eluting the residual ammonium and measuring its concentration. The results indicated that high levels of regeneration (80%) may be achieved in short periods of time (1–3 h) under the conditions tested and that the rate of regeneration increases as the concentration of nitrifying sludge increases. A mechanism of regeneration is suggested, and the application of a biological regeneration process is briefly discussed.

The naturally occurring zeolite, clinoptilolite, has been demonstrated to be effective in removing ammonium ions from secondary and tertiary effluents. However, the cost of chemical regeneration remains high and represents more than 50–60% of the total process costs even with regenerant reuse (1). As a result, a number of alternative regeneration schemes have been devised, and some have been tested (1–4). This paper presents the initial results of a study to determine whether nitrifying bacteria may be used to regenerate spent clinoptilolite.

In 1973 Sims et al. (5) reported that powdered clinoptilolite added to the aeration tank of an activated sludge pilot plant and recirculated with the sludge improved the nitrifying performance of the sludge. They suggested that clinoptilolite continually concentrated the ammonium at its surface where a layer of nitrifying bacteria oxidized it. In this way they believe the clinoptilolite was continually regenerated. However, the data and the arguments substantiating the biological regeneration mechanism were weak. The objective of this study was therefore to determine whether indeed nitrifying bacteria could regenerate clinoptilolite and, if so, to determine the extent of regeneration that could be achieved in different times and with different concentrations of nitrifying bacteria.

Experimental

Preparation and Characterization of Clinoptilolite. The clinoptilolite was supplied (in rock form) by the Double Eagle Mining Co., Casper, Wyo. The zeolite was ground and

sieved, and the fractions between U.S. Standard mesh numbers 18 and 50 were used in these studies. The zeolite samples were washed to remove fines and conditioned by alternate treatment with 0.25 M ammonium sulfate and 1 M sodium chloride. The zeolite was then rinsed thoroughly and stored dry in the sodium form.

The zeolite was characterized by its performance in column operation. Fifty- to 100-g quantities of the conditioned zeolite were transferred to a Plexiglas column measuring 2.5 cm i.d. by 60 cm. An ammonium chloride solution of known strength was applied to the column by a gravity feed constant head device so that the maximum deviation from the mean flow rate of 12 bed volumes per hour in each of the tests was less than 4%. The ammonia content of the column effluent was measured with time. The breakthrough curve so obtained was used to calculate the capacity of the zeolite for ammonium exchange.

Culturing Nitrifying Bacteria. A sample of waste sludge was taken from an activated sludge pilot plant which was being operated in the Environmental Engineering Laboratories at the University of Illinois. The plant was treating domestic sewage and was operated with a long mean cell residence time. The sludge sample was used as a source of nitrifying bacteria.

The nitrifying bacteria were cultured in a 16-l. aeration tank to which ammonia and other nutrients were added with a draw and fill technique. Once a day the air was turned off for approximately 20 min, and the sludge was allowed to settle. Eight liters of the supernatant solution was then replaced with 8 l. of dechlorinated tap water and nutrient solutions. Initially, low concentrations of ammonia were added to the reactor, and over a two-week period the concentration of ammonia was increased to 200 mg/l. as nitrogen and then maintained at that value. The nutrient solution addition provided the following concentrations in the reactor when aeration was resumed: $(NH_4)_2SO_4$, 200–400 mg/l. as N; $NaHCO_3$, 420 mg/l.; $K_2HPO_4 \cdot 3H_2O$, 1000 mg/l.; $CaCO_3$, 10 mg/l.; $MgSO_4 \cdot 7H_2O$, 100 mg/l.; $NaHPO_4$, 100 mg/l.; $FeCl_3$, 2 mg/l.; and $(NH_4)_6\cdot M_0O_{24} \cdot 4H_2O$, 2 mg/l.

The culture reactor was equipped with a Leeds & Northrup Model 7075-3 pH controller which maintained a pH of 7.9 ± 0.2 by regulating an ASCO 0.187-in., two-way stainless steel solenoid valve for the controlled addition of 1 M Na_2CO_3. The volatile suspended solids content of the reactor was monitored on a daily basis.

Nitrification Tests. To determine the nitrifying activity of the sludge in the culture reactor at the time of its use in regeneration tests, nitrification tests were conducted. The procedure consisted of taking a known volume of sludge from the aerated and well-mixed culture reactor and allowing it to settle in a graduated cylinder for ½ h. The clear supernatant was then decanted and replaced with deionized water to bring

the total solution volume to 1 l. The contents of the cylinder were transferred to a 1-l. beaker equipped with a pH electrode and air diffuser. Ammonium sulfate solution was added to the aerated contents of the beaker in sufficient quantity to provide an initial ammonium concentration of 100–150 mg/l. as N. The pH of the solution was maintained manually at pH 8 by the dropwise addition of sodium carbonate, and the rate of nitrification was determined by monitoring the ammonium ion concentration in solution with time. The temperature of the solution was not controlled, but initial and final temperature measurements were taken.

The concentration of volatile suspended solids in the culture reactor was determined at the time of these tests to relate the nitrifying activity to the weight of sludge employed in the nitrification test.

Clinoptilolite Regeneration Tests. These tests were also conducted on a batch basis. Preweighed samples, usually 5 g, of the conditioned zeolite in the sodium form were saturated with ammonium ions and washed with an excess of deionized water. The zeolite samples were transferred to a 1-l. beaker with approximately 700 ml of deionized water. The contents of the beaker were aerated and stirred for approximately 5 min, and the pH of the solution was raised and maintained at 8 ± 0.2 by the manual addition of 1 M Na_2CO_3. Simultaneously, a known volume of sludge was removed from the batch culture reactor, and the nitrifying organisms were allowed to settle for ½ h. The supernatant was decanted, and the nitrifying sludge contained in approximately 100–200 ml volume was added to the beaker containing the zeolite. The volume of solution in the beaker was adjusted to 1 l., and the starting time was recorded. The temperature of the reactor was not controlled, but initial and final temperature measurements were taken.

At timed intervals the ammonia content of the solution and the amount of base added for the maintenance of pH were measured and recorded. At the conclusion of the test, the ammonium concentration in solution was recorded, and the zeolite was separated from the nitrifying sludge which was returned to the culture reactor for subsequent reuse. The regenerated clinoptilolite was then transferred to a small Plexiglas column, and its residual ammonia content was measured by elution with an excess of 1 M sodium chloride.

Analytical

Ammonium and nitrite concentrations were measured by use of Orion ion selective electrodes coupled with an Orion Model 701 expanded scale digital pH/millivolt meter. The electrodes were calibrated for each test and checked routinely. Several investigators have previously reported on the interferences and the accuracy of the ammonia electrode in measuring different concentrations in waters of varying quality (6, 7). Nitrate analyses were initially conducted with an Orion

model nitrate selective electrode; however, the electrode gave an erratic response, and it was abandoned in favor of the UV spectrophotometric method described by Goldman and Jacobs (8). These nitrate analyses were conducted on an ACTA III UV spectrophotometer at a wavelength of 220 nm. The volatile suspended solids measurements were made in accordance with the procedure described in the 13th edition of "Standard Methods".

Results

Characterization of Clinoptilolite. The total exchange capacity of the Wyoming clinoptilolite was determined from the breakthrough curves and from the subsequent elution of ammonia from the saturated columns. Three measurements were made of the zeolite capacity for two different mesh sizes: 30×40 mesh and 20×25 mesh. The same preconditioning treatment and the same technique for measuring capacity were used for each mesh size, and the results are tabulated in Table I.

The mean capacity for the 30×40 mesh zeolite was determined to be 2.0 meq/g of dry clinoptilolite and that for the 20×25 mesh zeolite 2.04 meq/g. These measured capacity values are in agreement with values reported for clinoptilolite from the Hector deposit in California (1, 9).

Cultivation of Nitrifying Bacteria. Nitrifying bacteria were cultivated readily using the draw and fill technique, and the solids level in the reactor rose quite rapidly. The unit was operated for three weeks prior to being used in any tests. However, since sludge was not wasted during the test period, the mixed liquor volatile suspended solids in the reactor continued to increase slowly from approximately 200 mg/l. at the start of testing, to values in the region of 500 mg/l. at the conclusion of the test period (a period of 30 days). The nitrifying sludge so generated was very flocculent in nature and settled extremely well leaving a very clear supernatant.

The ammonium ion concentration fed to the reactor was depleted very rapidly, being reduced to near zero within a matter of 4–5 h; consequently, the feeding procedure was modified, and the reactor was fed on a twice daily basis midway through the testing period.

Nitrification Tests

Prior to any nitrification or regeneration studies, tests were made to determine the extent of ammonia stripping under the test conditions. A liter of deionized water containing 150 mg/l. of ammonia nitrogen was held at pH 8.0 and 29 °C and aerated. The air flow rate was measured and corresponded to 10 standard ft^3/h. This air flow rate was the maximum ever used in nitrification studies since any increase caused excessive turbulence and loss of solution from the test reactor. Aeration over long time periods indicated an hourly ammonium loss of 1.1 mgN/l./h. Very similar rates of ammonia stripping may be calculated from the data of Srinath and Loehr (10) who analyzed ammonium desorption by diffused aeration. The very low rates of ammonia stripping were negligible in this study since the rates of nitrification were very much greater as shown below.

Nitrogen balances were not conducted in the majority of the nitrification and regeneration tests owing to the failure of the nitrate electrode that was used initially. When Goldman's method was employed for nitrate analysis, however, good nitrogen balances were obtained. An example of the data obtained from a nitrification test is presented in Figure 1. Nitrite nitrogen concentrations were less than 0.2 mg/l. at all times and thus were negligible.

The good nitrogen balances that were obtained, however, and the observations that nitrogen losses through ammonia stripping or nitrite accumulation were negligible made it valid to monitor the rate of nitrification by means of the rate of

Table I. Clinoptilolite Capacity Measurements Recorded as Milliequivalents of NH_4^+ per Gram of Dry Clinoptilolite in Sodium Form

| Test no. | 30 × 40 Mesh | | 20 × 25 Mesh | |
	A[a]	B[b]	A	B
1	1.84	...	1.74	...
2	2.04	2.00	1.98	...
3	2.04	2.06	2.25	2.21

[a] Total ammonium capacity as measured from the breakthrough curve. [b] Total ammonium capacity as measured by elution of ammonium from the saturated clinoptilolite.
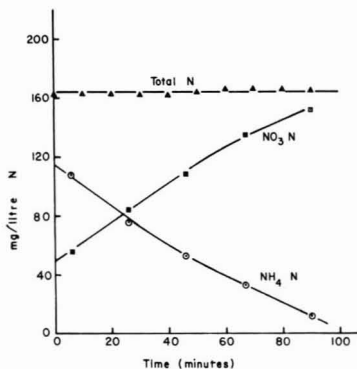
Figure 1. Example of nitrogen balance obtained in nitrification test

ammonium disappearance from solution. All of the oxidation rates reported in this paper were based upon the measured rates of decrease in ammonium concentration.

Each time a regeneration test was made, a simultaneous nitrification test was conducted. The total ammonium content of the solution in the nitrification reactor corresponded closely to the total ammonium content of the clinoptilolite (approximately 140 mg NH_4-N). Since the mixed liquor volatile solids content of the culture reactor was also measured, it was possible to determine the activity of the nitrifying sludge. The activity of the sludge measured as mg N oxidized/h/mg MLVSS varied between 0.1–0.2 with a mean of 0.15 during the test period.

A typical nitrification test curve showing the ammonia concentration as a function of time is shown in Figure 2. This figure indicates that the oxidation of ammonia is zero order with respect to ammonia concentration at high ammonium ion concentrations; however, the nonlinear relationship observed at low ammonium ion concentrations indicates that the nitrification rate is a function of ammonium concentration in this range. The deviation from zero order kinetics was observed at concentrations of NH_4-N as high as 40 mg/l., but most frequently it was below 30 mg/l. N.

The deviation from linearity was checked to determine whether it resulted from any nutrient deficiency; however, the addition of nutrients did not influence the nitrification kinetics. Temperature variations could not be held to account for the observed behavior because of the narrow temperature range investigated (25–29 °C). Furthermore, the behavior appeared to be independent of MLVSS concentration.

The rate of nitrification that was used to characterize the activity of the sludge was determined from the linear portion of the curve shown in Figure 2.
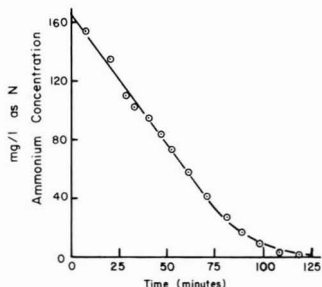

Figure 2. Typical nitrification test result showing nonlinearity below 30 mg/l. of ammonium
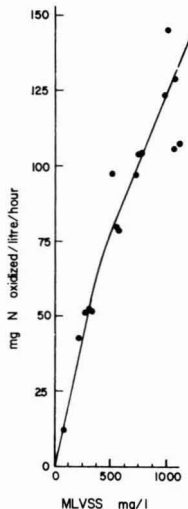
Figure 3. Influence of sludge concentration on rate of nitrification in nitrification test reactor

Different volumes of sludge were withdrawn from the culture reactor and used in nitrification tests to identify the influence of sludge concentration on the rate of nitrification. In Figure 3 the rate of nitrification, measured as mg N oxidized/l./h, is plotted vs. the concentration of mixed liquor volatile suspended solids concentration in the nitrification reactor. The line drawn through the data is not linear, and the slope of the curve tends to decrease with increasing MLVSS.

Measurements of dissolved oxygen concentration (DO) were not taken during the initial nitrification tests. However, subsequent tests, duplicating the nitrification rates shown in Figure 3 and collected under identical experimental conditions, indicated that the DO ranged from 6 down to 1 mg/l. at the highest sludge concentration tested. Since the data of Nagel and Haworth (11) showed that the nitrification rate was depressed at low dissolved oxygen concentrations, it is likely that the nonlinearity in Figure 3 results from the low DO levels in the reactors tested with high sludge concentrations.

The amount of base added to the nitrification test reactors was monitored with time to determine whether the base addition could be used to monitor the extent of nitrification. The amount of base added per meq of ammonium oxidized, however, varied widely from 50 to 150% of the stoichiometric requirement of 2 meq/meq ammonium oxidized. When alkalinity measurements were made before and after each test, it was determined that alkalinity changes in solution were in part responsible for the variation in the amount of base required for the maintenance of pH. When the alkalinity changes in solution were accounted for, the consumption of base ranged from 1.6 to 1.9 meq/meq of ammonium oxidized. It is probable that the stripping of CO_2 during aeration may account for the remaining differences between the measured and stoichiometric base requirements.

The rate of addition of base reflected the rate of nitrification observed during nitrification tests, being greatest when nitrification was greatest and slowing down as the ammonium concentration dropped to near zero. However, since the alkalinity of the solution varied during the test and since there was no consistent relationship between the amount of base added to the amount of ammonium oxidized, the rate of base addition could not be used to monitor the rate of nitrification with any accuracy.

Table II. Regeneration Test Results

Run no.	MLVSS, mg/l.	Temp range, °C	Regeneration time, h	Rate of nitrification, mg/l./h	% Regeneration achieved
1[a]	93	27–28	3.92	9.7	5.4
2	218	27–28	4.75	24	82
3	696	28–29.5	3.50	29	72
4	1096	28–29.5	1.78	66	81
5	1458	25–27	1.52	75	80
6	261	27	3.58	28	70
7[b]	1674	28	2.15	113	87
8	570	27–28	3.05	37	78
9	1185	28–29	2.00	58	79
10	1850	28–29	1.30	80	73
11	2864	28	1.00	110	76
12	1098	27	1.68	57	68
13	1060	26–27	2.00	59	84
14	1044	27	1.67	65	76
15	998	27–28	1.67	58	70
16	972	27–28	1.67	64	76

[a] 25 g of clinoptilolite in reactor. [b] 10 g of clinoptilolite in reactor.

Figure 4. Influence of sludge concentration on average rate of nitrification in regeneration test reactor

Figure 5. Ammonium concentration observed in solution during two regeneration studies

Regeneration Studies

The results of 16 regeneration tests are shown in Table II. The percentage regeneration for each test was calculated by dividing the amount of ammonia removed from the clinoptilolite by the total original ammonium content of the clinoptilolite. The amount of ammonium removed from the zeolite was estimated by subtracting the amount of ammonium eluted from the regenerated clinoptilolite from the total ammonium content of the saturated clinoptilolite.

The tests were varied so that a variety of sludge concentrations and regeneration times were studied. The tabulated data indicate that regeneration levels in the range of 70–80% were routinely achieved in a time frame of 1–3 h depending upon the sludge concentration (MLVSS) employed in the regeneration reactor.

The data in Table II were used to construct a plot of the amount of ammonium oxidized per hour vs. MLVSS shown in Figure 4. This figure is analogous to Figure 3 calculated for the nitrification tests. It is likely that the nitrification rate in the regeneration reactor varied during the test period, and one cannot assume it was constant. Figure 4 therefore reflects the influence of sludge concentration on the average nitrification rate during the test period. The data points shown in Figure 4 are (like Figure 3) described by a curvilinear plot. The data exhibit slightly more scatter than Figure 3; however, the same trend is apparent. From Figures 3 and 4, the rate of nitrification is much slower during regeneration than it is when the ammonium is present in free solution. This is not surprising since the ammonium ions within the crystalline cages of the zeolite are not accessible to nitrifying bacteria. For the ammonium to be oxidized, it must first diffuse to the particle surface or into solution where it becomes accessible to the bacteria. The rate of nitrification during regeneration may therefore be governed by the rate at which ammonium becomes accessible.

The free concentration of ammonium in solution in the regeneration reactor was monitored with time during each test, and the typical variation in ammonium concentration is shown in Figure 5 for two MLVSS concentrations.

The curves in Figure 5 indicate a trend that was apparent in the data collected on solution ammonium concentrations in the regeneration reactors. The use of higher sludge concentrations resulted in the displacement of higher ammonium concentrations from the clinoptilolite. This was explained by considering the experimental technique. The sludge used in the regeneration studies incorporated some of the nutrient solution drawn from the cultivation reactor; thus, higher ambient salt concentrations prevailed in the regeneration reactors operated with large sludge concentrations. The higher ambient salt concentration encouraged the exchange displacement of ammonium ions and resulted in the higher solution concentrations observed. The curves also indicate that the free concentration of ammonium in solution was never more than 50 mg/l. and dropped to lower levels as regeneration proceeded. Since the nitrification rate was a function of ammonium concentration in this range, the lower nitrification rates observed during regeneration may be a reflection of this. The rate of nitrification may therefore have been limited by the free concentration of ammonium in solution.
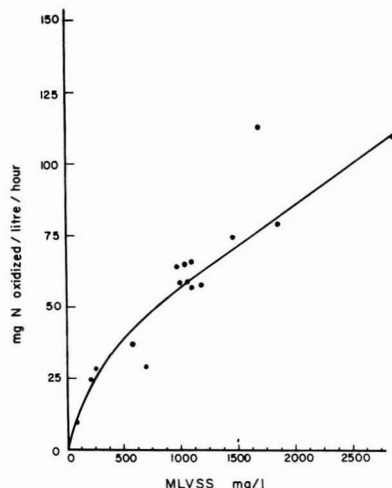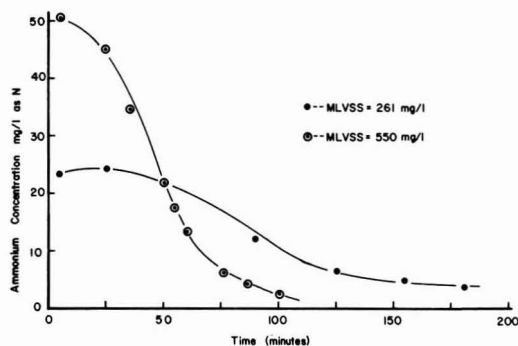
Discussion

These batch studies have clearly shown that it is possible to regenerate ammonium saturated clinoptilolite through the use of nitrifying bacteria. Furthermore, the regeneration process is quite rapid. The time required for regeneration depends very much upon the nitrifying activity of the sludge

used. For example, with high sludge concentrations, as much as 80% regeneration was achieved in less than 2 h of contact time.

The rate of nitrification during regeneration was always observed to be much slower than the rate of nitrification of free ammonium in solution.

Similar batch tests were conducted by Sims et al. (5) except that they added 10 mg/l. NH_4–N to a batch reactor containing both a nitrifying sludge and varying quantities of the clinoptilolite. They observed that the presence of 10 g of clinoptilolite caused no significant difference in nitrification rate. The presence of 100 g of clinoptilolite reportedly enhanced the nitrification rate. However, the authors did not maintain exactly the same pH in all their tests; the control pH averaged 6.9 and the zeolite tests averaged 7.5. Sawyer et al. (12) recently summarized the literature regarding the influence of pH on observed rates of nitrification. This summary suggests that the improved nitrification kinetics that Sims et al. (5) observed in the presence of zeolite may stem from the pH difference alone. Nevertheless, these authors' data also suggest that ammonium associated with clinoptilolite can be nitrified.

It is questionable whether the slower nitrification rates observed during regeneration arise from the availability of the ammonium since ammonium was shown to be present in solution. However, the solution concentrations of ammonium present in the regeneration reactor were in the range in which nitrification rate was a function of ammonium concentration. As such, the amount of available ammonium may have limited the nitrification rate. This remains unclear, for it is not possible to estimate the availability or the quantity of ammonium ions associated with the external surface area of clinoptilolite particles.

If it is the free ammonium concentration present in solution that is controlling the rate of nitrification, then it may be possible to improve the rate of regeneration by increasing the salt concentration in solution. This would have the effect of increasing the amount of ammonium displaced from the zeolite, thereby increasing the solution concentration of ammonium. The salt concentration differences between reactors in this study were not marked enough to cause large enough increases in solution ammonium concentration. However, large salt concentrations may inhibit the activity of nitrifying bacteria, and research is needed to identify the best conditions for regeneration.

The study conducted by Sims et al. (5), in which clinoptilolite was added to an activated sludge treatment plant and recirculated continually with the sludge, clearly did not take full advantage of the capacity of the clinoptilolite to remove ammonium from the water. The capacity of the clinoptilolite may have been useful in reducing the ammonium content of the solution when first added, but once a slime layer of attached microorganisms developed, it is questionable whether any benefits were derived from the use of clinoptilolite that would not develop from the use of inert particulate material such as sand.

To take full advantage of the clinoptilolite's exchange capacity and selectivity for ammonium ions, it must be used as an ion exchanger first, and then regenerated biologically in the same way that chemical regeneration is practiced.

The biological regeneration process would result in the accumulation of nitrogen in the form of a nitrate brine rather than as a concentrated ammoniacal brine. The latter brine which results from the chemical regeneration process must be stripped of its ammonia content and reused for the chemical regeneration process to be economically attractive. The nitrate brine, however, may be denitrified in a number of ways; for example, the brine may be used to raise the redox potential of raw sewage entering a waste treatment facility. As such, this may be a significant advantage in favor of biological regeneration.

Conclusions

The data presented in this study indicate that 5-g quantities of ammonium saturated clinoptilolite may be 80% regenerated in a period of 1–3 h by 1 l. of nitrifying sludge at a temperature of approximately 27 °C. The rate of ammonia nitrification during regeneration was considerably slower than the nitrification rate of free ammonium ions in solution observed in control tests. The results obtained, however, indicate that the rate of regeneration of clinoptilolite may be increased by increasing the concentration of nitrifying sludge in solution.

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Biological Regeneration of Ammonium-Saturated Clinoptilolite
II. Mechanism of Regeneration and Influence of Salt Concentration

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■ The influence of high concentrations of sodium nitrate on the activity of a nitrifying sludge was investigated, and salt concentrations of up to 0.3 M stimulated nitrifying activity. When the nitrifying sludge was used to regenerate ammonium-saturated clinoptilolite in batch tests, the presence of salt concentrations up to 0.4 M accelerated the rate of regeneration, and complete regeneration was accomplished in only 3 h. The data collected in the batch regeneration tests indicated that the free ammonium concentration in solution controls the rate of nitrification during regeneration. Under the conditions tested, more rapid nitrification was achieved by decreasing the clinoptilolite particle size and by increasing the weight of clinoptilolite in a given volume of sludge. Ion exchange followed by oxidation of the liberated ammonium was the mechanism of regeneration.

Nitrifying bacteria may regenerate ammonia-saturated clinoptilolite in relatively short periods of time (1). However, the rate of nitrification during regeneration was always slower than that observed in ammonium-containing solutions, and it appeared as if this difference might stem from the solution concentrations of ammonium that developed during regeneration.

The early investigations of nitrification in soils led to two conflicting opinions of the availability of "sorbed" ammonium. One group of investigators ($2, 3$) obtained experimental data which suggested that the rate of oxidation of ammonium in soil was proportional to the amount of ammonium sorbed by the soil, and they believed that the nitrifying bacteria preferentially metabolized the adsorbed ammonium at the soil surface. A second group of investigators (4–8) collected experimental evidence to support their contention that certain soils or soil minerals may adsorb or "fix" ammonium in a form that retards nitrification. In 1955 Goldberg and Gainey (9) resolved these different views by conducting two carefully controlled experiments. In one experiment, clays in the potassium form were added to a nutrient solution containing a known amount of ammonium and an inoculum of nitrifying bacteria. In the second experiment an equivalent amount of ammonium was added to the inoculated nutrient solutions by adding the appropriate weights of ammonia-saturated clays. The results of their studies indicated that the extent of nitrification in both tests was directly related to the concentration of ammonium in solution.

These observations provide some evidence that the mechanism of regeneration may be ion exchange followed by nitrification of displaced ammonium. If we assume this mechanism, it is possible to outline a theory of the regeneration process. The first step is ion exchange, and as soon as the ammonium-saturated zeolite is placed in solution, a small amount of ammonium will be displaced according to Equation 1:

$$Z \cdot NH_4^+ + Na^+ + Cl^- \rightarrow Z \cdot Na^+ + NH_4^+ + Cl^- \quad (1)$$
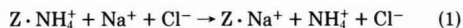
The ion-exchange equilibrium between ammonium and sodium ions for clinoptilolite has been studied by Koon and Kaufman (10). They calculated the selectivity coefficient of Hector clinoptilolite for ammonium over sodium to be 4.5 from batch isotherm studies at 23 °C. This value was calculated when the ionic fraction of ammonium ions in solution was 0.5 and higher values were indicated at lower ionic fractions. However, it is assumed that this value is appropriate in our analysis. The ammonium ion concentration in solution may be calculated using Equation 2 if equilibrium in a binary system is assumed.
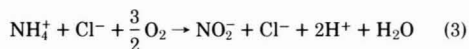
$$[NH_4^+] = \frac{\overline{X}_{NH_4^+} \cdot [Na^+]}{4.5 \, (1 - \overline{X}_{NH_4^+})} \quad (2)$$

The square brackets represent concentrations in solution expressed as meq/l., and the $\overline{X}$ values represent the ionic fraction of species in the zeolite phase.
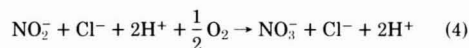
From this equation, the amount of ammonium displaced from the zeolite is influenced both by the amount of ammonium on the zeolite and the salt concentration in solution. Thus, even if only a very small salt concentration is present when there is an appreciable amount of ammonium on the clinoptilolite, a concentration of free ammonium ions will be found.

As the ammonium ions are liberated, they are oxidized by the nitrifying bacteria. The reaction stoichiometry is represented by Equations 3–5
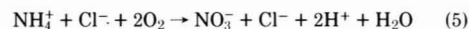
Nitrite Production (*Nitrosomonas*)

$$NH_4^+ + Cl^- + \frac{3}{2}O_2 \rightarrow NO_2^- + Cl^- + 2H^+ + H_2O \quad (3)$$

Nitrate Production (*Nitrobacter*)

$$NO_2^- + Cl^- + 2H^+ + \frac{1}{2}O_2 \rightarrow NO_3^- + Cl^- + 2H^+ \quad (4)$$

Overall Nitrification

$$NH_4^+ + Cl^- + 2O_2 \rightarrow NO_3^- + Cl^- + 2H^+ + H_2O \quad (5)$$

The hydrogen ions produced during the nitrification process are neutralized by the addition of sodium carbonate. Equation 5 may be rewritten to include the concurrent neutralization of hydrogen ions, and the overall equation is presented in Equation 6.

$$NH_4^+ + Cl^- + 2O_2 + Na_2CO_3$$
$$\rightarrow NO_3^- + Cl^- + 2Na^+ + 2H_2O + CO_2 \quad (6)$$
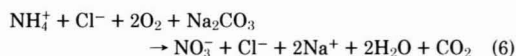
Combining Equations 1 and 6, we obtain Equation 7 which describes the overall regeneration process.

$$Z \cdot NH_4^+ + 2O_2 + Na_2CO_3$$
$$\rightarrow Z \cdot Na^+ + NO_3^- + Na^+ + H_2O + CO_2 \quad (7)$$

This equation indicates that for each equivalent of ammonia oxidized, two equivalents of sodium carbonate are required for pH control. One-half of the sodium ions so added replace the ammonium ions in the zeolite, and the other half remain in solution as sodium nitrate. The regeneration process therefore results in the buildup of sodium nitrate in solution.

The buildup of salt is desirable in that it may improve the rate of regeneration in the subsequent regeneration cycle. However, too high a brine concentration may be undesirable since it may cause inhibition of nitrifying bacteria. Brine must therefore be wasted after each cycle and replaced with makeup water to maintain a desirable salt level. The amount of brine

wastage will depend upon its concentration; for that reason, it would be desirable to operate at as high a brine concentration as practicable.

From the above discussion, any research on the biological regeneration of clinoptilolite must take into account the very important influence of salt concentration. Unfortunately, there is very little information available which characterizes the behavior of nitrifying bacteria in waters of high salt content. The main objectives of this research were, therefore, to identify the influence of salt concentration upon nitrification and regeneration and to obtain experimental data to support the ion-exchange mechanism postulated.

Experimental

Nitrifying bacteria were cultivated in a continuous flow reactor with sludge recycle. The 30-l. aeration tank was equipped with a Leeds & Northrup Model 7075-3 pH controller set to maintain a pH of 7.8–8.0 through the controlled addition of 2 M Na_2CO_3. The composition of the influent was the same as previously described (1) except that the ammonium nitrogen concentration was elevated to 1000 mg/l. The influent flow rate to the aeration tank was 20 ml/min, corresponding to a hydraulic detention time of approximately 1 day. The reactor was operated at room temperature, 25–30 °C. The sludge was recycled after sedimentation in a 4-l. baffled sedimentation tank. A timer-controlled, variable speed Masterflex pump recycled the sludge at a flow rate of approximately 500 ml/min for 1 min in every hour.

Effluent ammonium concentrations and the mixed liquor volatile solids were measured routinely every other day. The nitrification tests, regeneration tests, and analytical methods used in this study were all the same as described previously (1).

Results

The cultivation of nitrifying bacteria in a continuous flow unit proved trouble free, and the unit required little attention over a five-month operating period. Sludge was wasted to maintain a mean cell residence time of 16 days. Over the two-month test period the MLVSS ranged between 600 and 750 mg/l. at this wastage rate.

The effluent ammonia concentration from the culture reactor was always 0.1 ~ 0.5 mg/l. as nitrogen, being unaffected by variations in the sludge age. Maximum nitrogen oxidation rates ranged between 0.01–0.1 mgN/mg MLVSS/h and did not appear to be related to sludge age either.
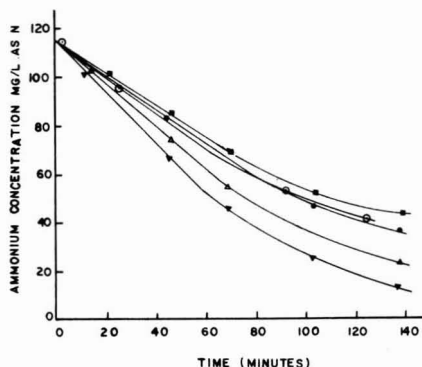

Figure 1. Influence of sodium nitrate concentration on nitrification rate
⊙ No salt added, ▼ 100 meq/l. $NaNO_3$, △ 190 meq/l. $NaNO_3$, ● 260 meq/l. $NaNO_3$, and ■ 364 meq/l. $NaNO_3$

Nitrification Studies

The influence of salt concentration on nitrifying activity was examined first. Nitrification tests were conducted under identical conditions except that the solution salt concentration was varied. Nitrification rates observed with sodium nitrate concentrations ranging from 0 to 800 meq/l. suggested that the rate of nitrification may be increased slightly by the addition of 200 meq/l. of $NaNO_3$. The addition of 400 meq/l. salt caused a slight decrease in the rate of nitrification, but the addition of higher salt concentrations caused significant inhibition. In Figure 1 the range of salt concentrations studied was narrowed to observe the range 0–400 meq/l. of salt more closely. The results clearly indicate that the addition of 100 meq/l. gave the most rapid nitrification rate. The 190-meq/l. concentration also exhibited a better nitrification rate than the control which contained very little salt. The nitrification rate at a concentration of 260 meq/l. of $NaNO_3$ was very similar to that of the control; however, 363 meq/l. caused the rate to decrease somewhat.

The study indicates that the nitrification rate was stimulated by salt concentration in the range of 100–300 meq/l. with the most rapid rate of nitrification being recorded for 100 meq/l. It is possible that higher salt levels may be tolerated without ill effects in cultures of nitrifying bacteria that are acclimated to high salt levels. The test procedure employed in this study was harsh. The bacteria were taken from the continuous culture reactor and an ambient salt concentration of 75 meq/l., washed in deionized water, and remixed with a solution containing the test salt concentration. Their behavior may well be influenced by this chain of events, and the maximum nitrification rate observed at 100 meq/l. may only be a reflection of the fact that the culture reactor was operated at a salt concentration of 75 meq/l. However, if we recognize the shortcomings of such a technique, the nitrification data remain valid for the purposes of this study since the bacteria used in the regeneration tests were treated in the same fashion. The intermediate wash with deionized water was required to reduce the initial nitrate level in the reactor so that any change in nitrate concentration could be determined accurately.

Very few studies have been conducted to determine the influence of salt concentration upon nitrifying activity. Lipman and Burgess (12) observed that the rate of nitrification in soils could be accelerated by the addition of small quantities of NaCl or Na_2SO_4, and they observed inhibition when concentrations exceeded 49 meq/l. Na_2SO_4 or 17 meq/l. NaCl. Much higher concentrations of salt were reported by Meiklejohn (13), however, who observed that substantial or complete inhibition of nitrifying bacteria was caused by sodium chloride concentration of 0.5 M. Mills and Wheatland (14), using salt concentrations similar to those employed in this study, reported that the addition of 6600 mg/l. of NaCl (113 meq/l.) to domestic sewage caused no inhibition of nitrification in a trickling filter. When 20 000 mg/l. (342 meq/l.) of salt was added, 10–17% inhibition was noted.

In other studies the addition of salt to nitrifying cultures caused a variable response. Coleman (15) noted that the nitrification in certain soils was stimulated by the addition of $NaNO_3$, while no effect was observed in other samples. Similarly, Loveless and Painter (16) reported that the addition of sodium sulfate to a number of activated sludge samples resulted in increased nitrification rates in only some of the samples. These differences may possibly be caused by variations in the type of nitrifying bacteria present in the individual test units. Recently, investigators ($17, 18$) have observed that pure cultures of nitrifying bacteria isolated from saline waters respond in different ways to salt (NaCl) concentration. Alternatively, these differences may be explained by differences in the cationic composition of the solutions in different test
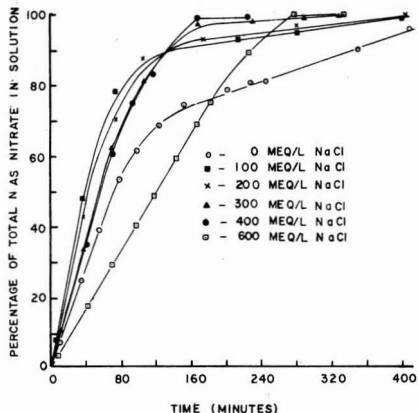
Figure 2. Influence of varying salt concentrations on rate of nitrification in regeneration reactor

units. McCarty et al. (*19*) reviewed the influence of salt concentration on the physiological processes of a variety of organisms and noted that while high concentrations of salt inhibit biological activity, the toxicity of a cation varies with the presence of other cations in solution.

In this study the concentrations of metals other than sodium were negligible. However, if nitrifying bacteria are repeatedly used to regenerate spent clinoptilolite, significant concentrations of magnesium, calcium, and to a lesser extent potassium may develop in solution. Since these ions may cause antagonism or synergism when present together with a high sodium concentration, further studies are needed to determine their influence upon nitrification rates.

Regeneration Studies

Kinetic studies were made of the rate of nitrification in solutions containing ammonia-saturated clinoptilolite and varying salt concentrations. The results are reported in Figure 2 where the percentage of the ammonium nitrogen initially on the zeolite that is oxidized to nitrate is plotted as a function of time. The total initial ammonium nitrogen content of the clinoptilolite was calculated from the amount of nitrate produced during regeneration plus the amount of ammonium eluted from the zeolite at the conclusion of the regeneration process. The curves obtained indicate that the salt concentration exerts a strong influence on the rate of nitrification in this system as well.

All of the curves obtained were linear during the initial stage of regeneration; however, the rate of nitrification characteristically decreased as the extent of nitrification increased. The decrease in the rate of nitrification was most pronounced in the regeneration tests conducted with no added salt or with low salt concentrations. At the higher salt concentrations studied, the curves were almost linear up to complete regeneration of the zeolite.

The initial slopes of the curves in Figure 2 vary with salt concentration. Nitrification rates computed from these slopes are presented in Table I and compared with the measured nitrifying activity of the sludge on the days of the tests. The data show that the nitrification rate in the regeneration reactor is lower than that observed in the nitrification study except when 100–200 meq/l. of NaNO₃ is present in the regeneration reactor. As observed above, the salt concentrations in the regeneration reactor first enhance the rate of nitrification, and then as higher concentrations are used, inhibition occurs. The difference in nitrification rates observed in the

case where no salt is added to the regeneration reactor may be explained by the free ammonium ion concentration in solution during this test. If the ammonium on the zeolite is inaccessible for nitrification, the rate of nitrification will be controlled by the availability of ammonium in solution. The nitrification rate data collected at the time of the test indicated that the rate of nitrification decreased when the free ammonium–nitrogen concentration fell below 20 mg/l.

The deviation from linearity observed in Figure 2 as the extent of nitrification increases correlates well with the ammonium ion concentrations present in solution. The ammonium concentration in solution is plotted as a percentage of the total nitrogen in the reactor for each of the regeneration tests, and the data are presented as a function of time in Figure 3.

The curves in Figure 3 for different salt concentrations very clearly show that as the salt concentration in the reactor is increased, the initial fraction of ammonium-N in solution increases as expected. The concentration of ammonia in solution then decreases as nitrification occurs.

The percentage regeneration at any time is equal to the fraction of nitrogen that has been transferred to the solution phase. The percentage is therefore defined as shown below in Equation 8, where [ ]s refers to equivalent concentrations in solution.

% Regeneration

$$= \frac{[NH_4-N]s + [NO_3-N]s}{\text{Total equivalents N originally on clinoptilolite}} \quad (8)$$

A plot of % regeneration is therefore obtained by combining Figures 2 and 3 as shown in Figure 4. The crosshatched area in each curve represents the contribution of free ammonium to the extent of regeneration. The dashed line under the crosshatched area represents the extent of nitrification and is the same as that shown in Figure 2. The heavy solid line describes the extent of regeneration at any time.

Considering the curves presented for different salt concentrations in Figure 4, it is apparent that during the early stages of regeneration the linear portion of the nitrification curves corresponds to the time at which a large ammonium ion concentration exists in solution. As the ammonium ion concentration dropped, the rate of nitrification tended to decrease, in accord with the nitrification studies. Eventually ammonium concentrations were reduced to very low levels, and the approach to complete regeneration was governed by the rate of nitrification. For example, in the reactors con-

Table I. Influence of Salt Concentration on Initial Rate of Nitrification in Regeneration Reactor

Salt concn in reactor, meq/l.	Av NH₄⁺–N concn in soln, mg/l.	Nitrifying[a] activity of sludge, mgN/ l./h (NA)	Nitrification[b] rate during first 50% of nitrification, mgN/l./h (NR)	$\frac{NR}{NA} \times 100$, %
~0	18	83	63	76
100	42	83	105	127
200	53	83	106	127
300	58	93	78	84
400	66	95	72	76
600	71	95	33	35
800	...	0	0	0
1000	...	0	0	0

[a] Determined in a nitrification control test in which the salt concentration ~0–10 meq/l. and ammonia concentration are approximately 140 mg/l. as N.
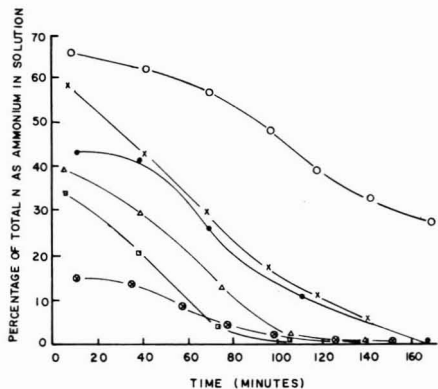[b] In regeneration reactor.

Figure 3. Concentration of ammonium in solution as function of time and salt concentration in regeneration reactor

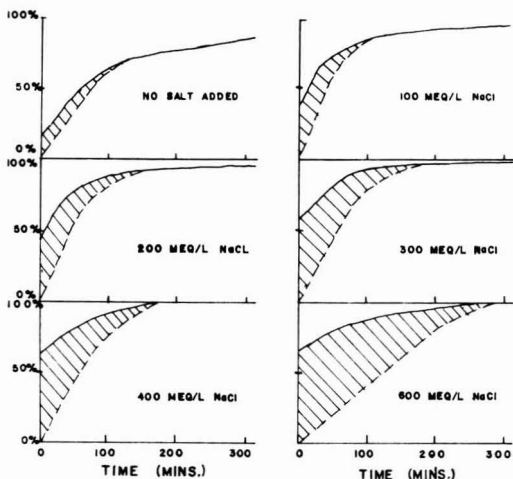⊗ No salt added, ⊡ 100 meq/l. NaCl, △ 200 meq/l. NaCl, ● 300 meq/l. NaCl, x 400 meq/l. NaCl, ○ 600 meq/l. NaCl

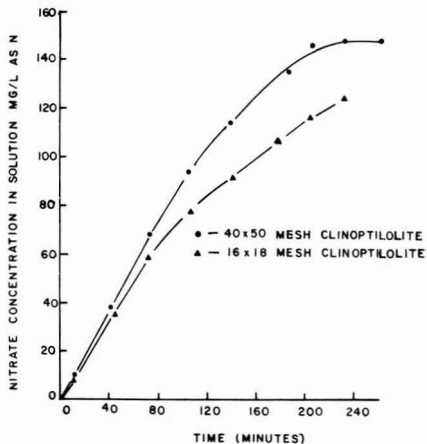**Figure 4.** Variation in rate of regeneration with varying salt concentration

Figure 5. Influence of particle size upon rate of nitrification in regeneration reactor

taining 0, 100, and 200 meq/l. NaNO$_3$, nitrification was extremely slow after 140 min since in each case the ammonia concentration in solution was only 1–4 mg/l. as N.

The rate of nitrification and thus regeneration were therefore limited by the extent of ion exchange during the final stages of regeneration. If the salt concentration in the reactor was increased so that a greater amount of ammonium was displaced from the clinoptilolite, then the rate of nitrification was more rapid, and complete regeneration of the clinoptilolite was accomplished sooner. Thus, Figure 4 indicates that the reactor containing 400 meq/l. achieved complete regeneration first, even though the initial rate of nitrification in this reactor was not as great as that measured in the reactors of lower salt content.

Further studies were conducted to determine the influence of particle size upon the rate of regeneration; a typical result of these studies is presented in Figure 5. When clinoptilolite particles of different sizes were regenerated in a solution containing 200 meq/l. of NaCl, the initial rate of nitrification was not altered significantly. However, the approach to complete regeneration was always observed to be more rapid with particles of smaller size.

As shown previously (1), the capacity of the clinoptilolite for ammonium may be considered independent of particle size. As the particle size is reduced, however, the kinetics of ion exchange are increased. The faster approach to complete regeneration with the smaller clinoptilolite particles may therefore be explained in terms of their more rapid release of ammonium ions.

Many investigators have observed that the provision of a large surface area enhances biological activity (20). This phenomenon has been explained primarily as a result of the fact that a large surface area may provide an interface at which bacteria and their nutrients tend to concentrate. Thus the provision of a large surface area would clearly enhance biological activity where the ambient nutrient concentration is low or where attachment to a solid surface would prevent organism washout in a continuous flow system. It may therefore appear that the surface area effects could also account for the difference in the curves shown in Figure 5, and one could perhaps argue that in the latter stages of regeneration when the ammonium concentration is low, the additional surface area in the reactor with the smaller particle size may enhance the rate of nitrification. This is considered improbable for two reasons, however: the clinoptilolite particles showed no signs of any attached growth at the conclusion of the tests, and even if any bacteria were attached to the particle surface during the test, their mass would represent an insignificant fraction of the total organism mass in the system. For these reasons, surface area effects were considered negligible, and the differences in the rates of ion exchange must be invoked to account for the observed rates of nitrification.

Some tests were also conducted to determine the rates of regeneration of different weights of clinoptilolite. One, two, five, and ten-gram quantities of ammonium-saturated zeolite were each added to a liter of nitrifying sludge containing 50 meq/l. NaCl. A low salt concentration was selected for this study to ensure that the ammonium concentrations that developed in solution were not too high. With Equation 2 it was calculated that with 50 meq/l. NaCl, maximum concentrations of 24, 43, 85, and 134 mg/l. NH$_4$–N would develop in the reactors containing 1, 2, 5, and 10 g of clinoptilolite, respectively. The observed ammonium concentrations in solution and rates of nitrification are presented in Figures 6 and 7, respectively. The ammonium concentrations that actually developed were significantly less than predicted values. This may in part reflect the use of an inappropriate value for the ammonium–sodium selectivity coefficient, but it may also be explained by slow ion-exchange kinetics and the relatively rapid rate of
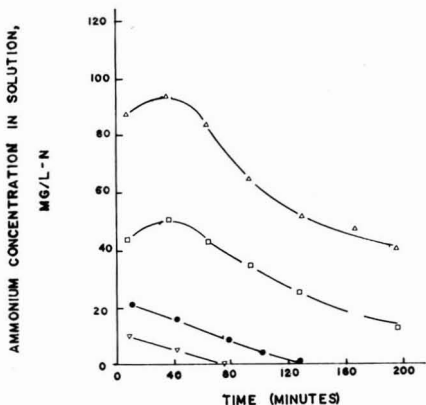
Figure 6. Influence of clinoptilolite quantity on ammonium concentrations present in solution during regeneration

△ 10 g/l., □ 5 g/l., ● 2 g/l., ▽ 1 g/l.

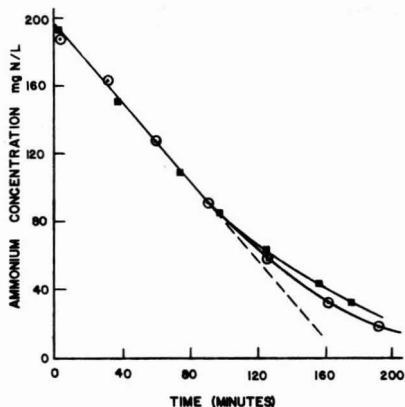**Figure 8.** Observed dependence of nitrification rate on ammonium concentration during tests depicted in Figures 6 and 7
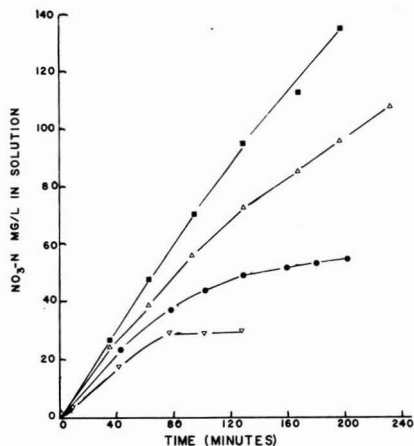
■ First test date, ⊙ second test date

Figure 7. Influence of clinoptilolite quantity on rate of nitrification in regeneration reactor

■ 10 g/l., △ 5 g/l., ● 2 g/l., ▽ 1 g/l.

nitrification. The curves shown in Figure 7 indicate that the nitrification rate increased with increasing weight of clinoptilolite. This result was not anticipated but may be accounted for by considering the nitrification kinetics on the days of the tests.

These data, which are shown in Figure 8, indicate that rate of nitrification was dependent upon the solution concentration of ammonium when it was less than 100 mg/l. Since the ammonium concentrations in the regeneration reactors were generally less than 100 mg/l., the rates of nitrification in each of the regeneration reactors were limited by the free ammonium concentration. A comparison between the initial rates of nitrification in the regeneration reactors and the rates of nitrification computed from the slope of Figure 8 at the average ammonium concentrations.shown in Figure 6 showed very close agreement and thus confirmed that the free ammonium ion concentration is controlling the rate of nitrification in the regeneration reactors.

Complete regeneration of the clinoptilolite should increase the nitrate content of the water by approximately 28, 56, 140, and 280 mg/l. NO_3–N for the reactors containing 1, 2, 5, and

10 g of clinoptilolite, respectively. Figure 7 indicates that complete regeneration of the 1-g batch of clinoptilolite was achieved in 80 min, and after 200 min the 2-g batch was completely regenerated, whereas only 65 and 48% nitrification was achieved in the 5- and 10-g reactors.

Summary

These results all confirm the observations of Goldberg and Gainey (9) and indicate that it is the solution concentration of ammonium which controls the rate of nitrification. The ammonium concentration in solution is in turn controlled by the amount of ammonium displaced by ion exchange. Decreasing the particle size of the clinoptilolite and increasing the salt concentration in solution increased the rate of regeneration by increasing the rate of ion exchange. The nitrifying bacteria were however inhibited significantly by salt concentrations higher than 0.6 M, and no nitrification at all was observed in a regeneration reactor tested at 1 M salt concentration.

Not only did salt accelerate regeneration by increasing the extent of ion exchange, but it also stimulated the nitrifying bacteria in low concentrations, 0–0.4 M, a result which is consistent with a number of previous studies. Since sodium nitrate increases in concentration naturally during the biological regeneration process, advantage may be taken of this effect by operating at a salt concentration of, say, 0.4 M.

These studies also indicate that it is possible to achieve higher levels of regeneration than previously recorded (1). In this study, for example, 99% regeneration was achieved in less than 3 h when 400 meq/l. of sodium chloride were added to the regeneration reactor.

These results and the confirmation of the mechanism of regeneration have two major implications with respect to the design of a biological regeneration process. Firstly, they indicate that nitrification can take place in concentrated salt solutions which is prerequisite to the economical operation of a biological regeneration process; it means that the volume of waste brine to be disposed of is not excessive. Secondly, they suggest that regeneration may be accomplished just as satisfactorily if a salt brine is used to extract the ammonium and the brine is biologically restored for reuse.

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Heavy Metal Concentrations in Water, Sediments, and Fish from Mediterranean Coastal Area, Israel

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■ Samples of water, sediment, and fish were collected along the northern part of the Mediterranean coast of Israel and analyzed for cadmium, lead, copper, zinc, nickel, and chromium by atomic absorption spectrophotometry. The obtained values showed no significant heavy metal pollution in the studied area, compared with values found in literature for metal concentrations in other parts of the world.

The Bay of Haifa receives domestic, industrial, agricultural, and natural runoff from a heavily populated and fairly industrialized area. The Qishon and Na'aman Rivers, both flowing to the Haifa Bay area, are heavily polluted, the former by industries and the latter by agriculture and domestic sewage. The Bay is also an important fishing ground for trawl, pelagic, and reef fishes.

Trace elements introduced into the marine environment from effluents and river runoff may be concentrated in marine organisms by a factor ranging from 1 000 to 10 000 (*1*). Metal concentrations in water and sediments of four streams and estuaries were studied by Roth and Hornung (*2*). Of these, only the Na'aman River flows into Haifa Bay. The values for metal concentrations (Cd, Pb, Cu, Zn, Ni, and Cr) in the water and sediments of the Na'aman River were similar to, or only slightly higher than, those found along the Israeli shore. Since no previous data on the concentration of trace elements in the Bay of Haifa are available, this survey was undertaken to initiate a routine monitoring of the heavy metal concentration in that Bay.

Water, sediment, fish, and random samples of algae were collected to determine the trace metal concentrations. The primary objective of the fish analyses was to ascertain whether the most commonly caught species contained concentrations of heavy metals hazardous to public health, and to establish the general levels and ranges for each of the metals in the edible parts of fish species.

Materials and Methods

Nearshore samples of water and sediments were collected at stations between Rosh Hanikra and Haifa. Fishes were collected from catches taken along the whole Mediterranean coast of Israel. Samples of some common marine algae were

collected at the water's edge on the Nahariya, Acre, and Haifa seashores.

Water Samples. Surface seawater was sampled with a plastic bucket, and subsurface samples with Niskin PVC water bottles. The water for determination of Cd, Pb, Cu, Zn, and Ni was filtered through a 0.45-μm membrane filter immediately after sampling, so that there was no need to test the possible adsorption of the metals onto the containers. Each 2-l. sample was then passed through a glass column containing ion-exchange resin (Chelex-100) and treated according to the procedure outlined by Riley and Taylor (*3*). The resulting solutions were then analyzed by atomic absorption spectroscopy. The analyzed filters showed low values of the adsorbed metal.

The blanks and efficiency of the columns were determined on stripped seawater (filtered seawater which passed the Chelex-100 resin). Part of this water was spiked with known amounts of metals to be analyzed at levels approximating twice their seawater concentrations. The spiked samples were analyzed in the same way as the other samples. The efficiency of this procedure and the limit of detection for each metal are given in Table I. The values of the blanks were below the limit

Table I. Percent Efficiency for Concentration of Metals with Chelex-100 Resin

Experiment no. [a]	Cd	Pb	Cu	Zn	Ni
I	88.0	81.7	78.5	87.8	82.5
II	84.4	87.0		86.0	
III	83.3	86.6	92.3	86.2	89.9
IV	84.9	80.0	80.0	86.7	92.7
V	88.9	76.2	72.6	87.6	84.2
VI	83.9	65.8	72.2	89.1	73.5
VII	79.2	68.2	82.2	84.0	78.5
Mean value	84.7	78.0	79.6	86.8	83.6
Standard deviation	3.2	8.4	6.8	1.6	7.1
% coefficient of variation	3.8	11.0	8.5	1.9	8.5
Standard error	1.2	3.2	2.6	0.6	2.9
Limit of detection (ppb)	0.6	20	2	2	8

[a] Each experiment was replicated.

Table II. Trace Element Concentration in Waters of Northern Israeli Coast Compared with Other Regions in the World in μg/l. (ppb)

	Cd	Pb	Cu	Zn	Ni
Drinking water standards (13)	10	50	100	1000	100
Unpolluted seawater (14–16)	0.11	0.03	3.0	10.0	0.7–7.0
Present work, northern shoreline	0.6–2.9	2.1–11.4	0.8–31.2	1.0–256.0	2.0–5.4
Present work, average	0.94	6.4	3.7	38.3	3.3
Mediterranean off Crete (17)			0.65	24.7	
Red Sea, surface (17)			0.2–0.4	2.4–24.8	
Suez Canal (17)			3.9	40.0	
Ligurian Sea (18)			0.7–4.8	3.3–86.0	
Adriatic Sea, coast & Gulf of Trieste (19, 20)		0.5–5.0			11.8
English coast, Liverpool Bay (21)	0.14–0.74	0.7–4.2	0.9–3.0	2.3–47.6	
English coast, Bristol Channel (21)	0.3–4.2	0.4–5.1	1.0–4.7	3.6–21.4	
Clyde Bay, Scotland (22)	0.01–0.18	0.02–0.36	0.3–1.5	1.8–11.8	
Menai Straits, Wales (23)			0.5–3.0	5.0–60.0	0.8–2.6
Irish Sea, shoreline (24)	0.03–1.4	0.6–2.9	0.9–3.1	3.8–49.1	0.9–9.8
Northeast Atlantic (25)	0.07–0.71		0.4–12.3	1.0–22.0	1.1–4.0
Northeast Atlantic, nearshore (26, 27)	0.04–0.3		0.3–3.8	0.6–12.6	0.5–5.2
Monterey Bay, California (28)	0.02–4.7	0.2–2.0	0.5–4.5	0.7–35.0	
California & Florida, shoreline (29, 30)		nd–36.0[a]	20		
Hong Kong, shoreline (31)	45	660	69	92	

[a] nd = not detected.

of detection. Corrected values for the metals studied are presented in Table II.

Sediments. Nearshore sediment samples were collected by hand, and deep water samples were taken with a bottom grab covered with epoxy paint to eliminate contamination. Each sample was washed, oven-dried at 100 °C, and ground in an agate mortar. The particles which passed through a 200-μm (70 mesh) nylon sieve were analyzed.

Samples for Cd, Pb, Cu, Zn, Ni, and Cr analysis were determined using the combined acid-reducing technique of Chester and Hughes (4). The concentration measurements were taken on a Techtron AA-5 atomic absorption spectrophotometer.

Fish. For the determination of the trace elements (Cd, Pb, Cu, Zn, Ni, and Cr), the homogenized fish tissue was oven-dried at 105 °C. The dry material was weighed in the Teflon vessel of the Uni-seal decomposition bomb, digested with concentrated nitric acid, and heated for 1 h at 130 °C. The cooled acid digest was evaporated to dryness, diluted to a standard volume (10 ml) with 0.1 M HNO_3, and analyzed by AAS (Techtron AA-5). The advantage of bomb decomposition

is the rapid and complete digestion of the biological material, especially fatty matter. This was in contrast to the methods of Leonard (5) and Anderson (6), tried by us, in which fatty matter caused difficulties.

All analyses of water, sediments, and fish samples were done at least in duplicate, but most were done in triplicate. Blanks and standards were prepared in triplicate, using the same procedure as that for the samples. No significant interference from other ions was detected when samples of water, sediments, and fish were treated by spiking with standard solutions.

Results and Discussion

Water. The preliminary results presented here illustrate the general levels found in the waters of the Israeli northern shore. The data show that only slight variations occur in the concentrations of lead, cadmium, copper, and nickel in the water, and most of the values are close to the overall mean given in Table II. High values of Cd (2.0–2.9 ppb), Cu (22.1–31.2 ppb), Pb (10.7–11.4 ppb), and Ni (5.0–5.4 ppb) found in the surface samples opposite densely populated

Table III. Concentration (ppb) of Trace Metals in Water Samples of Three Coastal Stations (20 October–10 November 1974)

	Acre					Kiryat Yam					Haifa				
	Cd	Pb	Cu	Zn	Ni	Cd	Pb	Cu	Zn	Ni	Cd	Pb	Cu	Zn	Ni
20 Oct	0.8	8.3	2.5	87.2	3.8	1.5	9.3	3.7	24.4	5.0	0.6	6.7	1.5	52.9	2.6
21 Oct	0.7	6.9	1.6	86.5	3.4	0.7	7.6	3.2	24.6	3.6	0.5	5.9	1.8	57.4	2.3
22 Oct	0.6	7.9	2.3	13.4	3.2	0.9	7.5	2.9	17.3	3.7	0.7	8.0	3.2	48.8	3.1
23 Oct	0.6	5.5	1.6	8.9	2.7	0.6	6.7	1.9	67.6	3.1	0.8	6.2	1.9	17.3	3.0
25 Oct	0.7	7.5	2.3	33.3	3.1	0.7	5.8	2.3	17.5	2.7	0.8	6.2	1.8	32.4	2.8
5 Nov											0.8	7.7	2.1	15.9	3.0
10 Nov	0.8	7.3	2.0	32.1	3.5										
Mean	0.7	7.2	2.0	43.6	3.3	0.9	7.4	2.8	30.3	3.6	0.7	6.8	2.1	37.5	2.8
Min	0.6	5.5	1.6	8.9	2.7	0.6	5.8	1.9	17.3	2.7	0.5	5.9	1.5	15.9	2.3
Max	0.8	8.3	2.5	87.2	3.8	1.5	9.3	3.7	67.6	5.0	0.8	8.0	3.2	57.4	3.1
Max:min	1.3	1.5	1.6	9.8	1.4	2.5	1.6	2.0	3.9	1.9	1.6	1.4	2.1	3.6	1.3

Table IV. Concentration of Heavy Metals in Particulate Matter in μg/l. (ppb)

Sampling area	Cd	Pb	Cu	Zn	Ni	Cr
Our data, range	nd–0.8[a]	0.1–13.3	nd–2.1	0.4–24.2	nd–2.4	nd–5.8
Our data, mean	0.2	2.4	0.4	5.7	0.5	0.4
Clyde Bay (22)	0.01–0.06	nd	0.4–4.4	0.2–11.2		
Trieste Bay (19)		0.6–3.5				
North Sea, shoreline (32)	0.1–0.3		0.1–8.9	3.9–16.3	0.1–1.3	

[a] nd = not detected.

Table V. Concentration Range of Heavy Metals in Sediments from Various Marine Areas (ppm in Dry Sediment)

Area	Cd	Pb	Cu	Zn	Ni	Cr
Present work, range	0.3–2.2	3.9–19.7	0.3–2.9	2.1–18.2	2.3–9.3	1.7–12.4
Present work, average	0.7	8.4	1.6	7.0	4.8	4.2
Israel coast, Tel-Aviv-Gaza (8)			1.4–24.2	5.4–49.6	2.1–7.3	2.7–17.3
English coast, Southampton (27)	0.6–0.7			115.0–224.0		
English coast, Tor Bay (33)	0.2–0.7	21.3–65.7	2.4–7.6	17.2–42.0	4.2–15.0	5.8–17.0
Cardigan Bay, Wales (34)	1.1	25	11	36		
Swansea Bay, Wales (35)	15	195	75	170		
Clyde Bay, Scotland (22)	0.4–1.5	12.0–45.0	2.7–17.1	34.0–102.0		
Clyde Estuary, Scotland (36)	1.0–3.0	24.0–67.0	9.0–20.0	60.0–130.0	15.0–50.0	10.0–65.0
Atlantic Ocean (37)		16.0–35.0			55	100
New York Bight (38)		12.0–25.0	3.0–8.0	18.0–26.0	3	2.0–6.0
Harbor Island, Gulf of Mexico (39)	0.4–1.1	3.4–9.0	2.7–5.2	14.0–28.0	5.0–10.9	

Table VI. Trace Metals in Marine Algae

Location	Date (1974)	Algae	Dry weight (%)	Cd	Pb	Cu	Zn	Ni	Cr	No. of samples
Acre (shore)	11 Jan	Chlorophyta	7.6	1.2	5.6	2.9		5.2		5
Haifa (beach)	24 Jan	Rhodophyta	22.7	2.1	22.2	7.6		5.8	6.7	3
Na'aman R. Estuary	28 Jan	Chlorophyta	7.6	0.9	1.9	5.5	218	5.3	2.6	3
Nahariya (shore)	3 Jul	Chlorophyta	8.0	1.2	5.3	5.4	117	5.5	2.8	3

(Concentration (ppm dry weight) header spans Cd, Pb, Cu, Zn, Ni, Cr columns)

settlements and in the vicinity of a chemical plant's sewage outlet were exceptional. Considerable variations were found also for zinc, with high levels of 175.1–256.0 ppb in Haifa Bay. These high values of the trace elements could be attributed to the runoff from the two polluted rivers in this area. Comparison of sea areas in Table II confirms the general view that the water at the shoreline, near densely populated and industrialized areas, contains higher levels of heavy metals than do coastal and ocean waters.

Daily fluctuations of heavy metal concentrations were checked at sampling stations along the shore of Haifa Bay between 20 October and 10 November 1974. The three stations chosen are close to the shore (10–20 m from the water's edge), and hence were expected to be most affected by runoff. The data in Table III show that except for Zn, there were no significant daily fluctuations in the metal concentrations.

Particulate Matter. With the exception of lead and zinc, heavy metals are found in solution rather than associated with particulate matter. The mean values obtained from all our data are close to the values found in Clyde Bay, Scotland, Trieste Bay, and the North Sea (Table IV). The high values of lead (5.8–13.3 ppb) and zinc (10.0–24.2 ppb) may have resulted from contamination or from organisms (retained on the filter pad) which concentrate these two elements (7).

Sediments. The heavy metal concentrations in the sediments are presented together with data from other areas in Table V. A comparison of our results with those of Amiel and Navrot (8) shows that the concentrations of copper, zinc, and chromium along the southern shoreline are considerably higher than those obtained by us in the Haifa Bay area. The concentrations of nickel are the same for both areas. Most of the values for trace metal concentrations found in this study

are low when compared with values from other regions in the world. The present low levels of the trace metals in the near-shore sediments may represent an early stage in the accumulation of these elements, which may increase as pollution continues. The highest values of Cd (2.2 ppm), Pb (19.7 ppm), Cu (2.9 ppm), Zn (18.2 ppm), Ni (9.3 ppm), and Cr (12.4 ppm) were found along the shores of Akhziv, Nahariya, and Acre.

The presence of high concentrations could be explained by the proximity of domestic and industrial sewage outfalls. Trace elements in estuarine sediments are often much higher than those observed in sediments from the adjacent coastal areas (Clyde Bay–Clyde Estuary, Table V).

Marine Algae. Only two species of algae were examined, *Corallina virgata* (red algae, Rhodophyta), collected on the seashore near Haifa, and *Codium tomentosum* (green algae, Chlorophyta), collected at the Na'aman Estuary, Nahariya, and Acre seashores. Both species are commonly found washed up on the beach and do not necessarily represent the dominant algae in the sea. The method applied for the determination of the metals was taken from Bernas (9), and the results are summarized in Table VI. The values obtained are useful only as a rough comparison with data in the literature. The ranges for Cd in marine algae found by Mullin and Riley (10) (0.3–2.1 ppm dry weight) and levels for the other elements detected by Black and Mitchell (11) (Pb: 2.0–26.0, Cu: <3.0–31.0, Zn: 40–136, Ni: 1.5–9.3, Cr: 0.4–3.7, all ppm dry weight), are very close to the ranges found here (Table VI).

Fish. The concentrations of six elements (Cd, Pb, Cu, Zn, Ni, and Cr) only in the edible muscle tissue of twelve species of sea fish are summarized in Table VII.

Cadmium. Most of the fish contained Cd concentrations of less than 0.4 ppm (dry weight). The highest values of Cd

Table VII. Trace Metals in Fish from Mediterranean Coastal Waters of Israel

Species	Collection date (1974)	Area + depth (fms)	Mean total length (cm)	Mean weight (g)	No. of individuals analyzed	Dry weight (%)	Concentration (ppm/dry weight)					
							Cd	Pb	Cu	Zn	Ni	Cr
Sardinella	4 Sept	Haifa Bay	17.0	42	16	24.8	0.6	0.6	3.4	81.6	2.3	3.4
aurita		off Qishon R.	18.5	56	7	25.1	0.6	0.7	6.0	84.3	2.3	3.4
	9 Sept	Haifa Bay 14	11.2	14	8	29.7	0.6	0.4	4.7	61.3	2.6	2.2
			13.5	21.5	30	31.8	0.6	0.3	2.8	40.2	1.6	2.1
			17.2	50	4	26.8	0.5	0.5	4.9	78.6	3.4	2.5
Saurida	25 Mar	Haifa Bay 14	26.0	116	4	25.4	0.3	2.8	1.3	5.3	2.9	1.4
undosquamis			28.8	127	3	25.4	0.3	2.7	0.9	0.5	6.3	1.2
			30.5	230	1	24.4	0.4	2.8	0.7	5.0	10.8	1.7
			33.0	271	1	24.4	0.4	3.2	3.9	7.7	1.5	1.7
	13 Jun	South coast 16	20.2	62	10	24.1	0.3	2.7	6.4	32.1	2.4	2.2
			27.5	150	4	24.5	0.3	2.5	2.5	20.2	1.2	0.9
	7 Sept	South coast 20	24.2	43	3	24.3	0.2	0.3	2.0	20.5	0.3	0.6
			26.8	140	4	24.0	0.2	0.3	2.5	32.2	0.8	0.8
			31.8	238	3	23.2	0.2	0.4	2.4	20.8	0.9	1.0
Merluccius	6 Mar	Central coast 40	21.5	70	2	20.5	0.2	2.6	5.2	26.8	nd[a]	2.2
merluccius			24.5	128	2	21.4	0.2	4.4	2.9	7.9	0.1	2.3
			26.5	157	3	21.4	0.3	2.7	3.8	2.7	0.2	2.7
			31.5	276	1	21.4	0.3	4.8	3.1	12.7	1.0	2.3
Epinephelus aeneus	26 Jul	Central coast 27	48.0	1200	1	23.3	0.1	0.04	5.4	33.0	1.6	
	28 Aug	South of Haifa Bay 70	36.0	556	1	23.1	0.2	0.3	2.6	21.7	1.1	1.0
	28 Aug	Haifa Bay 14	37.0	614	1	21.5	0.2	0.3	2.6	23.3		
Epinephelus guaza	8 Sep	Central coast 30	60.0	2150	1	18.8	0.1	0.3	3.3	25.5	0.8	2.4
Mullus barbatus	6 Mar	Central coast 48	16.0	54	18	20.4	0.7	3.4	6.4	14.9	1.4	2.8
	13 Jun	South Coast 16	11.0	30	2	21.4	0.6	3.2	4.2		1.6	4.9
	7 Sep	South coast 20	14.0	32	10	24.7	0.2	0.4	5.3	22.0	1.8	2.9
Upeneus moluccensis	6 Mar	South coast 10	17.5	62	5		0.3	5.3	5.0	23.1	0.7	4.1
	13 Jun	Haifa Bay 30	16.5	48	3	27.0	0.4	2.9	8.3	27.2	1.6	2.0
	1 Sep	South coast 20	14.5	35	10	23.8	0.2	0.3	4.5	25.1	1.7	2.3
Diplodus vulgaris	1 Aug	Central coast 8	18.9	133	6	23.4	0.3	0.3	4.2	26.5	1.7	1.0
Sphyraena sphyraena	20 May	Haifa Bay 5	31.5	108	4	26.8	0.3	5.2	23.5	20.7	0.1	2.0
			40.5	285	2	24.5	0.3	1.8	4.8	20.2	0.5	1.7
Siganus rivulatus	8 Sep	Central coast	24.5	236	10	25.1	0.2	0.3	3.1	25.8	0.7	1.4
Solea solea	7 Sep	South coast 20	20.5	62.7	10	23.6	0.2	0.3	1.4	22.1	1.1	1.1

[a] nd = not detected.

were detected in *Mullus barbatus* (benthic) and *Sardinella aurita* (pelagic) (0.6–0.7 ppm). The World Health Organization (12) provisional tolerance level for human consumption is 0.4–0.5 μg Cd/person/week, which means that to exceed this tolerance, a person must consume more than 5 kg of these fish per week.

Lead. The tolerance level for lead in fish for human consumption set by the Canadian Food and Drug Directorate is 2 ppm wet weight—a value higher than all the measured concentrations in the analyzed fish.

Copper. The copper concentrations varied according to the sampling area. An exceptionally high value (23.5 ppm) was found in one sample of *Sphyraena sphyraena* (pelagic) and in one sample of *Upeneus moluccensis* (benthic) (8.3 ppm) from Haifa Bay (this area ia polluted by industrial sewage).

Otherwise, the range of values is similar to those from other unpolluted areas (Table VIII).

Zinc. The concentration of zinc in fish from different fishing areas followed the same pattern as that for copper. The highest values (61–84 ppm dry weight) were found in *Sardinella aurita* from Haifa Bay, the most highly polluted of the areas sampled. Except for these high values, there was, however, very little difference in the concentration of zinc.

Nickel. The majority of values [with the exception of one high value, 10.8 ppm in *Saurida undosquamis* (benthic) from Haifa Bay] in all the species are within a limited range close to the mean value of 1.8 ppm dry weight.

Chromium. The mean concentration of Cr found in the fish samples was 0.5 ppm, being the same as for fish from England and Wales (0.5–0.6 ppm, Table VIII).

Table VIII. Heavy Metal Levels of Commercial Fish in Catches from Coast of Israel and Other Selected Areas (Concentrations in ppm)

Location			Cd	Pb	Cu	Zn	Ni	Cr
Present paper, range		Dry wt	0.1–0.7	0.04–5.3	0.7–8.3	0.5–84.0	nd–10.8[a]	0.6–4.9
		Wet wt	0.02–0.17	0.01–1.3	0.17–2.0	0.1–20.3	nd–2.6	0.14–1.2
Present paper, mean	,	Dry wt	0.33	1.8	3.8	27.2	1.8	2.1
		Wet wt	0.08	0.4	0.9	6.6	0.4	0.5
Scottish waters (40)		Dry wt						
		Wet wt	0.03–0.12	<0.2–1.2	0.05–4.3	1.6–23.0		
England and Wales (41)		Dry wt						
		Wet wt	<0.05–0.16	0.5–1.0	0.5–1.8	4.4–6.6		<0.5–0.6
North Atlantic (42)		Dry wt	<0.1–2.1		1.5–3.2	8.0–20.0		
		Wet wt						
Northeast Atlantic (43)		Dry wt	0.05–0.98			44		
		Wet wt						
New Zealand (44)		Dry wt						
		Wet wt	0.001–0.2	0.04–1.6	0.03–3.4	0.9–56.0	0.01–0.1	0.01–0.05

[a] nd = not detected.

Conclusions and Recommendations

From the data presented in this study, we can infer that the concentration of the heavy metals investigated both in water and sediments is similar to those found in literature for unpolluted regions.

The results obtained from the analyses of the edible muscle tissue of the 12 most common commercial fish show low concentration levels of the six trace elements investigated.

We conclude that the area is still relatively unpolluted and recommend continuing the monitoring of heavy metal concentrations to improve our understanding of their cycle in the marine environment.

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Phenalen-1-one: Occurrence in a Fuel Oil and Toxicity to Microalgae

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■ Phenalen-1-one (perinaphthenone) was isolated and characterized from the water soluble fraction of a No. 2 fuel oil. Phenalen-1-one had two very different effects on the growth of microalgae. With blue-green algae there was an abrupt toxicity, independent of wavelength, at 5 ppm. With two green algae toxicity was strongly wavelength dependent. In white light (Daylight fluorescent) 250 ppb was lethal; with this same lamp screened by a sharp-cut yellow filter (530 nm), growth rate was not affected until the concentration reached 10 ppm. The growth inhibition of a diatom by phenalen-1-one was also wavelength dependent, but the concentration required was some twentyfold that for green algae.

There is an increasing body of evidence suggesting that crude oils and products derived therefrom inhibit growth and photosynthesis in microalgae (1–3). In a search for the basis of toxicity in water soluble extracts of fuel oils, we have isolated and identified phenalen-1-one (Figure 1) from an American Petroleum Institute (API) No. 2 fuel oil sample commonly used in toxicity testing.

Although we have not been able to find phenalen-1-one in water solubles of four other No. 2 fuel oils, its toxicity to microalgae, especially green algae, merits comment.

It is interesting to note that phenalen-1-one has been isolated from organic extracts of airborne particulates (4, 5). In the context of these papers it was tested for potential carcinogenic activity via a photodynamic assay with *Paramecium caudatum*, an indirect index of carcinogenicity owing to polynuclear compounds. Its microalgal toxicity described herein may be cause for further concern for its presence in the environment.

Materials and Methods

Organisms and Growth Conditions. Strains PR-6 (*Agmenellum quadruplicatum*) and 17a (*Coccochloris elabens*) are coccoid blue-green algae. They are isolates of this laboratory. Strains DUN (*Dunaliella tertiolecta*) and 580 (*Chlorella autotrophica*) are green algae and were originally obtained from R. L. Guillard, Woods Hole. AMP-1 (*Amphora sp.*) is an estuarine diatom recently isolated into pure culture in this laboratory by J. C. Morgan (6). PR-6 and 17a were grown on medium ASP-2 (7) containing 8 $\mu g/l.$ of vitamin B_{12}, DUN, and 580 on medium ASP-2 plus 8 $\mu g/l.$ vitamin B_{12} and

Figure 1. Structures of phenalen-1-one (I) and 9-fluorenone (II)

1 mg/l. vitamin B_1; AMP-1 was grown on medium ASP-2 containing 8 $\mu g/l.$ vitamin B_{12}, 1 mg/l. vitamin B_1, and 250 mg/l. $Na_2SiO_3 \cdot 5H_2O$.

All liquid culture work was done in a water bath at 30 ± 0.1 °C under continuous illumination from Sylvania F20T12-D Daylight fluorescent lamps, two on each side of the bath, 7.5 cm from the lamp center to the position of the tubes in the bath. The growth tubes were Pyrex 22 × 175 mm test tubes fitted with bubbling tubes, through which was passed continuously $1 \pm 0.1\%$ CO_2-in-air. This general procedure is an adaptation of the methods of Myers (8).

With each organism the inoculum was preconditioned to the above growth conditions. The inoculum size used to start each growth run was approximately 10^5 cells/ml. Specific growth rate constants were determined from a plot of $\log_{10} N/N_o$ vs. time, where N = cell number, determined turbidimetrically using a Model 402-E Lumetron colorimeter. For convenience in data presentation the specific growth rate constants are herein given as generations/day.

An algal lawn technique was used to test pure compounds. Exponentially growing cells (final concentration 5 000–10 000 cell/ml) were added to agarized medium (1% Difco agar, 0140) held at 42 °C; 20 ml was then immediately distributed to plastic Petri dishes. The test materials, with absolute ethanol as solvent, were presented to the algal cells embedded in the agar by absorbing them on antibiotic sensitivity discs (12.7 mm) and placing the discs directly on the agar surface. The plates were then sealed with Scotch tape and incubated in the light for 3–7 days, 28–30 °C. The experimental endpoint was the zone size of growth inhibition around the pad, judged visually and microscopically. No inhibition was observed with appropriate ethanol controls.

Isolation and Characterization of Phenalen-1-one. Water extracts were prepared by gently stirring 8 parts distilled water with 1 part American Petroleum Institute #2 fuel oil for 24 h as previously described (2). This fuel oil is one of four oils set aside by API for use by the scientific community as reference oils. Our sample was obtained from Jack Anderson, Texas A&M University, College Station.

Organic components of the water extract were reextracted into benzene and analyzed on a Perkin-Elmer Model 900 gas chromatograph. A Dupont 21-491 mass spectrometer interfaced to a Varian 2700 gas chromatograph was also used for qualitative analysis. A component was identified as phenalen-1-one on the basis of its mass spectra (Figure 2) and retention times on two stationary phases of different polarity (FFAP and Apiezon L). Authentic phenalen-1-one (perinaphthenone) was obtained from Aldrich Chemical Co., Milwaukee. Another sample purchased from ICN Chemicals, Plainview, N.Y., behaved similarly, both chemically and biologically.

Phenalen-1-one was isolated from other components of the water extract by chromatography on a 1.7 × 150 cm column of Sephadex LH20 in isobutyl alcohol. Purity of the material obtained was about 95% by gas chromatography. The absorption spectra of the sample and standard in 95% ethanol were obtained on a Cary 118 spectrophotometer. Infrared spectra in carbon tetrachloride were recorded on a Perkin-Elmer 237B. Sample and standard spectra were in good agreement over both spectral regions.

The concentration of phenalen-1-one present in the water extract, as determined by gas chromatography, was 0.2 ppm (mg/l.).
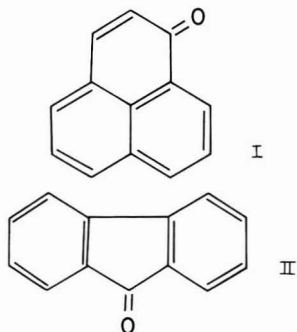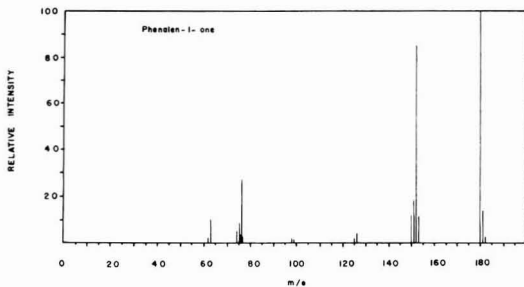
Figure 2. Mass spectrum of phenalen-1-one isolated from water soluble fraction of API No. 2 fuel oil

Results

Table I shows the effects of phenalen-1-one on the growth of five microalgae, representative of three major groups. For the two blue-green algae tested, strains PR-6 and 17a, phenalen-1-one had no effect on growth until the concentration reached 5 mg/l., wherein an abrupt toxicity was evident. The inhibition of growth of these two marine, coccoid, blue-greens was independent of the wavelength distribution of the light source used for growth. In contrast, the two green algae tested, strains DUN and 580, were remarkably sensitive to phenalen-1-one but only when the fluorescent lamp source was not screened by a sharp-cut yellow Plexiglas filter (transmission > 530 nm). When the light source was screened by the yellow filter, these two organisms were even more resistant than the two blue-greens. The response of the diatom, strain AMP-1, was intermediate between the blue-green and green algae.

The extreme toxicity of phenalen-1-one toward the green algae 580 and DUN manifested only in white light suggested that photochemical alteration was occurring. Since the yellow Plexiglas filter also screens out radiation into the region of bulk carotenoid absorption in an algal cell, the possibility existed that phenalen-1-one toxicity was being sensitized by carotenoids. The latter was not the case since the toxicity picture for strains 580 and DUN was not changed by further experiments with colored filters in which the actinic beam contained wavelengths down to 440 nm; the long wavelength absorption of phenalen-1-one extends to 450 nm.

Table II sets in perspective the extreme toxicity of phenalen-1-one in white light to organism 580 vis a vis other toxic compounds. An instructive comparison can be made with p-toluidine. p-Toluidine is the most toxic compound we have yet found in water soluble extractives from fuel oils for blue-green algae (3). With 1 μg per pad of p-toluidine in the same type of assay as used in Table II with organism 580, there was a clear inhibition of growth with organism PR-6. For organism

Table II. Effect of Pure Compounds on Growth, as a Lawn, of Green Alga, *Chlorella autotrophica*, Strain 580[a]

Amt on pad, μg	Compounds						
	Phen[b]	Cres	Tolu	TMPh	MeInd	DiMeAn	DMN
1	0	0	0	0	0	0	0
10	2	0	0	0	0	0	0
50	11	0	0	0	2	0	0
100	20	0	0	0	10	0	0
500	36	0	0	2 (10)	36	0	1
1 000	36	0	4 (15)	20 (36)	36	2	2
2 000	36	0 (3)	36	36	36	5 (10)	3
10 000	36	36	36	36	36	36	36

[a] Numbers indicate zone of inhibition of growth around pad in mm; 36 mm means no growth on Petri dish. Numbers in parentheses are zone sizes of reduced colony size indicative of some but not complete inhibition. [b] Compound identification: Phen = phenalen-1-one, Cres = o-cresol, Tolu = p-toluidine, TMPh = 2,3,5-trimethylphenol, MeInd = 7-methylindole, DiMeAn = 2,4-dimethylaniline, DMN = 1,4-dimethylnaphthalene.

580 in white light, phenalen-1-one approaches the toxicity of p-toluidine to blue-green algae.

Discussion and Conclusions

We can only speculate as to the biochemical reason phenalen-1-one, or possibly a photochemically produced product, is so lethal to green algae. Strain 580 does show a small degree of adaptation. When grown in sublethal levels (0.125 mg/l.) in white light, organism 580 then acquires resistance to 0.500 mg/l. but not to higher concentrations. Phenalen-1-one is without immediate effect on photosynthesis as measured on the oxygen electrode at light saturation in white light. However, some 6–8 h (about one generation time) after incubating organism 580 with a 0.50–1.0 mg/l. of phenalen-1-one in white light, the typical yellow-green of the cells' color perceptibly lightened. After 10–12 h the cells bleached completely, that is, the suspension became white. Correlating with this progressive destruction of the photosynthetic pigments was a decline in rate of photosynthesis (O_2 output) to zero some 6 h after addition of phenalen-1-one. This latter observation suggests that the basis of phenalen-1-one toxicity may lie in a photochemically induced, highly oxidizing species which causes oxidation of general cellular components. However, prediction of a photochemically formed strong oxidant as the basis for phenalen-1-one toxicity to green algae is greatly weakened by its lack of effect under similar lighting conditions and at a similar level in blue-green algae.

Phenalen-1-one and its 6-hydroxy derivative have demonstrated antibacterial activity (9). Perhaps of more interest

Table I. Effects of Phenalen-1-one on Growth[a] of Five Pure Cultures of Microalgae

Phenalen-1-one concn, mg/l.	Organisms									
	PR-6[b]		17A		DUN		580		AMP-1	
	W[c]	Y	W	Y	W	Y	W	Y	W	Y
0.0	6.0	4.0	6.0	4.0	3.3	2.0	2.7	1.8	3.5	3.2
0.125	6.0	4.0	6.0	4.0	3.3 (2)	2.0	1.0 (4)	1.8	3.5	3.2
0.25	6.0	4.0	6.0	4.0	NG	2.0	NG	1.8	3.5	3.2
0.50	6.0	4.0	6.0	4.0	NG	2.0	NG	1.8	2.3 (1)	3.2
1.00	6.0	4.0	6.0	4.0	NG	2.0	NG	1.8	0.5 (11)	3.2
5.00	NG	NG	NG	NG	NG	2.0	NG	1.8	NG	NG
10.00	NG	NG	NG	NG	NG	1.3 (2)	NG	0.4 (4)	NG	NG

[a] Numbers given are generations/day, reproducible to ±0.2/day. Values in parentheses are lag times in days as compared to controls. Notation NG means no growth. [b] Organisms PR-6 and 17A were grown at 39°, DUN, 580 and AMP-1 at 30°. [c] W means illumination used for growth included all wavelengths common to emission spectrum of a Daylight fluorescent lamp; Y the same lamp but wavelengths restricted to 530 nm and beyond by Rohm and Haas, 3-mm (⅛ in.), transparent, yellow Plexiglas filter, No. 2422.

in connection with our results are the observations on the occurrence of phenalenone derivatives in the seed capsules and roots of *Lacanthus tinctoria* ("red-root") and in the mycelium of *Penicillium herquei* (*10–12*). Phenalen-1-one or related compounds have not, so far as we know, been reported in green algae. However, the extreme toxicity of phenalen-1-one suggests that biochemically significant phenalen-1-one pigments may occur in green algae.

The extent of phenalen-1-one distribution in petroleum and petroleum products is unknown. It is improbable that the compound is unique to this fuel oil. The presence of phenalen-1-one in urban airborne particulates appears to indicate a widespread occurrence in, or production from, fossil fuels. Phenalen-1-one may be a product of combustion and/or refinery processes, although its occurrence in crude oils is not unlikely. Alkyl substituted fluorenones (Figure 1) have been reported in a crude oil (*13*). Compounds with molecular weights corresponding to C_1, C_2, and C_3 substituted fluorenones were described. The parent compound, fluorenone, an isomer of phenalen-1-one, was not found.

Wherein phenalen-1-one occurs in a petroleum derived product, its relatively high water solubility, low volatility, and herein demonstrated high and selective lethality toward green algae suggest that it could be environmentally dangerous.

Acknowledgment

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Synchronous Fluorescence Spectroscopy and Its Application to Indigenous and Petroleum-Derived Hydrocarbons in Lacustrine Sediments

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■ A comparison of conventional fluorescence emission spectra and spectra produced by synchronously scanning both excitation and emission monochromators is made on a series of standard oils to demonstrate the increased resolution achieved by the synchronous technique. Greater information on the aromatic content of the oils is obtained by separating the aromatic hydrocarbon fractions by liquid-solid column chromatography prior to fluorescence analysis. Fluorescence spectroscopy, in particular the synchronous method, is used to characterize the indigenous and petroleum-derived aromatic hydrocarbons in sediments of Lake Washington, Wash.

Fluorescence spectroscopy is a useful technique for the analysis of aromatic hydrocarbons in the environment (*1*). Zitko and Carson (*2*), Thruston and Knight (*3*), and Coakley (*4*) have summarized the use of ultraviolet fluorescence spectroscopy to identify oils by differences in their aromatic composition which produce the spectra. A number of workers have used fluorescence spectroscopy to estimate petroleum hydrocarbon concentrations in seawater (*5–10*) and in marine sediments (*11*). Ultraviolet fluorescence spectroscopy offers the advantages of greater sensitivity and selectivity for aromatic molecules than conventional ultraviolet absorption measurements.

An improvement in the fluorescence analysis of complex mixtures of fluorescing compounds has recently been made by Lloyd (*12*). Satisfactory resolution of complex mixtures often cannot be achieved by the usual technique of recording emission spectra produced by excitation at fixed wavelengths which have been specifically selected for individual compounds. However, Lloyd has shown that considerable improvement in resolution of the spectra may be made by varying the excitation and emission monochromators simultaneously, with the excitation wavelength maintained 20–30 nm less than the emission wavelength. In a study of the synchronous excitation of emission spectra of pure aromatic hydrocarbons and several motor oils, Lloyd (*13–15*) has demonstrated that the wavelength of maximum emission is a function of the number of fused aromatic rings in a molecule. Gordon and Keizer (*9*) have recently applied synchronous fluorescence analysis to a determination of petroleum hydrocarbons in seawater.

This report presents further data comparing conventional fluorescence emission spectra with spectra obtained by the synchronous scanning technique. In addition, the synchronous fluorescence method has been applied to an investigation of indigenous and petroleum-derived hydrocarbons in sediments of Lake Washington, Wash. Of particular interest is a com-

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parison of the fluorescence spectra for aromatic hydrocarbons isolated from sediments contaminated with petroleum, for hydrocarbons from uncontaminated sediments, and for the hydrocarbons from the several possible sources of organic matter to the lake (rivers, stormwater runoff, atmospheric dustfall, plankton, and terrestrial plant material).

Experimental Methods

Fluorescence spectra were obtained using a Farrand Optical Corp. MK-1 spectrofluorometer equipped with a corrected excitation module. The advantages of corrected fluorescence spectra, discussed in detail by Porro et al. (*16*), are the elimination of shifts in excitation peak positions, distortions of band shapes, and changes in relative band intensities caused by nonconstant output of the excitation source and nonlinear response of the photomultiplier. Corrected excitation (200–450 nm) and emission (220–580 nm) scans were made on the samples of interest to determine the general fluorescence characteristics of the hydrocarbons present. Synchronous scanning of the excitation and emission wavelengths was performed in a manner similar to that employed by Lloyd (*12*). Excitation and emission monochromators were offset by 25 nm, and the emission between 245 and 500 nm was recorded. Throughout this investigation, slits for the excitation and emission monochromators were 2.5 and 5 nm, respectively. Spectral grade cyclohexane was used as the solvent for the fluorescence analysis.

To ensure that concentrations of sample solutions were not so high as to cause quenching and distortion of the fluorescence spectra, a series of spectra was obtained for solutions of varied concentrations. Even at the highest concentrations tested, which were about an order of magnitude higher than sample concentrations normally used in this study (10–40 μg/10 ml), no significant distortion of the spectra was observed.

The four American Petroleum Institute reference oils (South Louisiana, Kuwait, Bunker C, and No. 2 fuel oil supplied by J. Anderson, Texas A&M University) of known composition were used as qualitative fluorescence standards. Excitation, emission, and synchronous spectra were obtained for the whole oils (40 μg/10 ml) as outlined above. In addition, a sample of the Kuwait crude oil was separated into aliphatic, mono- and di-aromatic, and polynuclear aromatic hydrocarbon fractions by silica gel/alumina column chromatography as described in more detail below. Fluorescence spectra of the aromatic hydrocarbon containing fractions were recorded to determine if this preseparation results in increased resolution of the aromatic constituents.

Sediments containing the hydrocarbons to be analyzed by the fluorescence techniques were collected from Lake Washington by use of procedures to minimize contamination by petroleum-type hydrocarbons. Sediment cores were collected in solvent-rinsed stainless steel barrels using a corer having a hydrostatically damped rate of penetration, thus reducing disturbance of the sediment/water interface. Following collection, the cores were frozen upright in the barrels and stored until analysis. Details of the collection, extraction, and hydrocarbon isolation procedures may be found elsewhere (*17*). In brief, lipids were Soxhlet extracted from the sediment with benzene:methanol (1:1). Fatty acids and their esters were removed by saponification. Hydrocarbons were isolated from other nonsaponifiable lipids by solid-liquid chromatography with alumina beds packed on top of silica gel beds. Three hydrocarbon fractions were routinely collected—aliphatic hydrocarbons were eluted with pentane, mono- and di-aromatic hydrocarbons were eluted with 20% benzene in pentane (in some cases, two fractions were collected by elution with 10 and 20% benzene in pentane), and the polynuclear aromatic hydrocarbons were eluted with pure benzene. The aliphatic
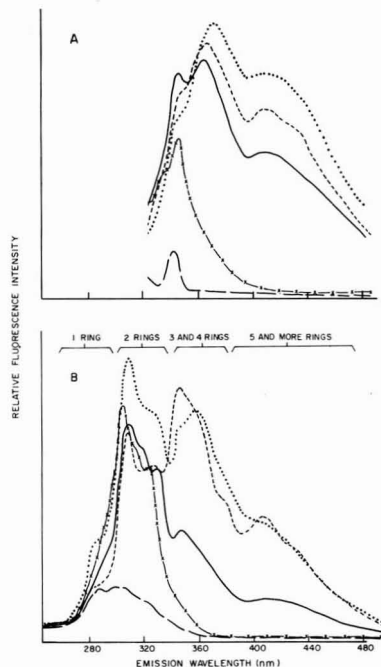
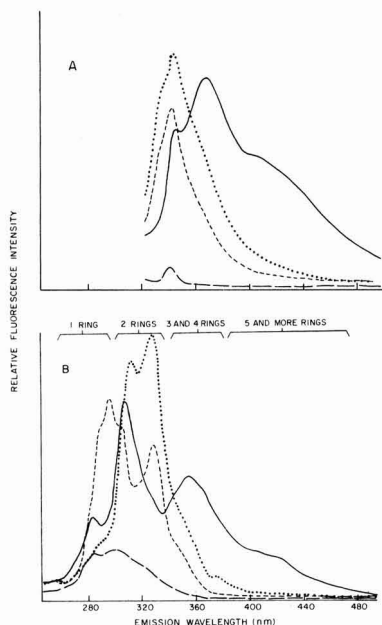**Figure 1.** Conventional emission (excitation wavelength 310 nm) spectra (A) and synchronous spectra (B) of four API reference oils
Concentrations are 40 μg/10 ml. No. 2 fuel oil —x—; Kuwait · · · ; South Louisiana ——; Bunker C - - -; cyclohexane solvent ——

hydrocarbons were analyzed by gas chromatography, radiocarbon dating, and stable carbon isotope ratio measurements (*17*), while the aromatics were analyzed by fluorescence spectroscopy as discussed in this communication.

To compare the aromatic hydrocarbon content of Lake Washington sediments with that of the several suspected hydrocarbon sources of the lake, samples of sediment from the rivers which feed Lake Washington, terrestrial plant material (peat and humus) from local areas, mixed plankton hauls (vertical tows with a standard 64-μm nylon net) from Lake Washington, and atmospheric dustfall (separated from rainwater by filtration with preextracted glass fiber filters) were collected and analyzed for hydrocarbons as discussed above. Urban stormwater runoff which drains into the lake was also collected in stainless steel containers. Lipids were extracted from the water with pentane, and hydrocarbons isolated by means of silica gel/alumina chromatography.

Results and Discussion

One of the primary concerns of this investigation was to document the differences between conventional emission spectra and the synchronous scanning method, and to point out the advantages of the latter technique. This difference is illustrated in Figure 1, where conventional and synchronous emission spectra of the four API oils are plotted together. The major peaks in the synchronous spectra are identified according to Lloyd's data (*15*), with the number of fused aromatic rings present in the sample determining the wavelength at which maximum emission occurs. Thus, benzenes emit most strongly in the 280–290-nm region, and naphthalenes emit at about 310–320 nm. Aromatics having three and four rings generally emit between 340 and 380 nm; compounds having five or more fused rings emit above about 400 nm. Clearly more fine structure is apparent using the synchronous mode

if the sample being analyzed is a complex mixture of fluorescing aromatic molecules. At fixed excitation wavelengths, much of the fluorescence of polynuclear aromatic hydrocarbons is masked. For pure compounds, however, the synchronous approach does not offer significant advantages over normal emission spectra.

Separation of the aromatic hydrocarbons into fractions based on their polarity as determined by elution from the silica/alumina columns helps to resolve the individual aromatic compound classes which are responsible for the fluorescence spectrum of the total hydrocarbon sample. Fluorescence spectra for four column chromatography fractions of the Kuwait crude oil are shown in Figure 2. No fluorescing material is apparently present in the pentane eluted fraction, which is expected since the fraction consists largely of aliphatic hydrocarbons. Benzenes and naphthalenes are present in those fractions eluted by 10 and 20% benzene in pentane, while the pure benzene eluate contains aromatics having three or more rings. It is interesting to note that while the normal emission spectra of the 10 and 20% benzene in pentane fractions are nearly identical in band shape, the synchronous spectra for these two fractions are quite different (Figure 2), providing further evidence of the increased resolution achieved by the synchronous scans.

Once the utility of the fluorescence technique, especially the synchronous approach, had been shown for the analysis of complex mixtures of aromatic hydrocarbons, the technique was applied to an investigation of the indigenous and petroleum hydrocarbons in sediments of Lake Washington. Previous work has shown that surface sediments in the lake contain elevated aliphatic hydrocarbon levels (about 1400 μg/g dry weight) relative to sediments at depth in the sediment column (30 μg/g). Gas chromatograms and radiocarbon measurements indicated that the aliphatic hydrocarbons in surface sediments were largely of petroleum origins. The
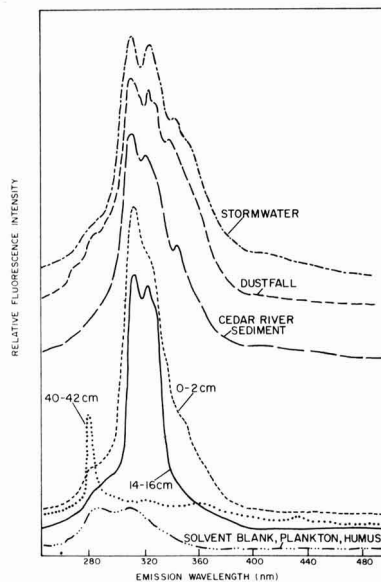
Figure 3. Synchronous spectra of aromatic hydrocarbons in 20% benzene in pentane fractions of Lake Washington sediments and several sources of hydrocarbons

primary source of the petroleum hydrocarbons in the surface sediments was determined to be stormwater runoff from the urban areas around the lake. The stormwater contained high levels of hydrocarbons from lubricating oils and pyrolysis products released by automobile traffic (17).

It was of interest to characterize by fluorescence spectroscopy the aromatic composition of both contaminated surface sediments and uncontaminated sediments at depth in the sediment column. Conventional and synchronous emission spectra were obtained for the pentane, 20% benzene in pentane, and 100% benzene eluted hydrocarbon fractions from 0–2, 14–16, and 40–42-cm sections of a Lake Washington sediment core. In addition, spectra were also recorded for the aromatic hydrocarbons isolated from the several known sources of hydrocarbons to the lake (river sediments, dustfall, stormwater, plankton, peat, and humus).

Fluorescence spectra of the pentane eluted hydrocarbons for all samples and solvent blanks were not significantly different, thus indicating the absence in this fraction of any fluorescing aromatic molecules. In contrast, the 20% benzene in pentane and the 100% benzene eluates contain a complex assemblage of aromatic hydrocarbons. Synchronous spectra of these two fractions from Lake Washington sediments and several hydrocarbon sources are illustrated in Figures 3 and 4.

Spectra of the aromatic hydrocarbon containing eluates from the 0–2-cm sediment in Lake Washington show the presence of naphthalenes in the 20% benzene in pentane fraction (Figure 3), and aromatic compounds containing three and four fused rings in the benzene cut (Figure 4). In addition, the presence of lesser amounts of more highly condensed aromatics in the benzene fraction is indicated by fluorescence bands at 400, 440, and 460 nm in the synchronous scans (Figure 4). Such a wide range of aromatic compounds is typical of the aromatic composition of petroleums, as shown in the petroleum spectra above.

The naphthalene and three- and four-ring components of the hydrocarbon spectra of surface sediment are quite similar to the components observed in the spectra of the aromatic

Figure 2. Conventional emission (excitation wavelength 310 nm) spectra (A) and synchronous spectra (B) of four column chromatography fractions for Kuwait crude oil

Cyclohexane solvent and pentane — —; 10% benzene in pentane - - -; 20% benzene in pentane · · ·; 100% benzene ——
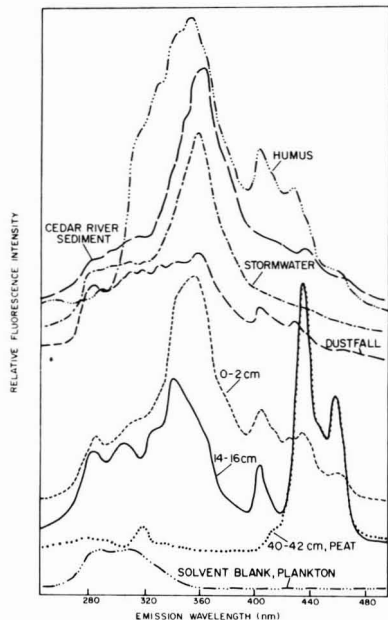
Figure 4. Synchronous spectra of aromatic hydrocarbons in 100% benzene fractions of Lake Washington sediments and several sources of hydrocarbons

hydrocarbons isolated from urban stormwater runoff (Figures 3 and 4), providing further evidence of the importance of urban runoff as a source of petroleum hydrocarbons to Lake Washington surface sediments.

Polynuclear aromatics are also predominant in the atmospheric dustfall, Cedar river sediment, and humus (from a local evergreen forest) samples (Figures 3 and 4), although the input from these sources is believed to be minor compared to stormwater.

The aromatic hydrocarbons containing five and more rings in surface sediments of Lake Washington (indicated by fluorescence bands at 400, 440, and 460 nm in Figure 4) are believed to be coming primarily from atmospheric dustfall, as these components appear to be present in the dustfall (Figure 4) and absent in the stormwater. These multiringed aromatic hydrocarbons are usually of pyrolytic origins and are often present in urban atmospheric fallout (18, 19). It is possible that these highly condensed molecules are the product of incomplete combustion of fossil fuels as has been previously discussed by Giger and Schaffner (19) in relation to the presence of these compounds in sediments of a Swiss lake. It is interesting to note that fluorescence bands indicative of these highly condensed aromatic hydrocarbons are also present in the spectrum of hydrocarbons isolated from the humus sample (Figure 4). While the source of these hydrocarbons is presently unknown, it is possible that the hydrocarbons are ultimately derived from atmospheric fallout.

The aromatic hydrocarbons isolated from the 14–16-cm sediment of Lake Washington (deposited about 1900 as determined by ^{210}Pb dating and containing about 400 μg/g hydrocarbons) generally are similar to those in surface sediments (Figures 3 and 4). However, these deeper sediments appear to contain, in addition to the naphthalenes and three- and four-ringed compounds, significant amounts of perylene, as indicated by the large doublet centered at about 450 nm in the synchronous spectrum of the benzene eluted fraction (Figure 4). Corrected excitation, emission, and synchronous spectra

of the sediment hydrocarbons all have bands with the correct shape and wavelength that were recorded for authentic perylene. The identity of this component as unsubstituted perylene has been confirmed by gas chromatography, high-pressure liquid chromatography, combined capillary gas chromatography–mass spectrometry, and high-resolution mass spectrometry (17). The significance of perylene in recent sediments will be briefly discussed below.

Of the hydrocarbons in the 40–42-cm sediment of Lake Washington (deposited about 1850 and having about 30 μg/g hydrocarbons), perylene is the predominant fluorescing compound in the benzene eluate (Figure 4), although minor amounts of some other aromatics are also present. The presence of such a complex mixture of aromatics (although without the predominance of perylene) has been reported by Giger and Blumer (20), Blumer and Youngblood (21), and Youngblood and Blumer (22) for sediments and soils believed to be uncontaminated by petroleum hydrocarbons. The actual origin of these hydrocarbons in recent sediments is presently unknown. Perylene is also the primary aromatic hydrocarbon constituent of the peat sample analyzed in this investigation (Figure 4).

The presence of perylene in recent sediments has been reported earlier for deep sea, coastal, and estuarine marine sediments (20, 23–26), soils (27), peat (26, 28, 29), and freshwater lake sediments (30). In most cases, perylene determinations have been only qualitative. However, where quantitative data are available, perylene content in marine sediments ranges from ~0.001 μg/g dry sediment [Tanner Basin (24), Gulf of Mexico (26)] to 0.26 μg/g [Santa Barbara Basin (24)] and 2.4 μg/g [Saanich Inlet (25)]. An English Peat has been found to contain 3.0 μg/g perylene (26). Perylene content in sediment cores was generally found to increase with increasing depth in sediment cores, indicating in situ formation by some diagenetic process.

Perylene concentrations in Lake Washington have been roughly calculated [based on high-pressure liquid chromatography (17)] to be 1.0 μg/g dry sediment at 14–16 cm and 1.4 μg/g in the 40–42-cm section of the sediment core which was analyzed. Surface sediments are not believed to contain perylene (based on the fluorescence spectra), although at the present time the data are not conclusive. Perylene was also apparently absent from stormwater, river sediments, humus, and plankton (Figure 4), although it is present in the peat sample at a level of about 6.3 μg/g.

Aizenshtat (26) has proposed a possible mode of perylene formation in marine sediments which may also apply to Lake Washington. Perylene precursors are believed to be land-derived (as indicated by high levels of perylene in peat) nonhydrocarbon compounds, such as hydroquinones resulting from degradation of carotenoids and chlorophyll-derived chlorins. These compounds must be rapidly transported through the water column and deposited in reducing sediments where transformation into perylene may occur by reduction. If sedimentation is slow and/or the precursors remain in oxidizing sediments, the compounds may be oxidized and thus destroyed. In this manner, it is possible to account for low concentrations of perylene in Tanner Basin and the Gulf of Mexico sediments (farther offshore and with lower sedimentation rates) relative to Santa Barbara Basin and Saanich Inlet sediments (inshore and with high sedimentation rates). In the case of Lake Washington, there would be a relatively short period of transportation of large quantities of terrestrial plant matter to the lake's sediments, followed by fairly rapid burial (sedimentation rate of about 3 mm/yr based on ^{210}Pb measurements) in a mildly reducing (based on the presence of elemental sulfur) sediment column. Thus, the precursors would be preserved, and perylene may be formed by reduction of these precursors.

It is possible to make a rough estimate of the rate of perylene formation in Lake Washington based on the increase in perylene concentration between the 14–16 and 40–42-cm sediment intervals (~0.4 µg/g) and the time period involved (about 100 years). Thus, perylene appears to be forming within the lake sediment at a rate of about 4 µg/g-1000 years. This rate is compared to rough estimates of 0.2–0.8 µg/g-1000 years in Saanich Inlet [calculated using data of Brown et al. (25)] and 0.1 µg/g-1000 years in Santa Barbara sediments [based on data of Orr and Grady (24)]. It is not clearly understood why the rate in Lake Washington may be so high, except that the terrestrial organic matter content of the lake sediments may be somewhat higher than in either Santa Barbara Basin or Saanich Inlet sediments, and/or that greater amounts of the necessary precursors reach the sediments of Lake Washington. This suggestion is supported by the fact that Lake Washington sediments generally contain greater carbon content (4–6%) than sediments of Saanich [2–4% (25)].

Conclusions

Synchronous scanning of excitation and emission wavelengths yields more information about the aromatic composition of a complex mixture of aromatic hydrocarbons than conventional fluorescence spectra obtained at fixed excitation wavelengths. Note that the information obtained by fluorescence spectroscopy is primarily qualitative, and even semiquantitative measurements on such complex mixtures as petroleum and sediment hydrocarbons are most difficult. For more detailed quantitative data, one must rely on more elaborate instrumentation, such as gas chromatography, mass spectrometry, or a combination of the two.

Hydrocarbons isolated from sediments of Lake Washington were analyzed by fluorescence spectroscopy to show the usefulness of the synchronous method in investigations of aromatic hydrocarbons in sediments. Surface sediments, known to be contaminated with petroleum hydrocarbons, contain large amounts of naphthalenes, three- and four-ring aromatics, and some more highly condensed aromatic molecules. Fluorescence spectra of surface sediment hydrocarbons are remarkably similar to spectra of hydrocarbons isolated from stormwater runoff and atmospheric dustfall. In contrast, the indigenous hydrocarbons at depth in the sediment column are predominated by perylene, which is believed to be forming with the sediment in the time period of about a century.

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Partial Extraction of Metals from Aquatic Sediments

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■ Four procedures employing 0.3 M HCl, pH 3 or pH 7 citrate–dithionite, or acetic acid–hydroxylamine solutions are evaluated for their potential to remove the surface coatings from aquatic sediment particles. Ten test samples representing a range of sediment types and broad geographic distribution are examined. Data on the relative recovery efficiency of each method are reported. Selection of a procedure for use on large numbers of samples is made on the basis of recovery efficiency, limitation of structural degradation, and operational simplicity. Single operator precision data for the more efficient methods are reported.

Interest in the source, transport, deposition, biological utilization, and release of trace metals in the aquatic environment has necessitated the investigation of analytical methods for determining the more readily available forms of metals that are associated with organic and mineral sediments. It is generally recognized that sediments, both suspended and bottom, constitute a potential source for many dissolved chemical species. It is reasonable to expect that trace metals associated with degradable organics and with the surface coatings of mineral particles would be more available than those incorporated in primary minerals or occluded by secondary mineral structures. Metals in the surface coatings of sediments, both in suspension and in bottom deposits, may be brought into solution by changes such as the intrusion of water of significantly different quality. Processes operating under these conditions would be principally of the exchange type, although it is conceivable that strongly acidic or alkaline discharges could dissolve a portion of the surface coating. Changes in the oxygen regime, such as in stagnant pools and impoundments, may also contribute to the solution of metals. In addition, water treatment processes such as chlorination, dialysis, and reverse osmosis may cause solution of surface coatings.

The purpose of this study was to determine which of the evaluated procedures can provide an acceptable analytical tool for monitoring trace metals in the surface coatings of mineral sediment particles. Methods were selected from those that have been proposed for use in cleaning coatings from mineral particles prior to x-ray diffraction analysis and in investigating the partitioning of trace metals in sediments and soils. Method evaluation was based on the effectiveness of removal, minimization of structural degradation, and operational suitability for large numbers of samples.

Materials and Procedures

Test Samples. Bottom material samples were collected from 10 sites representing a wide range of natural and man-made environmental influences. Sample locations and comments are listed in Table I. The samples were collected by personnel of the U.S. Geological Survey and shipped to the laboratory in a moist condition. Upon receipt the samples were wet sieved through a 2-mm nylon screen and stored in tightly sealed, 1 gal, wide-mouth glass bottles at 4 °C. General characteristics of these samples are listed in Table II.

Subsamples for the individual partial extraction procedures were obtained by forcing a 20-mm o.d. glass tube to the bottom of the sample container, sealing the end, and removing the tube containing a vertical section of the sample. Several such vertical sections were taken when necessary to obtain sufficient weight of sample. The wet weight of each subsample was

accurately determined, and a separate subsample was dried at 105 °C to determine moisture content.

Test Procedures

Four partial extraction procedures were selected for evaluation. These involve the use of 0.3 M HCl (*1*), pH 3 buffered citrate–dithionite (E. A. Jenne, oral communication, 1972), pH 7 buffered citrate–dithionite (*2*), and 1 M hydroxylamine hydrochloride in 25% by volume acetic acid (*3*) solutions. For comparison purposes the samples were subjected to Na_2CO_3 fusion (*4*) for determination of total metals and silica, and to a rigorous HNO_3–dry ashing procedure (*5*).

Four replicate subsamples of each sample were taken for each analytical procedure. Prior to application of the partial extraction procedures, the samples were treated with 30%

Table I. Sample Identification and Location

Sample	Location	Comments
1	Raritan River at South Bound Brook, N.J.	Receives industrial and municipal waste
2	South Fork Coeur d'Alene River near Pinehurst, Idaho, above mouth of Pine Creek	Downstream of lead–zinc mine wastes. Lead and zinc sulfide minerals
3	Curwensville Reservoir on Bald Eagle Creek near Curwensville, Pa.	Impoundment receives coal mine drainage from upstream sources
4	Mississippi River at St. Louis, Mo. (Station 960)	Major river receiving municipal, agricultural, and industrial wastes
5	Antietam Creek below Hagerstown, Md., sewage treatment plant	A highly calcareous sediment containing shell fragments and organic material
6	New Almaden, Calif. area composite. Sample from Alamitos Creek and from an unnamed tributary to Alamitos Creek	Sediment contains waste from mercury mine spoils. Probably sulfide minerals
7	Susquehanna River flood sample (Ott composite), June 1972, approximately 15 miles north of Harrisburg, Pa.	Undisturbed sample from cellar of home on bank of river
8	Waikele Stream at Waipahu, Honolulu, Hawaii	Sample contains sediment of lateritic soil origins
9	Peacock Creek near McIntosh, Ga.	Muck sample
10	South River at Island Shoal Road near Atlanta, Ga.	Highly micaceous red sediment

Table II. General Sample Characteristics

Sample	Size distribution, %			Carbon content, %			
	Sand	Silt	Clay	Total	Inorganic	Organic	pH
1	68.8	20.7	10.5	2.48	0.05	2.43	6.6
2	81.0	15.7	3.3	2.12	0.95	1.17	5.7
3	11.0	61.9	27.1	7.02	0.05	6.97	6.5
4	98.9	1.1	0.0	0.19	0.11	0.08	7.6
5	88.0	7.6	4.4	2.05	0.92	1.13	7.1
6	76.9	19.6	3.5	2.77	0.34	2.43	7.3
7	19.2	57.1	23.7	5.32	0.10	5.22	6.6
8	27.9	51.5	20.6	3.32	0.05	3.27	6.1
9	35.2	21.8	43.0	4.28	0.04	4.24	6.6
10	27.5	44.6	27.9	1.70	0.08	1.62	7.2

hydrogen peroxide (H_2O_2) on a steam bath to destroy organic matter. All of the methods under evaluation incorporated the same peroxide pretreatment so that they could be compared on an equivalent basis.

To obtain measurable quantities of trace metals in the final solution for direct determination by atomic absorption spectrophotometry (AAS), wet sample weights were selected to give the equivalent of 5–10 g of oven-dry sediment. The exception to this was in the total analysis by fusion where the size of the available platinum crucibles limited the sample size to 1 g. As a result, the fusion data for trace metals were not acceptable because sufficient quantities of the metals were not available for measurement; the fusion data are valid for total SiO_2, Al, Fe, and Mn concentrations.

The extraction procedures result in solutions for analysis of widely differing pH, viscosity, and salt composition and concentration. To avoid matrix problems created by these variables, the standard solution for each metal for each procedure was prepared in the respective extraction solution.

The following are brief descriptions of the four partial extraction procedures and the HNO_3–dry ashing treatment:

0.3 M HCl. The sediment–water mixture, following H_2O_2 treatment, is diluted to 200 ml with deionized water. Ten ml of 6 M HCl is added, and the suspension is mixed and heated to just below boiling on a hot plate. Heating at this temperature is continued for 30 min. The hot mixture is filtered through a Whatman No. 42 filter paper, or equivalent, and the filtrate is collected in a 250-ml volumetric flask. The residue on the filter is washed at least three times with hot, dilute HCl (1 + 19), and the filtrate is cooled and brought to volume with HCl (1 + 19).

pH Buffered Citrate–Dithionite. Add 40 ml of pH 3 citrate buffer (160.0 g citric acid and 71.3 g sodium citrate dissolved in deionized water to give a final volume of 1000 ml) to the peroxide treated sample and heat with occasional swirling for 1 h at 80 °C in an oven. Add 80 ml of purified dithionite–citrate solution (95.6 g sodium citrate and 36.8 g citric acid dissolved in 1 l. of deionized water, extracted by shaking with

1 g APDC, 100 ml ethyl propionate, and 50 g sodium dithionite, and reextracted using only 100 ml of solvent) and hold at 80 °C with occasional swirling for 3 h. If the solution temperature exceeds 80 °C, insoluble sulfides will form. Remove from oven and flocculate the sediment with saturated sodium nitrate solution, centrifuge, and decant into a 250-ml volumetric flask. Wash the sediment twice with 10-ml citrate buffer, combine washing and extract, and adjust to volume with deionized water.

pH 7 Buffered Citrate–Dithionite. Add 50 ml 0.3 M sodium citrate (88 g $Na_3C_6H_5O_7 \cdot 2H_2O/l.$) and 5 ml 1 M sodium bicarbonate (84 g $NaHCO_3/l.$) to the peroxide treated sample. Heat to 80 °C in an oven, remove, and quickly add 10 ml of sodium dithionite solution (100 g $Na_2S_2O_4/l.$). Heat to 80 °C in an oven and continue heating for 15 min. If the solution temperature exceeds 80 °C, insoluble sulfides will form. Cool and flocculate sediment with saturated sodium chloride solution, centrifuge, and decant the clear supernate into a 250-ml volumetric flask. Wash residue twice with 10-ml portions of 0.3 M sodium citrate and combine washings with the extract. Adjust to volume with deionized water.

1 M Hydroxylamine Hydrochloride in 25% (v/v) Acetic Acid. Add 50 ml of mixed acid-reducing reagent [mix 150 ml of 25% (w/v) hydroxylamine hydrochloride and 350 ml of 35% (v/v) acetic acid] to the peroxide treated sample in a 250-ml conical flask. Place on a mechanical shaker and shake at room temperature for 4 h. Filter through No. 42 Whatman paper into a 250-ml volumetric flask. Wash the residue on the paper several times with deionized water, combine washings and filtrate, and adjust to volume with deionized water.

HNO_3 Dry Ashing Extraction. Add 35 ml concentrated HNO_3 and 5 ml 30% H_2O_2 to the sample in a beaker and evaporate to dryness on a hot plate. Ash at 400 to 425 °C for 1 h in a muffle furnace and cool. Add 25 ml of acid mixture (200 ml conc. HNO_3, 50 ml conc. HCl, and 750 ml deionized water), 20 ml 10% NH_4Cl and 1 ml $Ca(NO_3)_2 \cdot 4H_2O$ (11.8 g/100 ml). Heat gently for 15 min and cool for at least 5 min. Separate the residue by filtration or centrifugation, wash the res-

Table III. Mean Concentration of Major Constituents (All Values in $\mu g/g$ Unless Noted)

Determination	Method[a]	Sample 1	2	3	4	5	6	7	8	9	10
SiO_2, %	(a)	78.0	61.8	50.3	87.2	84.1	59.0	65.4	32.7	73.0	67.6
	(b)	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
	(c)	0.77	0.32	1.05	0.11	0.14	1.21	1.03	1.68	0.41	0.52
	(d)	0.32	0.28	0.84	0.096	0.18	0.59	0.51	0.73	0.50	0.34
	(e)	0.065	0.074	0.24	0.027	0.045	0.17	0.088	0.24	0.21	0.087
	(f)	0.068	0.095	0.36	0.011	0.024	0.13	0.074	0.30	0.26	0.072
Al	(a)	34600	28000	106000	24500	9890	41100	45000	115000	42700	79200
	(b)	11000	3340	31900	1510	4600	14900	15300	56400	10800	29700
	(c)	3930	1270	19200	522	1280	5280	7070	10300	2940	5200
	(d)	2310	898	21500	256	1440	2530	4620	7910	2950	4410
	(e)	830	187	10700	40.0	313	270	1560	1780	1440	976
	(f)	991	258	13400	33.9	223	432	1310	1900	1960	1090
Fe	(a)	21900	111000	61700	6960	13700	39700	36100	137000	16900	35800
	(b)	14400	76600	60200	4110	10000	38800	34000	57800	5010	31000
	(c)	7890	79800	36900	1600	3130	15000	17600	18000	2700	10500
	(d)	12300	18200	53000	2130	9000	20700	20600	69500	3830	25700
	(e)	5370	4550	25000	626	2390	4700	9900	13000	2390	7620
	(f)	2780	3100	12700	184	876	3020	2280	4980	2420	5610
Mn	(a)	331	9040	701	116	203	718	1320	1370	113	908
	(b)	139	3960	519	71.4	155	623	1170	613	31.3	680
	(c)	109	9600	693	52.9	139	523	1360	922	37.2	942
	(d)	119	1520	783	53.9	166	487	1380	1000	45.3	926
	(e)	26.8	805	524	8.62	17.8	220	1090	693	12.7	725
	(f)	76.8	1030	478	31.3	88.2	326	1040	813	43.9	931

[a] (a) Fusion, (b) ashing, (c) 0.3 M HCl, (d) pH 3 C-D, (e) pH 7 C-D, (f) acetic acid.

idue twice with deionized water, and combine washings and extract in a 250-ml volumetric flask; adjust to volume with demineralized water.

Results and Discussion

The mean concentration of four replicate analyses for the major constituents by each of the six analytical procedures is presented in Table III. Similar data for minor constituents are in Table IV. Because of the limited sample size used for the total analyses by fusion and because of the volatility of some constituents, no satisfactory data are available for the total concentration of trace metals. The ashing procedure is used

as a reference point to determine the relative recoveries of trace metals because trace metal concentrations recovered by the ashing procedure approach their total concentration in the sediments. Tables V and VI present data showing the mean recovery and standard deviation from the mean of major and minor sediment constituents relative to the total amount present and to the concentrations as determined by the HNO_3–dry ashing digestion, respectively. Note that the pH 7 citrate–dithionite and the 25% acetic acid extractions recovered significantly less of all constituents than the 0.3 M HCl and pH 3 citrate–dithionite procedures.

Examination of the data in Table VI indicates that 0.3 M

Table IV. Mean Concentration of Minor Constituents (All Concentrations in μg/g)

Determination	Method[a]	1	2	3	4	5	6	7	8	9	10
Cu	(b)	78.4	148	38.1	1.62	14.4	32.8	36.5	169	1.19	44.0
	(c)	73.8	66.9	57.2	0.67	12.7	22.4	32.3	172	2.06	34.8
	(d)	67.4	29.9	41.9	0.87	11.7	16.2	32.4	159	3.90	33.8
	(e)	1.98	1.09	3.42	0.12	0.00	0.17	1.25	4.77	0.60	0.87
	(f)	64.2	30.0	39.4	0.11	8.6	9.5	16.2	126	0.35	34.5
Ni	(b)	21.4	13.1	72.2	7.07	8.63	599	47.1	238	1.82	28.3
	(c)	12.7	7.95	48.8	5.83	5.03	367	30.5	67.6	1.36	12.4
	(d)	13.1	6.96	45.4	5.69	8.59	330	25.8	111	2.91	10.6
	(e)	4.06	1.72	19.2	1.06	2.04	61.7	9.02	35.5	1.18	7.37
	(f)	4.39	2.09	28.9	1.18	3.64	75.3	10.9	25.5	1.95	8.69
Pb	(b)	157	6010	121	50.9	93.9	67.5	233	91.9	51.0	153
	(c)	93.4	5160	56.6	5.64	44.2	25.6	158	28.4	17.4	104
	(d)	103	1480	65.9	20.3	40.8	34.6	151	45.4	31.0	103
	(e)	36.2	178	43.6	8.82	15.1	19.1	62.2	23.6	15.7	42.2
	(f)	70.5	4050	39.8	2.49	29.3	15.4	92.8	17.7	20.9	89.1
Zn	(b)	115	4310	300	12.9	79.6	74.9	276	123	11.3	442
	(c)	99.3	2040	254	7.03	76.2	55.8	230	73.6	7.75	460
	(d)	65.8	1780	241	5.27	75.0	35.2	169	82.5	5.03	400
	(e)	10.0	1280	108	0.00	31.0	0.00	92.5	39.2	7.45	436
	(f)	45.4	1200	141	0.01	47.4	14.3	80.5	35.2	4.60	382
Cd	(b)	0.98	27.5	1.37	0.06	1.69	0.60	1.44	0.88	0.25	4.46
	(c)	1.38	15.4	1.32	0.11	1.85	0.54	1.68	0.88	0.17	6.42
	(d)	2.02	7.40	1.57	0.64	2.04	0.84	2.38	1.22	0.62	6.83
	(e)	0.89	4.26	1.94	0.21	0.32	0.40	0.83	0.75	0.23	3.10
	(f)	0.98	10.2	1.21	0.04	1.31	0.16	1.22	0.62	0.66	7.24
Cr	(b)	13.0	3.20	27.7	2.90	30.2	368	20.2	118	9.07	55.5
	(c)	22.2	2.71	14.9	1.35	20.3	128	14.8	58.7	3.51	42.9
	(d)	25.5	2.55	22.7	1.64	29.2	114	13.6	184	4.73	54.4
	(e)	23.2	1.28	17.6	0.92	15.8	25.5	10.2	45.4	3.56	37.8
	(f)	16.6	.65	12.9	0.02	11.9	16.6	5.92	17.3	2.99	35.3
Co	(b)	8.03	12.5	37.7	3.44	4.83	44.8	32.4	53.3	2.24	15.2
	(c)	5.11	8.82	32.9	2.55	6.09	31.3	26.0	48.9	1.78	10.8
	(d)	9.42	8.27	33.8	3.99	9.08	26.0	27.0	49.1	3.59	10.0
	(e)	2.94	3.81	14.5	1.64	1.45	9.84	12.7	30.5	16.3	7.49
	(f)	2.38	4.25	22.5	0.74	3.50	15.6	15.0	30.1	1.44	8.08

[a] (b) Ashing, (c) 0.3 M HCl, (d) pH 3 C-D, (e) pH 7 C-D, (f) acetic acid.

Table V. Recovery of Major Constituents from All Samples Relative to Total Amount Present (All Values in Percent)

		Ashing	0.3 M HCl	pH 3 citrate–dithionite	pH 7 citrate–dithionite	Acetic acid
SiO_2	$\bar{X}$ (mean)	a	1.5	0.89	0.27	0.32
	R (range)	a	0.13–5.14	0.11–2.23	0.03–0.73	0.01–0.93
	σ (std dev)	a	0.50	0.24	0.09	0.12
Al	$\bar{X}$	30.9	10.0	8.2	2.7	3.0
	R	6.2–49.0	2.1–18.1	1.0–20.3	0.2–10.1	0.1–12.6
	σ	4.5	1.7	1.9	1.0	1.2
Fe	$\bar{X}$	71.5	35.8	50.9	18.0	9.3
	R	29.6–97.7	13.1–71.9	16.4–85.9	4.1–40.5	2.6–20.6
	σ	7.8	6.4	7.3	3.6	2.1
Mn	$\bar{X}$	62.0	73.2	68.1	36.3	49.8
	R	27.7–88.6	32.9–106	16.8–112	7.4–82.6	11.4–103
	σ	7.1	9.7	10.9	10.8	9.3

[a] SiO_2 is not brought back into solution following dry ashing of samples. No data are therefore available on SiO_2 concentration extracted.

HCl recovers more Zn and less Cd, Cr, and Co than the pH 3 extract. There is no difference in the recovery of Cu, Ni, and Pb by either procedure. Table VII indicates that this relationship is generally valid for samples of widely varying particle size distribution.

In addition to extraction efficiency, another criterion applied to the selection of a procedure is the limitation of structural degradation. The concentration of SiO_2 and Al in the extracts is assumed to reflect the extent of degradation since the principal mineral structure in the samples consists of alumino-silicates. Data in Table V show that both of the more efficient procedures recover approximately 1% of the total SiO_2 and 10% of the total aluminum. The lower end of the range in each case was for sample #4, a predominantly sand sample from the Mississippi River. Sample #8, a sediment of lateritic origin having highly weathered SiO_2, is at the upper end of the SiO_2 range. Sample #3, from Curwensville Reservoir in Pennsylvania, yielded the maximum aluminum values. This high yield of aluminum is to be expected since a relatively small percentage of the total aluminum is present as secondary minerals. The reservoir has received coal-mine drainage, and the native aluminum is present in greatest quantities as the sulfate.

To test the significance with regard to structural degradation of extraction of approximately 1% SiO_2 and 10% aluminum, five samples were selected and subjected to three successive extractions with 0.3 M HCl. The data for each sample are presented in Table VIII and for the mean of all five analyzed samples in Figure 1. From these data, the recovery of trace metals more closely approximates the recovery of Fe and Mn than SiO_2 and Al for the series of extractions. This does not ensure either that all of the minor elements present in the surface coatings are recovered or that there is no structural degradation. It does indicate that for a wide range of physical and chemical sample characteristics, a significant part of the surface coatings is being removed while solution of structural components is minimized. The extent to which a given sample will only be stripped of its surface coatings or will be degraded upon application of a specific chemical treatment is determined by mineral type, degree of weathering, composition of the coating matrix, and particle size.

Another factor examined was the extent to which the H_2O_2 pretreatment removes metals and SiO_2. Table IX gives the data for the mean relative recovery and the standard deviation from the mean of major and minor sample components as determined in the filtrate obtained after peroxide digestion only. If we compare these data with those in Tables V and VI, the H_2O_2 pretreatment accounts for from 10 to 20% of the recovery by the more efficient procedures, 0.3 M HCl or pH 3 citrate–dithionite. There is also an apparent loss of copper from the pH 7 citrate–dithionite extract. This may be due to readsorption at the more alkaline pH and is indicative of the

Table VII. Concentrations of Metals in Samples of Varying Particle Size Distribution (All Values in $\mu g/g$)

	HCl	pH 3 citrate–dithionite
Sample No. 4 (98.9% sand; 1.1% silt & clay)		
Al	522	256
Fe	1600	2130
Mn	52.9	53.9
Cu	0.67	0.87
Ni	5.83	5.69
Pb	5.64	20.3
Zn	7.03	5.27
Cd	0.11	0.64
Cr	1.35	1.64
Co	2.55	3.99
Sample No. 1 (68.8% sand; 31.2% silt & clay)		
Al	3930	2310
Fe	7890	12300
Mn	109	119
Cu	73.8	67.4
Ni	12.7	13.1
Pb	93.4	103
Zn	99.3	65.8
Cd	1.38	2.02
Cr	22.2	25.5
Co	5.11	9.42
Sample No. 3 (11.0% sand; 89% silt & clay)		
Al	19200	21500
Fe	36900	53000
Mn	693	783
Cu	57.2	41.9
Ni	48.8	45.4
Pb	56.6	65.9
Zn	254	241
Cd	1.32	1.57
Cr	14.9	22.7
Co	32.9	33.8

probable readsorption of other sample components during extraction at the comparatively high pH of this solution.

A further consideration in the evaluation of analytical procedures is the operational utility. In addition to extracting a high percentage of the components in surface coatings with minimum structural damage, a method should be suitable for use with large numbers of samples and involve a minimum of manipulation. All of the partial extraction procedures examined require that the extract be separated from the sediment residue by either filtration or centrifugation. The 0.3 M HCl extraction requires the use of a single reagent addition and heating at 90–95 °C for 30 min prior to separation. The acetic acid extraction similarly employs a single reagent addition but requires shaking for 4 h prior to separation. The strong acetate odor necessitates using a good exhaust system for all manipulations. Both of the citrate–dithionite procedures require several reagents yielding high salt concentra-

Table VI. Mean Recovery of Metals from All Samples Relative to Ashing Procedure (All Values in Percent)

	0.3 M HCl	pH 3 citrate–dithionite	pH 7 citrate–dithionite	Acetic acid
Al	34.1 ± 4.2	26.7 ± 5.2	8.8 ± 3.1	10.2 ± 4.0
Fe	50.0 ± 7.3	73.2 ± 8.9	26.0 ± 4.4	14.7 ± 4.5
Mn	117 ± 20.3	96.7 ± 15.9	51.7 ± 15.1	69.9 ± 14.0
Cu	93.0 ± 13.8	73.4 ± 9.7	3.2 ± 1.1	52.8 ± 10.5
Ni	60.1 ± 5.1	71.1 ± 11.9	23.2 ± 5.2	32.0 ± 9.5
Pb	48.9 ± 7.3	52.2 ± 4.5	23.5 ± 3.1	36.2 ± 6.1
Zn	75.9 ± 6.1	62.4 ± 6.7	34.3 ± 10.1	37.8 ± 7.8
Cd	110 ± 12.6	146 ± 22.0	70.9 ± 13.7	80.8 ± 15.6
Cr	59.8 ± 5.8	80.1 ± 11.3	46.5 ± 6.6	30.6 ± 6.9
Co	81.4 ± 5.9	104 ± 14.2	39.0 ± 3.9	47.2 ± 5.6

Table VIII. Percent of Component Remaining Following Successive 0.3 M HCl Extractions

Sample	Extraction no.	SiO$_2$	Al	Fe	Mn	Cu	Ni	Pb	Zn	Cd	Cr	Co
2	1	99.5	95.1	30.6	10.8	51.4	43.5	10.6	42.0	10.2	32.8	14.4
	2	99.2	92.5	24.9	8.6	46.7	20.8	9.2	29.3	0.0	25.3	3.3
	3	99.0	92.1	23.2	8.4	45.2	17.7	8.7	24.4	0.0	25.3	3.3
3	1	98.0	79.0	40.4	22.7	0.0	26.2	35.5	20.7	0.0	57.8	0.0
	2	97.1	76.5	21.9	16.7	0.0	15.9	12.0	9.3	0.0	47.0	0.0
	3	96.3	75.1	13.2	14.9	0.0	11.9	0.0	3.7	0.0	45.0	0.0
5	1	99.8	85.8	67.6	11.3	16.0	30.6	41.0	4.6	5.9	27.5	0.0
	2	99.6	81.5	43.8	0.0	12.6	13.7	21.1	0.0	5.9	17.0	0.0
	3	99.5	78.2	30.4	0.0	10.9	5.3	2.6	0.0	5.9	13.2	0.0
7	1	98.9	86.2	67.6	16.7	15.1	35.5	30.5	10.5	7.6	40.1	0.0
	2	98.3	81.8	50.7	13.5	3.8	22.5	18.2	0.0	7.6	33.1	0.0
	3	97.8	79.3	38.9	12.0	0.0	16.2	5.9	0.0	7.6	27.9	0.0
8	1	95.8	90.9	87.2	45.8	4.1	69.8	55.3	28.8	8.0	51.4	4.3
	2	93.4	87.7	80.7	43.4	0.0	60.3	29.9	14.3	8.0	38.0	0.0
	3	90.6	84.5	74.3	42.0	0.0	52.1	2.9	1.1	8.0	25.5	0.0
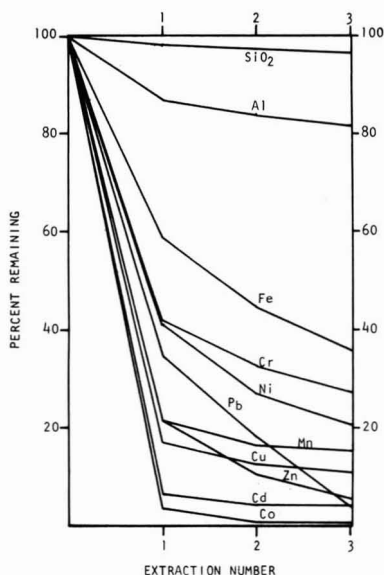
Figure 1. Mean recovery of metals by successive extractions with 0.3 M HCl solution

Table IX. Relative Recovery of Sample Components by H$_2$O$_2$ Pretreatment (All Values in Percent)

	Major components relative to total by fusion	Metals relative to total by ashing
SiO$_2$	0.13 ± 0.07	...
Al	0.90 ± 0.41	3.0 ± 1.5
Fe	1.4 ± 0.9	3.7 ± 3.0
Mn	15.8 ± 5.7	22.8 ± 8.1
Cu	...	19.7 ± 8.1
Ni	...	7.2 ± 2.2
Pb	...	5.4 ± 2.4
Zn	...	9.9 ± 4.2
Cd	...	9.5 ± 4.0
Cr	...	17.8 ± 5.4
Co	...	11.6 ± 3.9

tions in the extract which leads to frequent clogging of the atomic absorption three-slot burner and excessive flame noise when determining lead. Reagent purity is a problem and necessitates purification prior to use. The salt concentration and noise problems can be eliminated by chelation and extraction of the metals from solution, but this adds several additional manipulations to the procedure.

The precision statements for metals recovered by the 0.3 M HCl, pH 3 citrate–dithionite, and ashing procedures are listed in Table X for the stated concentration ranges. The expression of precision is based on the assumption that precision (S) varies linearly with concentration (x) over the range encountered in the 10 test samples. The data used for the statements were collected by a single operator in one laboratory using four replicates of each sample. Outlying values among replicates were tested and eliminated by applying the t test (6) using a limiting value of $t = 2.0$.

The precision data for the ashing procedure are included here for comparative purposes because this procedure has had wide use. The data for the three procedures compare favorably with published precision data for metal analysis by direct atomic absorption spectrophotometry (7).

Conclusions

Based on the results of this study, the following conclusions can be made:

• The acetic acid–hydroxylamine hydrochloride and pH 7 citrate–dithionite extractions are unacceptable because of low recovery efficiency and operational problems

• The pH 3 citrate–dithionite procedure, although possibly more efficient than the 0.3 M HCl extraction, is not suitable for high production large-scale laboratory use principally because of the number of manipulations involved and difficulties associated with analyzing the high solids concentration extracts by atomic absorption spectrophotometry

• The 0.3 M HCl extraction requires fewer manipulations than the citrate–dithionite procedure, yields approximately the same recovery efficiency with minimum structural degradation, and results in an easily analyzed solution

• Serial extraction with 0.3 M HCl indicates that the solution of trace metals more closely follows the solution of Fe and Mn than the structural components Si and Al

• The precision data obtained for the combined extraction analysis for metals by the three procedures reported compare favorably with published single operator precision data for direct metal analysis by atomic absorption spectrophotometric methods (7).

The numerous advantages of the 0.3 M HCl extraction

Table X. Precision Statements for Metals Determined (All Concentrations Expressed in $\mu g/g$)

Metal	0.3 M HCl		pH 3 citrate–dithionite		Ashing	
	Concn range	Precision	Concn range	Precision	Concn range	Precision
Al	522–19 200	$S = 0.014x - 0.28$	256–21 500	$S = 0.005x + 0.04$	1510–56 400	$S = 0.017x + 0.02$
Fe	1600–79 800	$S = 0.022x + 0.12$	2130–69 500	$S = 0.031x - 0.19$	4100–76 600	$S = 0.022x - 0.10$
Mn	37.2–9 600	$S = 0.039x - 13.0$	45.3–1 520	$S = 0.007x + 3.7$	31.3–3 960	$S = 0.061x - 19.7$
Cu	0.67–172	$S = 0.013x + 0.37$	.87–159	$S = 0.018x + 0.44$	1.19–169	$S = 0.019x - 0.21$
Ni	1.36–367	$S = 0.053x + 0.07$	2.91–330	$S = 0.016x + 0.12$	1.82–599	$S = 0.008x + 0.10$
Pb	5.64–5 160	$S = 0.022x - 0.22$	20.3–1 480	$S = 0.070x - 1.9$	50.9–6 010	$S = 0.013x + 0.98$
Zn	7.03–2 040	$S = 0.038x - 2.0$	5.03–1 780	$S = 0.002x + 3.9$	11.3–4 310	$S = 0.007x + 0.88$
Cd	0.11–15.4	$S = 0.032x - 0.03$	0.62–7.40	$S = 0.009x + 0.05$	0.06–27.5	$S = 0.008x + 0.03$
Cr	1.35–128	$S = 0.069x - 0.76$	1.64–184	$S = 0.014x + 0.29$	9.07–368	$S = 0.010x + 0.92$
Co	1.78–48.9	$S = 0.022x + 0.15$	3.59–49.1	$S = 0.022x + 0.28$	2.24–53.3	$S = 0.009x + 0.09$

procedure make it preferable for routine use in monitoring the readily acid-soluble minor elements in aquatic sediments. For samples requiring more detailed information, laboratories should be able to perform other procedures to provide data on the concentration of exchangeable and total metals.

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Distillation/Headspace/Gas Chromatographic Analysis for Volatile Polar Organics at ppb Level

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■ The distillation technique was used to concentrate volatile polar water-soluble organics in the distillate for later headspace gas chromatographic analysis. A fast, easy, and reliable headspace gas injection system equipped with an evacuated gas sampling valve was used. Methanol, ethanol, acetone, 2-propanol, and methyl ethyl ketone were determined at concentrations ranging from 0.008 to 13 mg/l. in many samples of membrane-treated hospital wastewater. The detection limit was approximately 4 $\mu g/l$. for all of the compounds except methanol and ethanol for which the limit was 8 $\mu g/l$. Combining the headspace gas chromatographic method of analysis with sample preconcentration by the distillation technique made it possible to determine volatile polar organics at the ppb level. The basic principles, advantages, and applications of these techniques are discussed.

There is a need to develop sensitive analytical methods for determining the concentrations in drinking water of trace amounts of organics, especially some of the volatile polar organic compounds. Solvent extraction and sorption on solid adsorbents such as activated carbon and resins are the two methods most widely used for concentrating the less volatile organics from water for subsequent determination by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). For the determination of volatile water-insoluble (i.e., nonpolar) organics, the Bellar and Lichtenberg procedure of gas stripping, adsorption onto a suitable medium, and subsequent thermal desorption in combination with GC or GC/MS methods has received increasing interest (*1–3*). This method, however, is not successful for trace determination of volatile polar organic (VPO) compounds such as the low-molecular-weight alcohols, ketones, and aldehydes. Solvent extraction is unsatisfactory because either the extraction efficiency for VPO's is low or they tend to be lost via evaporation during the solvent concentration step. Likewise, poor stripping efficiency along with poor sorption efficiency on solid adsorbents makes the sorption method unsuitable. The Bellar and Lichtenberg procedure has been used with only limited success for determining VPO's in water (*2*). In view of their significant contribution to the total organic carbon level in wastewaters treated for reuse, the VPO's can by no means be overlooked.

Recently, gas chromatography using the headspace gas injection technique has been discussed for determining vol-

atile organics (4), and a septumless gas injection system has been developed for fast, easy, and reliable headspace gas injection (5). VPO's can be detected at the sub-ppm level with the headspace gas injection technique, whereas the detection limit could not be reduced below the ppm level with direct aqueous injection (6, 7).

To meet the need for monitoring trace organics in water, it is necessary to determine VPO's at the ppb level. Hence, it is necessary to improve the sensitivity by a factor of 10–100, which can be accomplished either by improving the sensitivity of the final analytical step (GC or GC/MS) or by preconcentrating the initial sample. Recently, a simple distillation procedure has been demonstrated to concentrate VPO's into a few milliliters of distillate by the distillation of a few hundred milliliters of sample solution. The resulting concentration factor was found to depend on the initial sample volume, the final volume of distillate collected, and the volatility of the specific VPO's relative to that of water. A concentration factor of 10–100 can be easily achieved with the distillation technique (8). Therefore, VPO's in the distillate can be determined at the sub-ppm and ppb levels by the direct aqueous injection/GC method and the headspace gas injection/GC method, respectively. The purpose of this study was to demonstrate the application of the distillation/headspace gas injection/GC (DHGC) method in determining VPO's in hospital wastewaters treated for nonconsumptive water reuse. Based on the composition of the synthetic wastewater and the nature of the treatment processes, the organic compounds present in the treated waters are mostly the low-molecular-weight polar compounds, either volatile or nonvolatile (9, 10).

Experimental

Samples. Synthetic MUST (medical unit, self-contained transportable) hospital wastewaters were treated by ultrafiltration, followed by reverse osmosis (RO) and final ozonation (O_3) by Walden Research Division of Abcor, Inc., Cambridge, Mass. (11). The integrated test protocol called for reusing the product water effluent from each test for the subsequent run's wastewater makeup. Samples of RO permeate and ozonated RO permeate from integrated tests 3–7 were sent via the U.S. Army Medical Bioengineering Research and Development Laboratory (USAMBRDL) to the University of Illinois where they were distilled and the distillates collected. A given amount of distillate from the samples and the standard solutions was stored in headspace serum bottles (5), and mailed to USAMBRDL where headspace gas injection/GC analyses were performed.

Reagents. Standard stock solutions were prepared from ACS reagent-grade chemicals using distilled water. These stock solutions were then mixed and diluted with distilled water, which was freshly stripped at elevated temperature with purified nitrogen gas, to prepare standard solutions with concentrations ranging from 0.008 to 16 mg/l.; *n*-butanol, internal standard, was added to give a 0.8 mg/l. concentration.

Procedures for Distillation. One hundred ml of each sample solution was spiked with *n*-butanol to give a 0.8 mg/l. level and saturated with 21.3 g of dried sodium sulfate in a 250-ml round-bottomed flask. A 7.75-in. Vigreux column was connected to the flask. A small distilling head with a thermometer and a small condenser attached was connected to the upper end of the Vigreux column. During the distillation process, the vapor temperature at the distilling head was controlled at 100 °C by regulating the voltage supply to the heating mantle. Distillation continued until the first 1.5 ml of distillate was collected. From that amount, 1 ml was injected with a 2-ml syringe into a 15-ml headspace serum bottle containing 1.2 g dried sodium sulfate. Distillations were done

in duplicate for each sample. The standard solutions and distilled water were distilled in the same way.

Apparatus and Procedures for Headspace Gas Analysis. Only a brief description of the valving system is given here, since it has been described in detail elsewhere (5). Headspace bottles were heated in a 70 °C water bath for at least 70 min. The headspace gas was injected via an eight-port gas sampling valve into a gas chromatograph equipped with flame ionization detectors. The gas chromatograph was fitted with a 183-cm, 2-mm i.d. glass column packed with GP 0.4% Carbowax 1500 on 60/80 mesh Carbopack A (Supelco, Inc., Bellefonte, Pa.). After injection the column temperature was held at 60 °C for 2 min, then increased at 8 °C/min to 150 °C and held for 5 min. The carrier helium flow rate was 10 ml/min. An electronic integrator was interfaced to the flame ionization detector for acquisition of retention time and peak area data. The ratios of the peak areas of the resulting chromatograms to internal standard peak area were used for standard curves.

Excluding the time required for heating and equilibrating the solution in serum bottles, which could actually be left unattended, the sample preparation and analysis time is less than 50 min. It takes approximately 25, 3, and 18 min, respectively, for distillation, headspace gas sampling and injection, and GC run.

Results and Discussion

The gas-liquid equilibrium headspace system has been used to determine the activity coefficient of solutes and the molar energy of mixing (12) as well as the partition coefficient of solutes (13). It has also been used to determine VPO's in water (6, 7, 14). The principle of this technique for quantitative analysis is that, by injecting into the GC the equilibrated gas over a liquid phase, the solute concentration in the gas (C_G) can be determined. By knowing C_G, K_T, the partition coefficient between the liquid and gas phases, and the volumes of the liquid and headspace (V_L and V_G), the initial solute concentration (C_L°) before equilibrium can then be determined according to the following equation,

$$C_L^\circ = C_G(K_T V_L + V_G)/V_L$$

However, by fixing V_L and V_G, a calibration curve can be made to relate C_L° and C_G permitting quantitation without knowledge of the values of K_T. The values of C_G were determined experimentally by measurement of peak area relative to an internal standard peak area, and C_L° values obtained by reference to the standard curve.

The basic principle of distillation for sample preconcentration has been described elsewhere (8, 15). The technique takes advantage of the difference in volatility between the more volatile organics and less volatile water so that the VPO's can be concentrated in a small volume of distillate. The concentration factor is higher for compounds having a higher relative volatility. For example, a higher concentration factor can be expected for methyl ethyl ketone than for methanol.

In this study a calibration curve was made for each solute to correlate its original concentrations in the standard solution to the GC peak area ratios obtained from the distillates of the standard solution using headspace gas analysis. A linear regression analysis of the calibration curve using five concentration points (0.008, 0.08, 0.8, 8, and 16 mg/l.) was performed to obtain a least-squares fit. Linear standard calibration curves for methanol, ethanol, acetone, 2-propanol, *n*-propanol, methyl ethyl ketone, ethyl acetate, 2-butanol, 3-pentanone, and *n*-pentanol were obtained. The proportion of explained variation due to the linear relationship, r^2, was better than 0.97 for all model compounds. This fact indicates that the areas
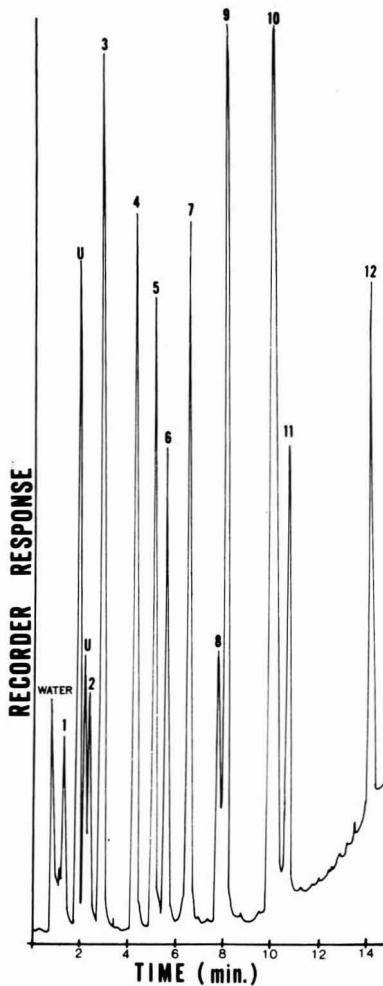
Figure 1. Headspace gas chromatogram of distillate from 0.08 mg/l. standard mixture of volatile compounds.

Peak 1 = methanol, 2 = ethanol, 3 = acetone, 4 = 2-propanol, 5 = diethyl ether, 6 = 1-propanol, 7 = methyl ethyl ketone, 8 = ethyl acetate, 9 = 2-butanol, 10 = n-butanol (internal std.), 11 = 3-pentanone, 12 = n-pentanol, u = unidentified peaks. (Range 1 × 16 attenuation)

of the GC peaks, relative to the n-butanol internal standard area, were directly proportional to the original sample concentration with the DHGC procedure.

VPO's were tentatively identified according to the relative GC retention time with n-butanol as the internal standard. A representative chromatogram of a standard solution is given in Figure 1.

The results of wastewater analyses are shown in Table I in which solute concentrations of the original wastewater samples were determined using the calibration curves described previously. As can be seen, 2-propanol and methyl ethyl ketone were determined at concentrations as low as 8 μg/l. The detection limit was estimated to be about 4 μg/l. for most of the compounds. This limit was determined by the background signal in distilled water blanks rather than by the sensitivity of the DHGC technique. The detection limit for methanol and ethanol was approximately 8 μg/l. The relative standard deviation, determined for independent triplicate runs of stock solutions containing 16 μg/l. of methyl ethyl ketone, was 9.2%. With the exception of methanol, the concentrations determined for other compounds in this study agreed fairly well with those obtained by direct headspace GC analysis of the original samples without distillation preconcentration as shown in parentheses in Table I. The discrepancies between the results of methanol determination using DHGC and headspace GC techniques are because the concentration of methanol in most wastewater samples is beyond the sensitivity limit and, thus, accuracy of the headspace GC analysis, i.e., 5 mg/l. Ethanol, however, was not detectable without the preconcentration step (Table I).

By use of the distillation preconcentration technique, the sensitivity of VPO determinations was greatly improved. The fact that the results of this study were obtained from distillates obtained in one laboratory and mailed to another for headspace analysis points to another potential advantage of the distillation technique: volatile organics can be distilled off from a large sample at the sampling site and can be preserved in a small bottle for ease of storage, shipping, and subsequent analysis at a second laboratory, thus eliminating the problems associated with shipping large samples required for analysis. Degradation of the volatile compounds as a result of the presence of microorganisms can also be avoided by preserving the distillate instead of the original sample.

The sensitivity of the DHGC method can be further improved by analyzing a highly enriched distillate. As has been mentioned, 1 l. of sample solution or more can be distilled to recover almost completely the VPO's in 100 ml of distillate. A second distillation can then be performed to further con-

Table I. Quantitative Analyses of MUST Hospital Synthetic Wastewater Samples by DHGC and Headspace GC Techniques

					Concentration, mg/l.					
Sample	Methanol		Ethanol	Acetone		2-Propanol		Methyl ethyl ketone	
IT-3-RO	13	(13)[a]	0.04	2	(3)	0.4	(0.4)	0.2	(0.2)
3-RO + O$_3$	0.6	(2)	0.05	2	(2)	0.04	(<0.08)	0.08	(0.1)
IT-4-RO	12	(11)	0.02	0.8	(2)	0.3	(0.2)	0.08	(0.1)
4-RO + O$_3$	0.2	(3)	0.02	0.8	(0.8)	0.02	(<0.08)	0.07	(<0.08)
IT-5-RO	0.3	(2)	0.02	0.6	(0.6)	0.05	(0.08)	0.08	(0.2)
5-RO + O$_3$	0.2	(2)	0.02	0.5	(0.2)	0.02	(<0.08)	0.02	(<0.08)
IT-6-RO	13	(5)	0.03	0.7	(0.6)	0.2	(0.08)	0.2	(0.08)
6-RO + O$_3$	0.6	(6)	0.03	2	(0.3)	0.02	(<0.08)	0.03	(<0.08)
IT-7-RO	4	(5)	0.02	2	(4)	0.5	(0.2)	0.2	(0.2)
7-RO + O$_3$	0.8	(3)	0.02	0.8	(2)	0.02	(<0.08)	0.08	(0.2)
7-RO + O$_3$[b]	0.08	(2)	<0.008	0.04	(<0.08)	0.008	(<0.08)	0.008	(<0.08)

[a] Data enclosed in parentheses were obtained by headspace GC technique. [b] Additional ozonation period of 3 h.

centrate the VPO's into a few milliliters of final distillate (8). Headspace GC analysis of VPO's from distillates thus obtained is then possible at the ppb (μg/l.) level or lower. Besides VPO's, other volatile, nonpolar, water-insoluble organics can also be determined by the DHGC method. The detection limit should theoretically be much lower because the concentration factor during the distillation step and the sensitivity during headspace GC analysis is much higher, a result of the higher relative volatility and smaller K_T of the volatile nonpolar compounds. Research is underway to investigate the application of the DHGC method in determining volatile, nonpolar compounds in water at the sub-ppb level.

Conclusion

VPO's at concentrations as low as 8 μg/l. can be determined in treated hospital wastewaters by the distillation/headspace/GC method (DHGC). Determinations at the ppb level or lower are attainable by applying headspace analysis to highly enriched distillate samples using two- or multistage distillation. It is expected that this technique can be applied to determining volatile nonpolar water insoluble organics at even lower concentrations. Besides the sensitivity of the DHGC technique, the possibility of processing samples on site and the ease of preserving and shipping the distillate in serum bottles will lead to even broader applications.

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Sulfate and Particulate Emissions from an Oxidation Catalyst Equipped Engine

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■ Particulate and sulfuric acid emissions were studied in the exhaust of a production Chevrolet V-8 engine, both without a catalyst in the exhaust system and with the engine equipped with a pelleted or a monolithic catalyst. The weight and sulfuric acid content of the particulate matter and the percent of fuel sulfur emitted as H_2SO_4 were determined under different operating conditions. Tests were performed at various constant speeds in the range 35–96 km h^{-1} to evaluate the effects of the following parameters: catalyst temperature in the range 573–773 K, fuel sulfur content in the range 0.1–0.3%, fuel consumption, exhaust gas flow rate through the catalyst (space velocity), amount of secondary air, and air–fuel ratio. The results showed that with the sulfur storage-release processes equilibrated, the sulfuric acid and particulate emissions and the sulfur conversion depended primarily on the first four of these parameters. Within the temperature range and secondary air range studied, the air–fuel ratio and the amount of secondary air did not seem to affect the results significantly. The weight and sulfuric acid content of the emitted particulate matter were also measured with different sulfur content fuels during a simulated seven-mode Federal Test Procedure.

Gasolines contain a small amount of sulfur which is emitted mostly in the form of sulfur dioxide if the engine is not equipped with a catalyst. When the engine is equipped with an oxidizing catalyst, some of the sulfur dioxide is converted into sulfur trioxide which combines rapidly with water vapor in the exhaust and is emitted in the form of sulfuric acid. Although oxidation catalysts reduce gaseous emissions, they give rise to the emission of sulfuric acid. In addition, the installation of oxidation catalysts in automobile exhaust systems causes an increase in the amount of particulate matter emitted.

Owing to the possible problems created by the increased sulfuric acid and particulate emissions from catalyst equipped engines, it would be desirable to understand the mechanisms and parameters which control such emissions and to determine the amounts of sulfuric acid and particulates emitted. In recent years several investigations have been addressed to this problem. Nevertheless, many aspects of the problem remain unresolved. Results are not yet available to indicate the full effects of engine variables, fuel sulfur content, and catalyst temperature on the sulfuric acid and particulate emissions from an actual spark ignition engine equipped with oxidation catalysts. The objective of this investigation was, therefore, to study the influence of these parameters on emissions from a Chevrolet V-8 engine operating on a test stand dynamometer.

Experimental Apparatus and Procedures

The apparatus used in this study was essentially the same as that used by Ganley and Springer (1) and Sampson and
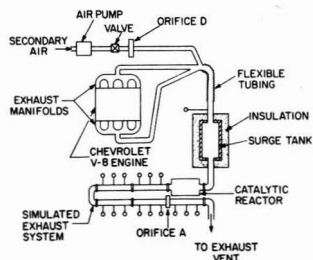
Figure 1. Experimental apparatus
Circles: thermocouple and sampling locations

Springer (2). Therefore, only a brief summary is given to indicate the changes made and to facilitate the reading of the paper.

The engine was a 1970 350 CID 250 HP Chevrolet V-8 production engine mounted on a dynamometer. The tests were conducted with Indolene HO 0 (clear) fuel, with di-t-butyl-disulfide added to adjust the sulfur content to the desired value. The physical and chemical properties of the fuel are given by Laresgoiti and Springer (3).

The exhaust system, connected to the engine, consisted of the standard exhaust manifolds and crossover pipe, a surge tank, a 4.27-m-long, 50-8-mm diameter pipe (simulated exhaust system), and a 22-mm diameter sharp-edged orifice (orifice A, Figure 1).

Tests were first performed under cyclic conditions without the catalysts. In turn, a pelleted and a monolithic catalytic reactor were installed in the exhaust system (50 cm downstream from the surge tank), and tests were performed with each catalyst under steady and cyclic operating conditions. The pelleted catalyst was a General Motors extrudate catalyst with a 5-to-2 platinum–palladium weight ratio and a nominal loading of 0.35 g l.$^{-1}$. The monolithic catalyst was an Engelhard PTX-type IIB catalyst. For the monolithic reactor only four of the eight cylinders were connected to the exhaust. The catalyst temperature was measured with a thermocouple inserted into the reactor. For the pelleted catalyst the thermocouple was near the middle of the reactor; for the monolithic catalyst it was near the exit.

For both catalysts secondary air was injected into the exhaust (before the surge tank) by an air pump driven by a V belt from the crankshaft pulley. The amount of secondary air was controlled by a valve and was measured by an 18-mm diameter sharp-edged orifice (orifice D, Figure 1).

The sampling train is shown in Figure 2a. The sampling probes were made of 316 stainless steel (2.6–4 mm i.d., 1 mm wall thickness). The probes were located in the center of the exhaust pipe facing the direction of the flow.
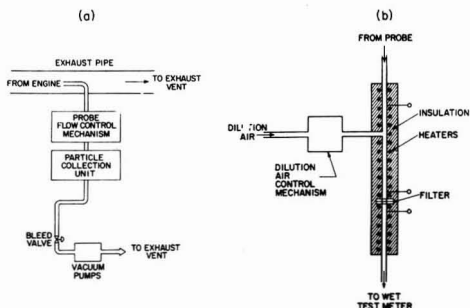
The particle collection unit housed a Gelman 47-mm diameter type A glass fiber filter placed in a modified Gelman 2220 filter holder (Figure 2b). The matter collected on the filter was analyzed to determine particulate and H_2SO_4 emissions. The entire collection unit was surrounded with beaded heaters and kaowool insulation. The current to the heaters was controlled by voltage controllers. The temperature of the gas sample was measured with thermocouples inserted into the gas stream on both sides of the filter holders. The exhaust gases could be diluted with ambient air. All the data given in the Results section were obtained by diluting the sample with air (dilution ratio 8:1) and by keeping the temperature of both the sample gas and the collection unit (including the filter) in the range 305–315 K. The reasons for selecting those sampling conditions are discussed subsequently.

The flow rate through the probe and the amount of dilution air must be carefully regulated through the tests. The flow rate through the probe must be adjusted to the proper value for isokinetic sampling (1). The dilution air must be adjusted to maintain an 8:1 dilution ratio. At steady operating speeds the flow rates of the dilution air and the total sample were measured by wet test meters installed in the system, and the flow rates were set appropriately. Under cyclic operating conditions the flow rates through the probe and the dilution system were modified and adjusted continuously.

The flow rate through the probe was regulated as follows (Figure 3). A standard 1.3-mm diameter sharp-edged orifice (orifice B) was installed in the sampling line (Figure 3). The pressure drop across this orifice was measured by a differential pressure sensitive transducer. The pressure drop across the orifice in the exhaust system (orifice A) was measured by a potentiometer-type differential pressure transducer. The signals from the two transducers were compared by an operational amplifier. The difference in the two signals was amplified by a dc servoamplifier and fed to a motor generator. This motor generator was connected to a stainless steel valve through a gear box. The flow rate through the probe was regulated by the valve. The amount of dilution air was controlled by a similar control system. The orifices were calibrated under steady-state conditions. The orifice in the exhaust system (orifice A) was calibrated with a rounded approach air cart. The orifices in the sampling line (orifice B) and in the dilution air line (orifice C) were calibrated using the wet test meters. The sampling system was also tested under cyclic conditions by comparing on a strip chart recorder the pressure fluctuations in the exhaust system (across orifice A) and in the sampling line (across orifice B). Excellent correlation was found between the two signals as the engine speed was varied.

Before taking the final data the engine and exhaust system were operated at the test conditions to allow the emissions to stabilize. When the pelleted catalyst was installed, the engine

Figure 2. a) Sampling train; b) schematic of collection unit
Open circles: thermocouple locations
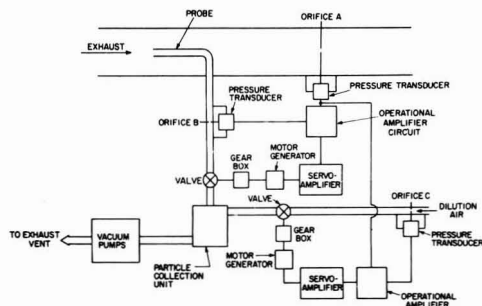
Figure 3. Schematic of automatic control system

was conditioned for a period equivalent to 8000 km at 88 km h^{-1} with fuel containing 0.017% sulfur and then for a period equivalent to 2500 km at 88 km h^{-1} with fuel containing 0.1% sulfur. When the pelleted catalyst was replaced by the monolithic catalyst, the engine was operated for a period equivalent to 2500 km at 88 km h^{-1} with 0.1% sulfur content fuel.

When the engine was started it was warmed up for 1½ h. Then, before each steady engine speed test the engine was operated for 3 h at the condition of the test. The sampling was done for a 30-min period. For cyclic tests the system was warmed up through 10 cycles before sampling. Each test was repeated five times, and the average of the five data points is shown in the results presented in the next section. There was a maximum of ±20% spread in the data. Within this spread there were no noticeable changes in any of the parameters measured. This suggests that within the time span of the tests, thermal storage did not have an appreciable influence on the results.

After each test the filters were placed for 24 h in an airtight container having within CaCl$_2$ as desiccant and were then weighed and prepared for chemical analysis. The sulfuric acid content of the collected particulate sample was determined by the Barium-Thorin titrimetric procedure (4, 5). The effect of filter material on the SO$_2$ to H$_2$SO$_4$ conversion was checked by making tests without the catalyst in the exhaust. Even at high SO$_2$ concentrations, H$_2$SO$_4$ could not be detected on the filters. For additional details of the apparatus and test procedures, the reader is referred to Laresgoiti and Springer (3).

Sampling Temperature and Sample Dilution. Sulfuric acid condenses and collects on the filters only below about 350 K, with the exact temperature being dependent upon the test conditions. The exhaust gas is generally above this temperature. To measure the sulfuric acid content, the sample had to be cooled. However, at low temperatures, water also condenses and collects on the filters. Water condensation may be prevented by diluting the sample with ambient air, and this method was adopted in the present tests. A series of preliminary tests was performed to establish the proper sampling temperature and to determine the effects of dilution on the emission of particulates.

First, particulate emission was measured with the engine operating without the catalyst (unleaded fuel). Above 400 K the particulate emission (g km^{-1}) was determined both with and without dilution (dilution ratio 8:1). When the sample temperature was higher than 400 K, the sample temperature was adjusted to the same value as that of the exhaust gas at the location of the probe. Above 400 K the results were unaffected by the dilution and were insensitive to changes in the sample gas temperature (Figure 4). This can be explained by the fact that particulates collected above 400 K are mostly carbon formed in the combustion chamber due to the dehydrogenation of hydrocarbons (1).

Below 400 K the sample was diluted with air. These measurements showed that below 390 K there is a large increase in particulate emission, due mostly to condensation of high-molecular-weight organic compounds present in the exhaust gas (6–9).

It is interesting that during a simulated seven-mode Federal Test Procedure, approximately twice the amount (by weight) of particulates is emitted as at 35 km h^{-1} steady speed (35 km h^{-1} corresponds to the average speed of the cycle). A similar trend was observed by Ter Haar et al. (10).

Second, particulate emission as a function of sample gas temperature was measured with fuel containing 0.017% sulfur (Figure 5). These tests were performed both with and without the catalysts with the objective of determining the sample gas temperature at which most of the sulfuric acid condensed.
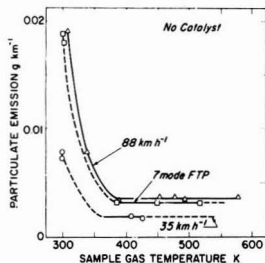
Figure 4. Particulate emission vs. sample gas temperature during seven-mode Federal Test Procedure, and 35 km h^{-1} and 88 km h^{-1} cruise conditions

(———- - - -) Fit to data
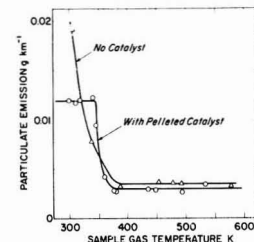
Figure 5. Particulate emission with and without pelleted catalyst 88 km h^{-1} cruise condition. Catalyst temperature, 755 K. Indolene HO 0 fuel with 0.017% sulfur content. (———) Fit to data

Above 400 K neither dilution nor the presence of the catalysts affected the amount of particulate matter emitted, suggesting that most particles were carbon emitted directly from the combustion chamber (1). Deposition in the catalyst may account for the small difference in the results.

Below 400 K the sample was diluted (dilution ratio 8:1). There is a sharp increase in the amount of particulate matter emitted below 390 K. In the absence of the catalyst this increase is due to condensation of heavy hydrocarbons. For the catalyst equipped engine the increase is most likely due to condensation of sulfuric acid. Below 350 K the amount of particulate matter collected remained nearly constant when using a catalyst, implying that most of the sulfuric acid condensed out of the gas stream. On the basis of these results, in all subsequent tests (i.e., for all the data reported in the next section) the collection unit was kept in the 305–315 K temperature range by diluting the sample with ambient air (dilution ratio 8:1). These temperatures were appropriate also when fuels with higher sulfur content (i.e., sulfur content above 0.017%) were used, since in this case the condensation process was completed at even higher temperatures.

Results

The major objective of this investigation was to evaluate the parameters which affect the sulfate and particulate emissions from spark ignition engines equipped either with a monolithic or with a pelleted catalyst. Particular attention was focused on the effects of catalyst temperature, fuel sulfur content, exhaust gas mass flow rate through the catalyst (space velocity), fuel consumption, air–fuel ratio, and amount of secondary air on the amount of particulate matter emitted, on the amount of sulfuric acid emitted, and on the sulfur conversion. Tests were performed at engine speeds and loads corresponding to a 1970 full size Chevrolet cruising at 35, 64, 88, and 96 km h^{-1}, and under a simulated seven-mode Federal Test Procedure.

Note that in the following tests the effects of the various parameters were separated. This was accomplished by varying one parameter at a time. For example, the temperatures of the catalysts were regulated by heating tapes and were thus unaffected by the engine speed and load or the secondary air. This must be borne in mind when evaluating the data and when comparing them to the results of other studies where generally several parameters were varied simultaneously.

Sulfur Conversion. The sulfur conversion (percent weight of sulfur in the fuel converted to sulfuric acid) as a function of space velocity, exhaust gas mass flow rate, speed, fuel sulfur content, and catalyst temperature is shown in Figure 6. The data points are from the measurements. The lines were computed from the expression (see Appendix),

$$C = (X_{SO_2})_E \left[1 - \exp \left(\frac{-km \left(\dfrac{m_f}{m_c + m_f} \right) \rho_{exh}}{m_f} \right) \right] \times 100$$

(1)

where $(X_{SO_2})_E$ is the fraction of SO_2 converted into SO_3 at equilibrium, k is the rate constant for the conversion of SO_2 to SO_3 inside the catalyst, m is the mass of the catalyst, m_f is the mass of fuel burned in the engine per hour, m_c is the mass of air entering the engine per hour plus the mass of secondary air entering the reactor per hour, and ρ_{exh} is the density of the exhaust gas (kg dm^{-3}). Values for $(X_{SO_2})_E$ and for the product km are given in the Appendix.

In Figure 7 the results of Figure 6 were crossplotted using temperature as the abscissa and the exhaust gas mass flow rate (and speed) as the variable parameter. The solid lines in Figure 7 were calculated from Equation 1 with the values of km given in the Appendix. The left side of the peaks corresponds to reactions in the kinetically limited region; the right side corresponds to reactions in the region limited by chemical equilibrium. The data of Creswick et al. (11), Trayser et al. (12), and Holt et al. (13) obtained with pelleted and monolithic catalysts are also included in Figure 7. The data reported by these investigators were shifted 70 K to the right (as suggested by W. R. Pierson) to allow for the fact that these investigators measured the catalyst temperature at the catalyst exit and not inside the catalyst. The results of Bradow and Moran (14) and Somers et al. (15) are not included in Figure
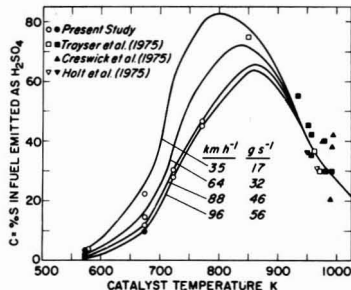
Figure 7. Sulfur conversion as function of temperature, speed, and exhaust gas mass flow rate through catalyst

Indolene HO 0 fuel with 0.1% sulfur content. A/F = 15.0, excess air 25% ($\sim$5% O_2). Open and closed symbols: pelleted and monolithic catalyst data, respectively. Solid lines calculated from Equation 1

7 because these investigators did not report the catalyst temperature. The data of Begeman et al. (16) and Irish and Stefan (17) are not included because these data were taken under transient conditions.

Mikkor et al. (18), Hammerle and Mikkor (19), and Hammerle and Truex (20) also measured sulfur conversion. Their data are not included here because instead of an engine they used a simulated exhaust system. Nevertheless, their results show a trend similar to the curves in Figure 7.

For all the temperatures used in the present tests (catalyst temperatures less than 800 K), the sulfur conversion increased with temperature (Figure 7). This indicates that the reaction in the catalyst was kinetically limited as opposed to being limited by chemical equilibrium (21). At catalyst temperatures above $\sim$900 K, where most other tests were performed, the reactions were in the chemical equilibrium region.

Figure 6 shows that in the temperature range of the present tests (i.e., below $\sim$800 K) the sulfur conversion decreased with increasing exhaust gas mass flow rate and increasing space velocity, the latter being defined as the exhaust gas volume flow rate at 273 K and 1 atm divided by the catalyst volume. The reason for this is that at higher flow rates (which correspond to higher engine speeds and loads), the flow rate through the catalyst increased, decreasing the residence time inside the catalyst. However, the residence time (inverse space velocity) affects the conversion only in the kinetically limited region. At catalyst temperatures above $\sim$900 K the reactions are in the chemical equilibrium region, and the conversion is not influenced by the flow rate.

At catalyst temperatures below $\sim$800 K, at the same space velocity the sulfur conversion is different for the two different types of catalysts. However, for a given exhaust gas mass flow rate (i.e., given engine speed and load), the sulfur conversion is practically the same for both the pelleted and monolithic catalysts. Thus, under the same conditions, in a given engine both catalysts would result in approximately the same sulfur conversion.

Figure 6 also shows the effect of fuel sulfur content on the sulfur conversion. The conversion is insensitive to the fuel sulfur content above $\sim$573 K indicating that the catalytic oxidation of SO_3 is limited by adsorption of SO_2 by the catalyst. By use of the monolithic catalyst the amount of sulfur emitted as H_2SO_4 and the sulfur conversion were also measured at 400 and 530 K. Because of the small scale the data thus obtained were not included in Figure 6. However, these results show that below $\sim$573 K the conversion decreases with fuel sulfur content indicating that the limiting mechanism is desorption of SO_3 from the catalyst.
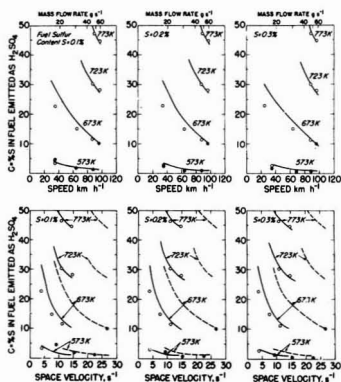
Figure 6. Effects of space velocity (at 273 K and 1 atm), exhaust gas mass flow rate through catalyst, catalyst temperature, and fuel sulfur content on the sulfur conversion

Indolene HO 0 fuel, A/F = 15.0, excess air = 25% ($\sim$5% O_2). O Pelleted catalyst data. ● Monolithic catalyst data. Solid and dashed lines calculated from Equation 1 for pelleted and monolithic catalysts, respectively

Sulfuric Acid Emission. Once the percent conversion of SO_2 into SO_3 (denoted by the symbol C) is known (see Figure 6), the amount of sulfuric acid emitted can be calculated from the expression

$$H_2SO_4 = 3.06(F)\left(\frac{S}{100}\right)\left(\frac{C}{100}\right) \text{ g km}^{-1} \qquad (2)$$

where F is the fuel consumption in g km^{-1} (Figure 8), and S is the sulfur content of the fuel (percent sulfur per weight in the fuel). The gravimetric factor between H_2SO_4 and sulfur is 3.06. Note that the engine speed, space velocity, and catalyst temperature do not enter into Equation 2 directly. These variables affect the H_2SO_4 emission through their effects on F, S, and C.

The measured H_2SO_4 emission and the values calculated from Equation 2 are shown in Figure 9. The sulfuric acid emission has a minimum at about 90 km h^{-1}. As shown previously, the sulfur conversion decreases continuously with increasing speed. However, the fuel consumption increases with speed giving rise to the minimum in the sulfuric acid emissions.

The sulfuric acid emission for the seven-mode Federal Test Procedure is shown in Figures 10 and 11. In these figures the ranges of sulfuric acid emission at the steady speed corresponding to the average speed of the cycle (35 km h^{-1}) are also shown. For the seven-mode Federal Test Procedure the amount of sulfuric acid emitted increased linearly with the fuel sulfur content. At 35 km h^{-1} a similar increase in sulfuric acid with fuel sulfur content was observed with the pelleted catalyst. With the monolithic catalyst at the steady 35 km h^{-1} speed, the sulfuric acid emission seems to be insensitive to the fuel sulfur content. The latter can be explained by noting that the rate of reaction at which the SO_2 to SO_3 conversion occurs depends on the concentration of SO_2 in the exhaust gas at the inlet to the catalyst and on the catalyst temperature (21). At low SO_2 concentrations and at high temperatures the mechanism limiting the formation of SO_3 is the adsorption of SO_2 by the catalyst. Under these conditions the reaction rate varies nearly linearly with the SO_2 concentration. At high SO_2 concentrations or low temperatures the rate of reaction becomes constant. In this region the reaction is controlled by desorption of SO_3 from the catalyst. In between the adsorption and desorption controlled regions the reaction is governed mostly by chemical reaction. That the amount of sulfuric acid emitted remained constant indicates that the reactions in the catalyst are in the desorption controlled region (high SO_2 concentration, low catalyst temperature) where the SO_2 concentration at the catalyst inlet does not affect the reaction. Since the amount of SO_2 is proportional to the fuel sulfur content, in this region the fuel sulfur content does not influence the results significantly. At higher catalyst temperatures the reactions are not in the desorption region, and the amount of sulfuric acid emitted depends on the fuel sulfur content.

Particulate Emission. There is a distinct similarity between the amounts of sulfuric acid and particulate matter emitted, because the particulates are composed mostly of sulfuric acid and water (22). Consequently, the amount of emitted particulate matter P is expected to be proportional to the amount of H_2SO_4 emitted, i.e.,

$$P = A(H_2SO_4 \text{ emitted}) \text{ g km}^{-1} \qquad (3)$$

where A is a proportionality factor accounting for the presence of the water. Equations 2 and 3 give

$$P = A(3.06)(F)\left(\frac{C}{100}\right)\left(\frac{S}{100}\right) \qquad (4)$$

The value of A was obtained by matching Equation 4 to data obtained at steady speeds (Figure 9). This procedure yielded A in the range 2.2–2.8. The lines in Figure 9 were computed
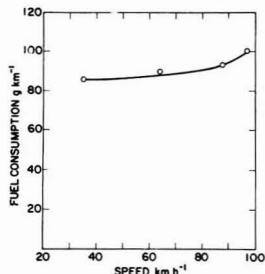
Figure 8. Fuel consumption vs. speed. (——) Fit to data
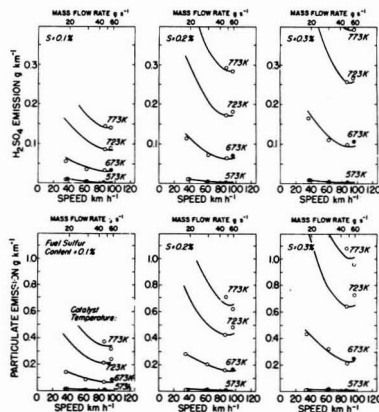
Figure 9. Effects of speed, exhaust gas mass flow rate through catalyst, catalyst temperature, and fuel sulfur content on H_2SO_4 and particulate emissions

Indolene HO 0 fuel, A/F = 15.0, excess air = 25% ($\sim$5% O_2) O Pelleted catalyst data. ● Monolithic catalyst data. Solid lines calculated from Equations 2 and 4
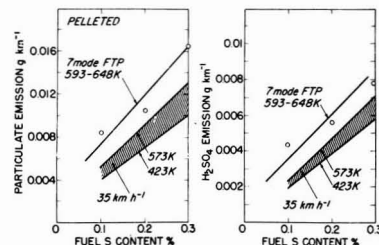
Figure 10. Particulate and H_2SO_4 emissions during seven-mode Federal Test Procedure and 35 km h^{-1} cruise condition

Pelleted catalyst. Temperatures indicated correspond to catalyst temperatures. Indolene HO 0 fuel
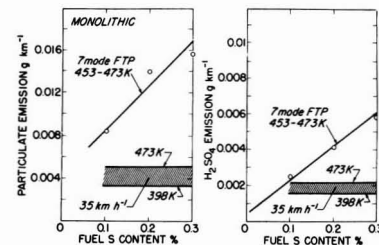
Figure 11. Particulate and H_2SO_4 emissions during seven-mode Federal Test Procedure and 35 km h^{-1} cruise condition

Monolithic catalyst. Temperatures indicated correspond to catalyst temperatures. Indolene HO 0 fuel

using the average value of $A = 2.4$. As in the case of sulfuric acid emission, the engine speed affects the particulate emission only through the parameters F, S, and C.

Particulate emission under cyclic operation (seven-mode Federal Test Procedure) is shown in Figures 10 and 11. As expected, the trend in the results is the same as for the sulfuric acid emission because of the relationship between the amounts of sulfuric acid and particulate matter emitted.

Space Velocity. Under the same engine operating conditions (speed and load), the effects of space velocity on particulate and sulfuric acid emissions and on the sulfur conversion are shown in Figures 12 and 13. A reduction in space velocity and a corresponding increase in residence time result in an increase in sulfuric acid conversion and hence in an increase in the amounts of sulfuric acid and particulate matter emitted.

Secondary Air and Air–Fuel Ratio. The effects of secondary air and air–fuel ratio on the particulate emission were investigated at various steady engine speeds. Sulfur conversion, sulfuric acid, and particulate emissions as a function of secondary air injected into the exhaust before the catalyst are given in Figures 14 and 15. The amount of secondary air does not seem to affect the results, suggesting that there is sufficient oxygen for the reaction to be completed. These results tend to agree with those reported by Mikkor et al. (*18*) and Hammerle and Truex (*20*). At smaller amounts of secondary air the secondary air might affect the results, but the amounts needed to observe these effects could not be achieved in the present tests.

The air–fuel ratio does not seem to influence the results provided the catalyst temperature is kept constant, and sufficient oxygen is supplied (through secondary air injection) to the catalyst to oxidize the unburned hydrocarbons, carbon monoxide, and sulfur dioxide (Figure 16).

Concluding Remark. As already noted, in the present tests the operating conditions were set to indicate the effects of the various parameters individually. In applying the results to actual operating conditions, the appropriate combination of these parameters must be selected.

Appendix. Calculation of Conversion of SO_2 to SO_3

SO_3 is produced by the reaction

$$SO_2 + \tfrac{1}{2} O_2 \rightleftharpoons SO_3 \qquad (A1)$$
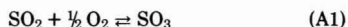
For this reaction the overall rate constant inside the reactor [$dm^3/(h) \times$ (catalyst mass in kg)] may be approximated by (*21*)

$$k = \frac{-r_{SO_2}}{C_{SO_2} - (C_{SO_2})_E} \qquad (A2)$$

where $(-r_{SO_2})$ is the rate of disappearance of SO_2 (moles of SO_2 reacted/catalyst mass kg $\times$ h), C_{SO_2} is the concentration of SO_2 (mol/dm^3) at a given position inside the catalyst, $(C_{SO_2})_E$ is the chemical equilibrium concentration of SO_2 (mol/dm^3). r_{SO_2} and C_{SO_2} are not known directly but must be determined from the information available—the amount of SO_2 entering the catalyst (reactor) and the amount of SO_3 leaving the catalyst. To tilize the available information we assume that the reaction takes place in a plug flow-type reactor shown in Figure 17. For a differential element containing a dm mass of the catalyst, an SO_2 mass balance gives (*21*)

$$(F_{SO_2})_{in} dX_{SO_2} = -r_{SO_2} dm \qquad (A3)$$

Upon integration Equation A3 becomes

$$\frac{m}{(F_{SO_2})_{in}} = -\int_{(X_{SO_2})_{in}}^{(X_{SO_2})_{out}} \frac{dX_{SO_2}}{r_{SO_2}} \qquad (A4)$$

where m is the mass of the catalyst in the reactor, (F_{SO_2}) is the
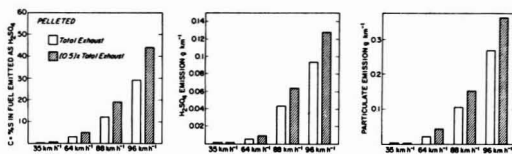
Figure 12. Effects of flow rate through pelleted catalyst on sulfur conversion, H_2SO_4 emission, and particulate emission
Open symbols: entire exhaust passing through catalyst. Shaded symbols: reduced flow rates. Indolene HO 0 fuel with 0.1% sulfur content. 25% excess air ($\sim$5% O_2). A/F = 15.0. Temperatures given are catalyst temperatures
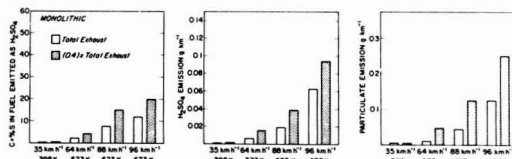
Figure 13. Effects of flow rate through monolithic catalyst on sulfur conversion, H_2SO_4 emission, and particulate emission
Open symbols: entire exhaust passing through catalyst. Shaded symbols: reduced flow rates. Indolene HO 0 fuel with 0.1% sulfur content. 25% excess air ($\sim$5% O_2). A/F = 15.0. Temperatures given are catalyst temperatures
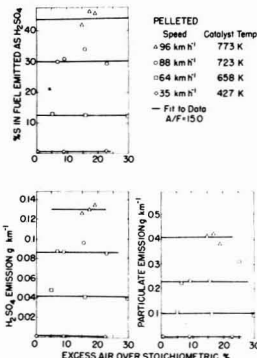
Figure 14. Effects of secondary air on sulfur conversion, H_2SO_4 emission, and particulate emission for pelleted catalyst
Steady engine speed. Indolene HO 0 fuel with 0.1% sulfur content

molar flow of SO_2, and (X_{SO_2}) is the fraction of SO_2 converted into SO_3. The subscripts in and out represent the conditions at the inlet and outlet of the reactor, respectively,

$$(X_{SO_2})_{out} = \frac{(C_{SO_3})_{out}}{(C_{SO_2})_{out} + (C_{SO_3})_{out}} \qquad (A5)$$

By assuming that $(X_{SO_2})_{in} = 0$, the substituting Equation A2 into A4, we obtain

$$\frac{m}{(F_{SO_2})_{in}} = \int_0^{(X_{SO_2})_{out}} \frac{dX_{SO_2}}{k[C_{SO_2} - (C_{SO_2})_E]} \qquad (A6)$$

With the definitions

$$X_{SO_2} = \frac{C_{SO_3}}{C_{SO_2} + C_{SO_3}} = \frac{(C_{SO_2})_{in} - C_{SO_2}}{(C_{SO_2})_{in}} \qquad (A7a)$$

$$(X_{SO_2})_E = \frac{(C_{SO_3})_E}{(C_{SO_2})_E + (C_{SO_3})_E} = \frac{(C_{SO_2})_{in} - (C_{SO_2})_E}{(C_{SO_2})_{in}} \qquad (A7b)$$

Equation A6 yields

$$\frac{(k)(m)}{(F_{SO_2})_{in}} (C_{SO_2})_{in} = \int_0^{(X_{SO_2})_{out}} \frac{dX_{SO_2}}{(X_{SO_2})_E - X_{SO_2}} \qquad (A8)$$
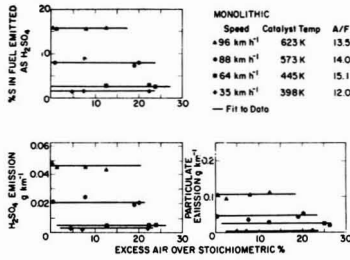
Figure 15. Effects of secondary air on sulfur conversion, H_2SO_4 emission, and particulate emission for monolithic catalyst
Steady engine speed. Indolene HO 0 fuel with 0.1% sulfur content
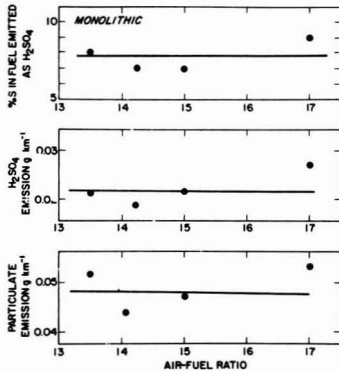
Figure 16. Effects of air–fuel ratio on sulfur conversion, H_2SO_4 emission, and particulate emission for monolithic catalyst
88 km h^{-1} cruise condition. Excess air 25% ($\sim$5% O$_2$). Catalyst temperature 623 K. Indolene HO 0 fuel with 0.1% sulfur content. (————) Fit to data

Figure 17. Plug flow reactor for calculating SO$_2$ conversion
X_{SO_2}: fraction of SO$_2$ transformed to SO$_3$. F_{SO_2}: molar flow rate of SO$_2$ (mol h^{-1}). Subscripts in and out: conditions at inlet and outlet of catalytic reactor, respectively
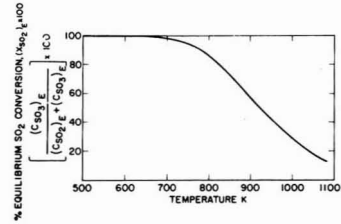
Figure 18. Conversion of SO$_2$ to SO$_3$ at chemical equilibrium (19)
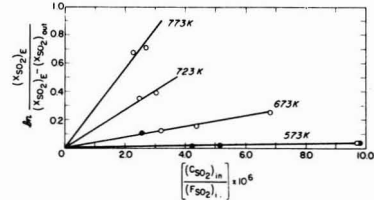
Figure 19. Relationship between fractions of SO$_2$ converted to SO$_3$ and SO$_2$ concentrations as function of temperature
(F_{SO_2})$_{in}$: molar flow rate of SO$_2$ (mol h^{-1}). Subscripts in and out: conditions of inlet and outlet of catalytic reactors, respectively
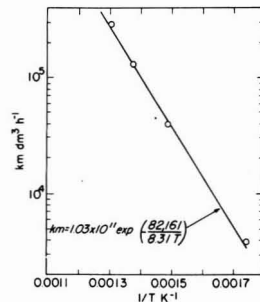
Figure 20. km as function of temperature

The subscript E denotes chemical equilibrium. Integration of Equation A8 gives

$$(k)(m) = \frac{\ln \left[\dfrac{(X_{SO_2})_E}{(X_{SO_2})_E - (X_{SO_2})_{out}} \right]}{\dfrac{(C_{SO_2})_{in}}{(F_{SO_2})_{in}}} \quad \text{(A9)}$$

$(X_{SO_2})_E$ as a function of temperature was calculated by Hammerle and Mikkor (19), and their result is reproduced here in Figure 18. $(X_{SO_2})_{out}$ (which is the same as $C/100$) was measured in the present experiments (Figure 6).

$(C_{SO_2})_{in}$ was determined as follows. The catalyst was operated with 25% excess over stoichiometric. This corresponds to an "air-fuel ratio" of 19:1 through the catalyst. The "air-fuel ratio" through the catalyst is defined as

$$\left(\frac{A}{F} \right)_{cat} = \frac{m_c}{m_f} = 19 \quad \text{(A10)}$$

The amount of sulfur (kg) per kg of exhaust gas is

$$m_s^* = \frac{m_f}{m_c + m_f} \frac{S}{100} \quad \text{(A11)}$$

where S is the percent sulfur in the fuel by weight. The number of moles of SO$_2$ per kg of exhaust gas is

$$(C_{SO_2})_{in} = \frac{m_s^*}{32} \frac{\text{kg mol}}{\text{kg exhaust}} \quad \text{(A12)}$$

since 1 mol of S in the fuel gives rise to 1 mol of SO$_2$. Equations A10–A12 give

$$(C_{SO_2})_{in} = \frac{1000}{(20)(32)(100)} \times S \quad \frac{\text{g mol}}{\text{kg exhaust}} \quad \text{(A13)}$$

or

$$(C_{SO_2})_{in} = \frac{1000}{(20)(32)(100)} \times S \times \rho_{exh} \quad \frac{\text{g mol}}{\text{dm}^3 \text{ exhaust}} \quad \text{(A14)}$$

where ρ_{exh} is the density of the exhaust gas (kg dm^{-3}). This density was calculated by assuming that the density of the

exhaust gas is the same as the density of air at the temperature and pressure of the exhaust.

In Equation A9, $(F_{SO_2})_{in}$ is the number of moles of SO_2 entering the catalyst per hour

$$(F_{SO_2})_{in} = m_f \times 1000 \left(\frac{S}{100}\right)\left(\frac{1}{32}\right)\frac{g \, mol}{hour} \quad (A15)$$

To obtain the product km the right-hand side of Equation A9 was plotted for various temperatures (Figure 19). The slope of the lines gives km as a function of inverse temperature in Figure 20. Equations A9–A15 yield Equation 1 in the main text.

Acknowledgment

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Fluorescence Immunoassay Technique for Detecting Organic Environmental Contaminants

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The need for monitoring pesticide residues has been met by numerous methods which have been previously summarized (1), and it is beyond the scope of this article to discuss them. Of all methods, however, gas chromatography–mass spectrometry has achieved the most notable success in the detection of pesticides at the residue level. In an effort to improve upon the sensitivity and provide a simpler technique capable of field operation, the use of a fluorescence polarization immunochemical technique has been investigated. The use of such a technique has been prompted by the development and application of these fluorescence techniques to the measurement of biological substances (2). Available evidence indicates that specific antibodies can be obtained against many organic compounds (3). In particular, antibodies have been obtained against DDT and malathion (4, 5) and other

pesticide residues (1). The availability of a specific antibody against the structure or molecule to be detected immediately opens up the possibility of using immunochemical methods as a highly specific and sensitive (2) detection technique.

2-Aminobenzimidazole, the degradation product of several carbamate fungicides such as Benomyl, was chosen as the compound for which the fluorescence polarization immunoassay would be developed.

Any means of applying an immunochemical reaction to a detection problem ultimately relies upon a reaction occurring between the substance of interest (antigen or hapten) and its specific antibody. Perhaps the most general means by which this interaction can be employed in measurement and detection has come to be known as "competitive binding assay". In principle, this method requires two essential reagents. These

■ The development of an immunological assay for 2-aminobenzimidazole, the degradation product of several carbamate pesticides such as Benomyl, is described. The specific technique is a fluorescence polarization immunoassay, and it may be applicable to the detection of many low-molecular-weight organic contaminants of organic concern. The preparation of the two required reagents, namely a fluorescent conjugate of the contaminant of interest, together with an antibody to the contaminant, is described in detail. The specific contaminant chosen for this study was 2-aminobenzimidazole (MW = 133), a metabolite of certain fungicide agents used in agriculture, and the particular fluorescent moiety chosen to form the conjugate with 2-aminobenzimidazole was fluorescein. A successful demonstration of the assay is accomplished, and a detection sensitivity in the subnanogram/ml range obtained.

are a labeled form of the substance to be detected or measured, and an antibody or receptor specifically directed against the substance. The principle of the assay involves a preliminary measurement of the binding of the labeled antigen (substance being detected) with its antibody and then a determination of the extent of the inhibition of this binding by known quantities of the unlabeled antigen, which corresponds to the unknown. From these data, a standard curve can be constructed which shows the degree of binding by the labeled antigen under certain specified conditions as a function of concentration of the unlabeled antigen or unknown added.

Fundamentals of Immunoassay Technique

A substance, which when injected into an animal stimulates the animal to produce antisera capable of reacting with it in a highly specific manner, is referred to as an immunogen, and the specific protein produced is referred to as an antibody. These antibodies belong to a group of serum proteins known as immunoglobulins. The production of these antibodies as a result of the injection of the immunogen takes place over a period of many weeks, and depends upon the immunization schedule. In general, "good" immunogens are usually of large molecular size (>40 000), partially digestible by enzymes, and are recognized as being foreign by the antibody-producing animal. It is immediately obvious, of course, that many compounds of environmental concern do not have a large molecular weight and would, therefore, appear to be incapable of stimulating antibody formation.

Fortunately, this is not the case, and so-called partial immunogens or haptens can be produced and are capable of reacting with specific antibody. Haptens or partial immunogens are defined as immunogens which alone cannot induce antibody formation, but in conjugation with a suitable carrier can produce antibody against themselves, as well as against the carrier-hapten complex. Examples of such carriers include ovalbumin, bovine serum albumin, and fibrinogen, as well as many others.

In summary, the hapten once conjugated with a suitable carrier can stimulate antibody production. The remarkable thing about this antibody stimulation is that some antibody will be produced which is highly specific in its reaction with the hapten alone. It is this phenomenon which allows the use of immunological techniques in the detection and quantitation of organic contaminants of relatively low molecular weight and under a variety of practical circumstances.

Review of Immunoassay Techniques

The usual method of labeling the antigen to be identified in an immunoassay requires the introduction of a radioactive label. When such a radiolabel is used, an essential and crucial step in the radioimmunoassay (RIA) is to separate physically that portion of the labeled antigen which is bound to the antibody from that which is unbound or free. Only in this way is it possible, by radioactive counting, to determine what fraction of the radiolabel remains bound, or is being bound, in the presence of the unknown. Hawker (3) has reviewed various radioimmunoassay and related techniques.

Alternatively, a direct way of implementing competitive binding principles in an immunoassay is to employ a fluorescent label which allows the assay to be carried out in principle, either by fluorescence polarization measurements (FPI), or in some cases by fluorescence intensity measurements. Unlike RIA, no separation of the bound and free forms of the labeled antigen is necessary, since a simple, rapid optical measurement gives the essential information without physical separation.

Examples of other radioassays include radioreceptor assay, which employs a partially purified tissue receptor as the active reagent, and immunoradiometric assay, which uses radioactive labeled antibody. In the latter case, separation of bound and unbound antibodies is accomplished by attachment to the antigen which is deposited on a solid substrate. Radioenzymatic assays involve enzymes as the reactive agent. Once again, a separation procedure is required. In this case, separation of the radioactive pools requires separation of two compounds, one formed from the other by the enzyme catalyzed reaction. These techniques, however, tend to be inferior to RIA and FPI in terms of sensitivity and specificity (1). The application of immunological techniques to the analysis of pesticide residue levels appears to be of relatively recent origin, and Ercegovitch (6) in 1971 gave an excellent review of work in this area. This work appears to be limited to research carried out on the herbicide aminotriazole and parathion with sensitivities in the microgram range, and by Centeno et al. (4) and Haas and Guardia (5) using a tanned cell hemagglutination inhibition test with detection limits of 0.1 and 1.0 μg for DDT and malathion, respectively.

Application of Fluorescence Polarization to Immunoassay Techniques

The essential feature of applying this phenomenon to an immunoassay consists in first labeling the antigen molecule with a fluorescent moiety and then observing the degree of polarization of the fluorescent light upon stimulation with polarized light of the correct wavelength, or in certain cases, the intensity of fluorescent light measured, when standard quantities of the labeled antigen and antibody together with the unknown are allowed to interact. The dependence of polarization (and also occasionally, the fluorescent intensity) upon the extent of reaction between the antigen and antibody forms the basis for the quantitation and immunoassay. Reaction between the antigen and antibody results in an increase in size of the kinetic unit and in a retardation of the rotary brownian motion, which in turn is manifested by an increase in the polarization of fluorescence. In the presence of unlabeled antigen in the sample, a smaller percentage of the labeled antigen is bound to the antibody, and in this circumstance the polarization observed will be lower. Hence, the standard immunoassay curve, which can be constructed from this type of data, would show the polarization of fluorescence for certain standard chosen experimental conditions plotted as a function of the amount of unlabeled antigen. This subject is treated more extensively by Dandliker et al. (7).

Organic syntheses are generally used to prepare the required fluorescent derivative of the hapten. The organic

syntheses adopted clearly depend on the structure of the contaminant itself and will vary widely.

Preparation of an antibody against a contaminant begins by coupling it to a highly immunogenic molecule such as ovalbumin, and introducing the complex into an animal, for example, rabbits, by means of intradermal injections. The initial immunization yields "primary response" antibodies, which are usually of fairly low specificity. Booster immunizations can be given at eight-week intervals, and secondary response antibody collected 10 days after the booster. This is generally more specific and of higher titer. Additional information regarding antibody generation is given by Vaitukaitis et al. (8).

Experimental

Preparation of Tagged Hapten. 2-ABZI and fluorescein isothiocyanate (FNCS) were reacted to produce a conjugate with fluorescein coupled to the 2-position of 2-ABZI by the following reaction.

The 2-FNCS-ABZI mixture was subjected to separation by a two-step, thin-layer chromatography procedure—firstly, on silica gel with 15% methanol in ethyl acetate until the faster moving unreacted dye was separated from the labeled product. The latter was removed from the silica gel with methanol and separated on cellulose TLC using borate buffer (pH 8.8). The fluorescent zone adjacent to the leading point contained the desired product which was removed with methanol.

Preparation of Antibodies to 2-ABZI. The preparation of immunogen was carried out by first reacting tetrahydrofuran solutions of 2-ABZI and thiophosgene to produce the isothiocyanate of 2-ABZI which precipitated:
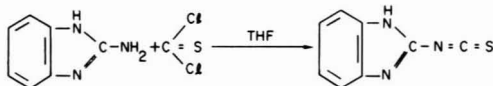
The precipitate was filtered, washed, and air dried. An 18-mg aliquot was dissolved in 1 ml of dimethylformamide and slowly added to an 8-ml, 0.15 M saline solution of 500 mg of ovalbumin. The solution was stirred overnight, dialyzed, and freeze dried to give a yellow-tan product. Spectral analysis (UV) indicated the product was a conjugate of 2-ABZI and ovalbumin in the mole ratio of ~2:1. This indicated that the reaction of 2-FNCS-ABZI with amino groups of the ovalbumin led to a successful conjugation:
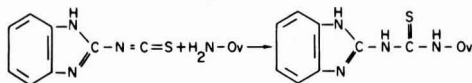
This will be designated 2-Ov-ABZI.

The ovalbumin conjugate was mixed 1:1 with Freund's complete adjuvant, and 2-mg portions were injected into two sites of each of three rabbits (female New Zealand Whites). After eight weeks, the rabbits were boosted and then bled 10 days later (15 ml per rabbit); the blood was allowed to clot, and the serum separated by centrifugation. The globulins were separated from the serum by precipitation with $(NH_4)_2SO_4$ (at 0.38 saturated ammonium sulfate), followed by centrifugation. The globulin fraction was solubilized to its original serum concentration in 0.15 M saline solution for testing by FPI.

Results

Analytical Sensitivity. With the successful production of antibody to 2-ABZI and also a fluorescent conjugate, a series of preliminary experiments was conducted to estimate the analytical sensitivity. In these experiments, varying concentrations of 2-ABZI were incubated with the globulin aliquot (which contains the antibody), labeled 2-ABZI was added, and the polarization was recorded as a function of time. The results of these experiments are shown in Figures 1 and 2. The initial rate of polarization was diminished in proportion to the logarithm of the 2-ABZI concentration, which is demonstrated by the data given in Table I and shown in graphical form in Figure 3. 2-ABZI acts as an inhibitor of the polarization rate; hence, it may be called an "inhibitor", and Figure 3 is referred to as an "inhibition curve". Least-squares fitting of these data points gives the regression line:

$$Y = 98.79 - 18.68\ X$$

The observed data points show a standard deviation of 16%, relative, about the regression line. The value of $(dp/dt)_o$ in the absence of 2-ABZI (67 × 10^{-4} in Table I) is intercepted by the regression line at $X = 1.7$; i.e., when the concentration of 2-ABZI is 50 pg/ml. This level cannot be differentiated from zero 2-ABZI concentration, i.e., this concentration corresponds to the "noise" of the system. However, changes in the initial rate of polarization of 3 × 10^{-4} units are readily observable. Thus, a rate of change of 64 × 10^{-4} units can be differentiated from the noise level. From Figure 3, this gives a log concen-
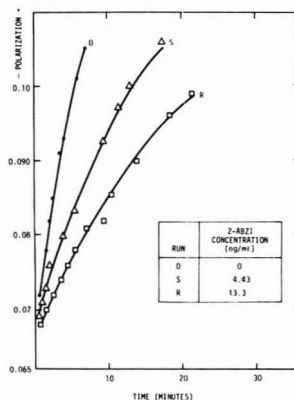
Figure 1. Rate of change of fluorescence polarization due to reaction of fluorescein-tagged 2-ABZI with its antibody as function of 2-ABZI concentration
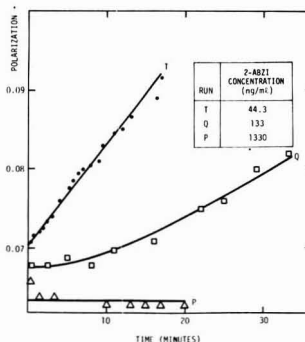
Figure 2. Rate of change of polarization as function of 2-ABZI concentration

Table I. Diminution of Initial Fluorescence Polarization Rate by Preincubation with Hapten

Log, pg of 2-ABZI/ml	Initial polarization rate,[a] $(dp/dt)_o$, units of polarization/min
...	67.0[b]
3.64	32.4
4.12	19.0
4.64	12.6
5.12	3.9

[a] Initial rate $\times$ 10^4. [b] Basic reaction of 1 μg 2-FNCS-ABZI with 200 μg of globulins in 3 ml of solution.
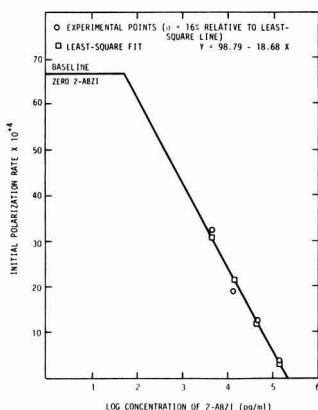
Figure 3. Standard inhibition curve
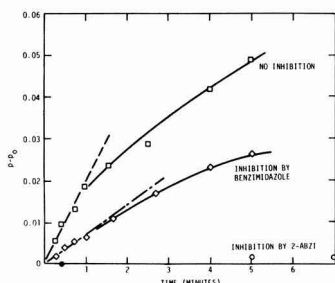
Figure 4. Comparative inhibition: comparison between 2-aminobenzimidazole and benzimidazole

tration of 2-ABZI (pg/ml) of approximately 2, which corresponds to a minimum detection sensitivity for 2-ABZI of 100 pg/ml.

Specificity. In devising an immunoassay, the degree of specificity attained is a prime factor in determining the ultimate usefulness of the test. No one parameter has been universally adopted as a measure of immunological specificity, but one of the best would seem to be the binding affinity between antibody and the antigen or hapten as compared to other, structurally similar compounds. The binding affinity is a reasonable measure of specificity, since cross-reacting antigens or haptens usually show lower affinities than that of the structure contained in the immunizing antigen. The physical factors contributing to the binding affinity finally reduce to the number and strengths of all the atomic interactions between the antigenic determinant group and the antibody combining site. The nature of these interactions includes hydrogen bonding, electrostatic attraction, hydrophobic bonding, and a variety of weaker dispersion forces. The better the match between groups of antigen and antibody, the greater will be the free energy of interaction when the two molecules combine, and the greater the "specificity".

To provide an initial estimate of the specificity of this assay, inhibition experiments involving 2-ABZI and benzimidazole were conducted. The structure of these two compounds and their respective molecular weights are as follows.
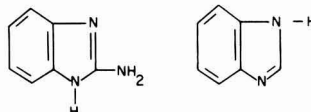
Since the complete immunogen developed in this study utilized coupling ovalbumin through the primary amino group of 2-ABZI, benzimidazole copies the structure of "exposed" or unbound portions of the hapten; thus, benzimidazole was expected to have greater affinity for the antibody than many of the available benzimidazole derivatives.

In these experiments, antibody (200 μl) was added to 3 ml of buffer, and then 3 μl of benzimidazole or 2-ABZI was added to achieve a 10^{-5} M solution of the respective benzimidazole compound. The fluorescence polarization was read at timed intervals after 50 μl of the 2-ABZI fluorescent conjugate was introduced.

The resulting data are shown in Table II, and in graphical form in Figure 4. The results for the case in which no inhibitor has been added are also given. The initial polarization rates for the cases of no inhibition, inhibition by benzimidazole, and inhibition by 2-ABZI were 158, 67, and zero (in 10^4 polariza-

Table II. Relative Inhibition Produced by Benzimidazole and 2-ABZI

2-FNCS-ABZI, no inhibitor			2-FNCS-ABZI vs. 2-ABZI inhibitor			2-FNCS-ABZI vs. benzimidazole inhibitor		
Time, min	p^a	$p - p_o$	Time, min	p^a	$p - p_o$	Time, min	p^a	$p - p_o$
(0)	(0.076)	0	(0)	(0.076)	0	(0)	(0.084)	0
0.28	0.0815	0.0055	0.30	0.076	0	0.30	0.086	0.002
0.38	0.086	0.010	0.55	0.076	0	0.48	0.088	0.004
0.75	0.0895	0.0135	1.0	0.074	−0.002	0.70	0.0895	0.0055
1.00	0.095	0.019	2.0	0.074	−0.002	1.0	0.0905	0.0065
1.58	0.100	0.024	3.0	0.074	−0.002	1.65	0.095	0.011
2.5	0.105	0.029	5.0	0.0775	0.0015	2.70	0.101	0.017
4.0	0.118	0.042	7.0	0.0775	0.0015	4.0	0.107	0.023
5.0	0.125	0.049	10.0	0.076	0	5.0	0.110	0.026

[a] p at time zero, p_o, obtained by extrapolation of observed data.

tion units), respectively. It may be noted that 10^{-5} M benzimidazole (1.18 μg/ml) halved the uninhibited initial polarization rate, whereas this was accomplished with 3.3×10^{-8} M 2-ABZI (4.4 ng/ml) in a previous experiment (see Table I). Thus, it required 270 times more benzimidazole by weight than 2-ABZI to halve the rate.

The significant difference between both the initial rate of change of polarization for the case of inhibition by 2-ABZI and benzimidazole demonstrates the high degree of specificity of the antibody for its hapten.

"Recovery" Experiment. The objective of this recovery experiment was to demonstrate the ability of the fluorescence polarization technique to determine on an absolute basis the presence of 2-ABZI in an unknown sample.

For these measurements, new reagents were prepared. Firstly, fresh tris buffer at pH 8.0 and 0.01 M concentration was prepared and filtered through 0.22-μm millipore filter to remove any microorganisms. Next, fluorescein-tagged, 2-aminobenzimidazole (FABZI) was prepared by reacting fluorescein isothiocyanate with 2-ABZI in tetrahydrofuran, and purified by sequential TLC procedures, as previously described.

Previously unused immunoglobulin preparation, which had been frozen immediately after preparation, was then thawed. This preparation, obtained from rabbits innoculated and boosted, was at normal serum concentration in the thawed preparation.

A set of inhibition curves was then developed for varying concentrations of inhibitor. All polarization measurements were made after mixing the reactants in 3.0 ml of tris buffer. The resulting curves are shown in Figure 5. The initial rate of change of polarization for each of the four different levels of inhibitor concentration is shown in Table III. These data points are shown in graph form in Figure 6. Analyzing these four points by least squares gives the following linear relationship:

Log Inhibitor Concentration (pg/ml)
$$= -0.00247 \, dp/dt_o + 4.171$$

Two aqueous solutions were then prepared containing known but different quantities of 2-ABZI, and the known values were not revealed to the analyst until after the experiment was completed.

The change in polarization as a function of time for these two unknowns, containing the antibody, tris buffer, and 1 μl of fluorescent-labeled 2-aminobenzimidazole was then recorded. The results are shown in graphical form in Figures 7 and 8.

The estimated initial rate of change from these two curves is 730×10^{-4} and 670×10^{-4}, which from Figure 6 corresponds to 272 and 347 pg/ml, respectively. The unknown had been prepared at concentrations of 270 and 330 pg/ml.

This demonstrates the ability of the technique to determine subnanogram quantities of 2-ABZI in an unknown aqueous sample to approximately 5% of the true value for the worst case analyzed in this experiment.

Figure 5. Polarization as function of inhibitor concentration and time
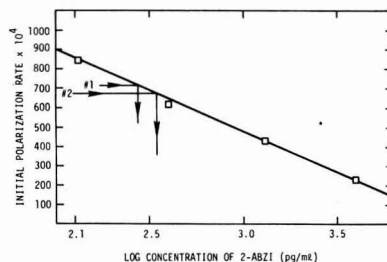
Figure 6. Standard inhibition curve
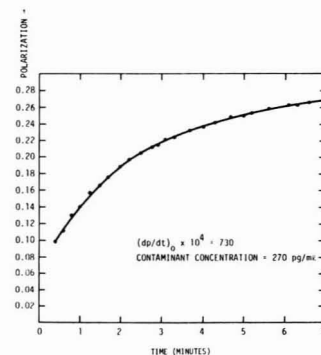
Figure 7. Polarization as function of time for unknown sample No. 1
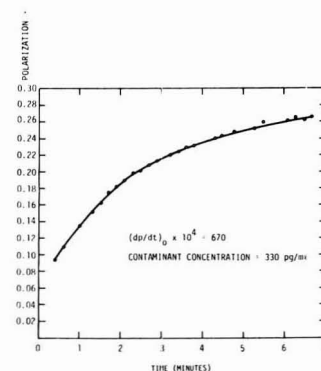
Figure 8. Polarization as function of time for unknown sample No. 2

Table III. Data for Standard Inhibition Curve

Log, pg of 2-ABZI/ml	Initial polarization rate,[a] $(dp/dt)_o$, units of polarization/min
3.60	227
3.12	433
2.60	617
2.12	842

[a] Initial rate $\times 10^4$.

Discussion of Results

It is of interest to compare the FPI system for 2-ABZI to that of a typical case, as represented by dinitrophenol (DNP) (9) and its antibody, and to the optimum system evaluated to date, i.e., fluorescein and its antibody (10, 11). The relevant parameters for these systems are given in Table IV. Comparison of the three systems shows that the FPI system for 2-ABZI performs better than average, but not as well as for the best test system evaluated to date, namely, fluorescein.

Despite the fact that fluorescein is a considerably larger and more complex molecule than 2-ABZI, there is reason to believe that the FPI system for the latter could be brought to perform nearly as well as the fluorescein system. In particular, it seems likely that affixing carrier protein to one of the positions of the six-membered ring of 2-ABZI would provide for greater participation of the unique triple amine constellation in antibody formation relative to the present case.

The present 2-ABZI-Ov conjugate presents the hapten with the six-membered ring foremost in a manner that apparently minimizes the uniqueness of the molecule as it appears to the antibody-forming system. Both the small production of antibody, which suggests that less than the usual number of lymphocytes recognized the antigen as a foreign entity, and the comparatively small rate constant, k, which suggests a relatively large steric factor in the antibody-hapten reaction, are consistent with this view.

The FPI method can be applied to the measurement of 2-ABZI with great sensitivity and specificity and indicates that this technique has a significant future potential for the analysis of environmental contaminants at the residue level. Presently, it is necessary that the contaminant be in a nearly neutral aqueous solution, and chemical processing of the material of interest may be necessary to achieve this condition.

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NOTES

History of Heavy Metal Pollution in Southern California Coastal Zone—Reprise

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■ The anthropogenic fluxes of lead, vanadium, and zinc to sediments of an outer basin off the coast of Southern California, 100 km from shore, are substantially less than those to deposits 30 km from shore. The values fall off as the square of the distance from shore. Atmospheric transport, as opposed to fluvial or sewer outfall inputs, appears to be in accord with these measurements. Anthropogenic Cr, Cu, Ag, and Cd are undetectable in the outer basin.

To what distances off the coasts of highly industrialized areas are heavy metal pollutants evident in the sediments? The answer will clearly depend upon the source of the metals and their intensity as well as their modes of transport (atmosphere vs. water). In a previous study we had found that there were readily definable entries of man-mobilized lead, chromium, zinc, copper, silver, vanadium, cadmium, and molybdenum in sediments approximately 30 km off the Southern California coast (1, 2). These basin deposits were anoxic, and their levels were not disturbed by the burrowing
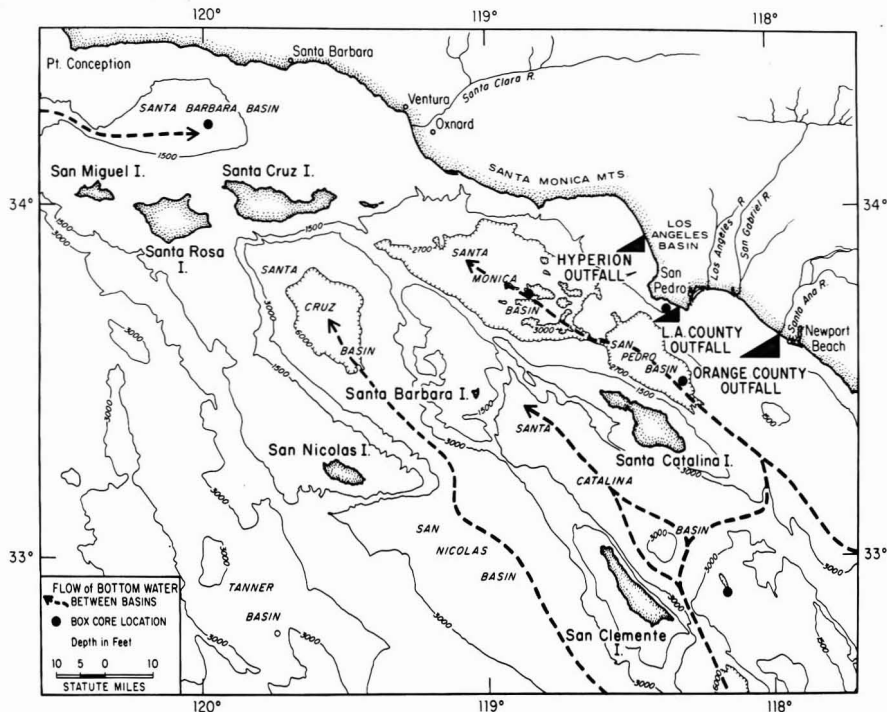
Figure 1. Location of box core in San Clemente Basin. In addition, flow of bottom water between basins is indicated

activities of organisms. Their rates of accumulation varied between 0.27 and 0.9 cm/year based upon Pb-210 geochronologies and varving. Anthropogenic contributions of Cr, V, and Mo in these sediments probably originated from the sewer outfall. We were unable to resolve the sources of Pb, Zn, Ag, Cd, and Cu.

More recently, we have introduced a time frame into a sediment from a bank slope between San Clemente and Santa Catalina basins, 100 km to the southwest (32°51'N; 118°10'W, depth of 665 m) of the previously studied basins (Figure 1) and directed away from the centers of industrial activity (3). The first meter of the accumulation is aerobic and appears to have been mixed by bioturbation. Its sedimentation rate is 5 cm/1000 years, about two orders of magnitude less than those of the inner basins. Is heavy metal pollution detectable in these deposits?

Experimental

The samples were analyzed by atomic absorption spectrophotometry on a Perkin-Elmer 406 unit using a deuterium background corrector where necessary. The results for Co, Ag, Cd, Pb, Cr, Cu, Mn, Ni, Zn, V, Fe, and Al are given in Table I. The absolute concentrations of aluminum and metal/aluminum ratios are given. Aluminum is assumed to have had a uniform flux to the deposits over the past 10 000 or so years. Thus, changes in water, salt, $CaCO_3$, or organic matter contents can be compensated through normalization of the metal concentrations to that of aluminum.

Discussion

Of the 11 elements analyzed, three (lead, zinc, and vanadium) are significantly enriched with respect to aluminum in the uppermost 2 cm. Three other elements (cadmium, man-

ganese, and cobalt) are higher in the first two levels, 0–0.5 and/or 0.5–1.0 cm, than those at greater depth.

Bioturbation resulting in downward mixing of sediments has been proposed to account for the Pu-239 + 240 and Pb-210 distributions (3). For instance, Pu-239 + 240 is found to a depth of about 10 cm, whereas with a sedimentation rate of 5 cm/1000 years, it should be found within the top 0.2 cm or last 40 years.

Anthropogenic fluxes for metals in the San Clemente deposits can be calculated by assuming that all of the higher metal values, normalized to aluminum, in the top 2 cm result from anthropogenic inputs of the metal, and by assuming that without bioturbation the higher values would have been restricted to the top 0.2 cm. This 0.2-cm level represents a time of about 1940 which is when the anthropogenic fluxes first became evident in the Inner Basin sediments. Anthropogenic fluxes for the metals in 1973 may then be calculated by determining the anthropogenic metal contents in the top 2 cm and compressing this amount into the top 0.2 cm. A linear increase is assumed from a zero value at 0.2 cm through the calculated anthropogenic amount at 0.1 cm to obtain the surface value. For example, the value of the Pb/Al ratio at 0.2 cm (0) is extrapolated through the total anthropogenic Pb/Al ratio (1.89) at 0.1 cm to obtain the surface value of 3.78. [The value 1.89 is the sum of the differences between the upper four Pb/Al ratios and the average Pb/Al ratio for the 2–22-cm interval (1.07).] Then by utilizing this value together with the sedimentation rate of 5 cm/1000 years, the average Al content (5.46%), the solids density (assumed to be 2.6 g/cm³), and the average solid content of 28%, the anthropogenic Pb flux in 1973 of 0.04 $\mu g/cm^2$/year is calculated.

Table II compares the anthropogenic fluxes for Pb, Co, Cd, Mn, Zn, and V so derived to the San Clemente Basin with the

Table I. Concentrations of Al and Metal/Aluminum Ratios in Units of ppm Metal/% Al in San Clemente–Santa Catalina Box Core

Depth, cm	Co/Al	Ag/Al	Cd/Al	Pb/Al	Cr/Al	Cu/Al	Mn/Al	Ni/Al	Zn/Al	V/Al	Fe/Al[a]	% Al
0–0.5	3.11	0.11	0.19	1.83	19.0	11.7	73.9	15.2	34.9	21.0	0.68	5.47
0.5–1.0	3.46	0.15	0.12	1.62	17.7	10.6	71.0	16.4	34.6	17.1	0.64	5.49
1.0–1.5	3.31	0.18	0.09	1.38	17.3	11.4	66.7	15.4	34.3	14.8	0.64	5.44
1.5–2.0	2.39	0.16	0.11	1.34	16.9	11.8	66.5	16.5	33.5	15.4	0.57	5.44
2.0–2.5	2.79	0.15	0.11	1.05	16.4	11.3	67.0	14.5	31.0	9.8	0.69	5.74
2.5–3.0	2.32	0.14	0.11	1.09	17.6	10.5	64.5	14.8	31.2	11.2	0.65	5.61
3.0–3.5	2.67	0.17	0.12	1.17	16.7	10.9	65.8	14.4	31.9	14.1	0.62	5.62
3.5–4.0	2.54	0.15	0.09	1.11	19.2	11.4	66.8	15.2	31.9	11.1	0.66	5.52
4.0–4.5	2.48	0.13	0.08	0.97	16.0	10.2	67.8	14.2	31.4	12.4	0.71	6.06
4.5–5.0	2.62	0.19	0.10	1.14	16.1	11.4	67.7	16.4	30.3	15.0	0.64	5.35
5–6	2.82	0.18	0.12	1.19	17.6	11.6	65.3	15.7	31.2	15.3	0.66	5.67
8–9	2.07	0.13	0.11	1.00	17.6	10.7	66.8	15.5	31.2	14.1	0.70	5.81
30–32	2.18	0.19	0.12	0.96	16.5	10.2	70.0	15.6	31.6	12.9	0.60	5.50
70–72	1.93	0.15	0.09	1.03	18.2	9.6	64.8	13.0	32.7	10.0	0.61	5.71
Av 0–2	3.07± 0.48	0.15± 0.03	0.13± 0.04	1.54± 0.23	17.7± 0.9	11.4± 0.5	69.5± 3.7	15.9± 0.7	34.3± 0.6	17.1± 2.8	0.63± 0.05	5.46
Av 2–72	2.44± 0.30	0.16± 0.01	0.11± 0.01	1.07± 0.08	17.2± 1.0	10.8± 0.7	66.6± 1.7	14.9± 1.0	31.4± 0.6	12.6± 2.0	0.65± 0.04	5.66

[a] Units of % Fe/% Al.

Table II. Anthropogenic Fluxes to San Clemente Basin Compared to Anthropogenic Fluxes for Inner Basins

Element	$\mu g/cm^2/yr$ San Clemente	Av Inner Basins[a]
Pb	0.04	1.6
Co	0.05	...
Cd	0.001	0.07
Mn	0.2	...
Zn	0.2	2.1
V	0.3	4.0

[a] From refs. 1 and 2.

average to the Inner Basin sediments. The anthropogenic fluxes of lead, vanadium, and zinc to the San Clemente sediments are considerably less than those for the Inner Basins.

Two concepts emerge from these results. First of all, the anthropogenic fluxes of zinc, vanadium, and lead from the highly industrial Southern California coastal zone to the ocean appear to roughly fall off as the square of the distance. The fluxes to the San Clemente Basin, 100 km from the coast, compared to those of the inner basins, about 30 km from the coast, are less by about a factor of 10 or so (Pb, 40; Zn, 10; and V, 13). This suggests that the transport of these metals is primarily atmospheric. Surface winds prevailing off Southern California can transport atmospheric particulates in all directions. Surface ocean currents are weak and variable but sometimes are in a counterclockwise gyre around the San Clemente Basin (4). By such a path, materials introduced to near shore surface waters off the Los Angeles area could be brought to the San Clemente region. More probably the materials would stay with the waters adjacent to the coast and move northward. The deep currents (5) between basins are shown in Figure 1 and, in general, move in a northwesterly direction. It is difficult to conceive of an oceanic transport to the outer basins of these highly reactive metals from the inshore zone, via the gyre, when their residence times may be of the order of months or less in coastal waters (1, 2).

Secondly, the record of anthropogenic fluxes of heavy metals to aerobic sediments off the coast of Southern California is distorted by the burrowing actions of organisms. Pollution histories of the coastal marine environment can most readily be found in the relatively undisturbed anoxic sediments.

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Sample Size Effect on Geometric Average Concentrations for Log-Normally Distributed Contaminants

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■ Sampling programs which utilize different sample volumes to redundantly monitor the same space may yield different geometric average concentrations, particularly if the material sought is scarce. Discrepancies approaching a factor of 2 should be expected if the standard geometric deviation is much larger than 3 and if the sample volumes differ by a factor of 5. This effect is statistical in nature and believed due to the sample volume being too small, comparable to the scale of heterogeneity for the substance sought, a concept described. An example utilizing PuO_2 particulate concentrations in air shows how to assess whether a sample is too small.

Concentrations of many contaminant and natural materials are distributed log-normally (1–3). For a set of such data, the geometric average is preferable as a characterizing central value (2). However, the arithmetic average is sometimes required (4), as, for example, when total environmental quantities are to be calculated. The two are related by Equation 1 (2, 5):

$$\overline{X}_a = \overline{X}_g \exp\left(0.5 \ln^2 s_g\right) \tag{1}$$

$$\overline{X}_a = \text{arithmetic average} = \frac{1}{n} \sum_{i=1}^{n} X_i$$

$$\overline{X}_g = \text{geometric average} = \exp\left[\frac{1}{n} \sum_{i=1}^{n} \ln X_i\right]$$

s_g = standard geometric deviation

$$= \exp\left[\frac{1}{n-1} \sum_{i=1}^{n} (\ln X_i - \ln \overline{X}_g)^2\right]^{1/2}$$

$\overline{X}_a$ always is greater than $\overline{X}_g$

Use of Equation 1 is preferred here for estimating $\overline{X}_a$ since it is less sensitive to uncertainties in a few high values. For example, 90% of the sum of a set of (log-normally distributed) data may be due to only 10% of the entries, whereas the sum of the logarithms is not so affected.

Sampling of continuous media, like air or water, is an additive process in the sense that each sample can be considered as a composite of smaller elements that are combined prior to analysis. Combining, in an additive way, volume elements which have log-normally distributed concentrations can have a curious effect. The geometric average concentration is larger if the sample sizes are larger. Accommodating this effect requires knowledge of the standard geometric deviation. The effect can be important in comparing data since discrepancies of 100% or more in apparent concentration are possible if the sampling methods involve greatly different volumes and if the standard geometric deviations are much larger than commonly observed (near 2.0). This effect will exist in the case (among others) where independent samplers operate side by side at the same time, differing only in the volume-rate at which they collect or filter a medium. The discrepancy has an appearance of a bias between the independent efforts, whereas in fact it is statistical in nature. In cases where agents in conflict monitor the same space, this effect may deserve special consideration.

This paper shows how a concentration discrepancy can arise between sampling efforts due only to differences in sample
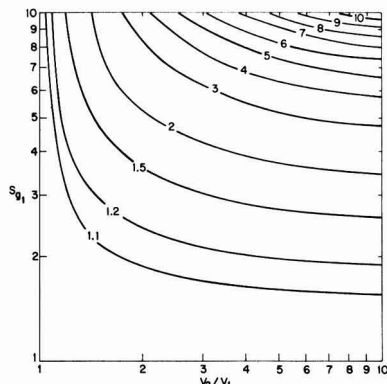
Figure 1. Isopleths of concentration ratios ($\overline{X}_{g2}/\overline{X}_{g1}$) due to sampling different volumes

volume. A graph (Figure 1) shows the size of discrepancy to expect based on the standard geometric deviation and the ratios of sample volumes. The effect is reduced if larger volumes are taken in sampling. How large is large enough depends on characteristics of dispersion for the substance at interest.

Derivation

Consider an environmentally large volume V_T which contains a quantity Q_T of contaminant distributed nonhomogeneously, specifically so that concentrations of small volume elements conform to a log-normal distribution. The arithmetic average concentration, $\overline{X}_a = Q_T/V_T$ can be estimated by Equation 1 if several samples are obtained and analyzed. [Development of this point ignores sampling and analytical problems while presuming that all differences in concentrations reported by analysis are real and due only to (empirically log-normal) random variations among the samples.] The same value of $\overline{X}_a$ should be obtained (within statistical limits) from different samplings that involved differently sized volume elements, as indicated by Equation 2:

$$\frac{Q_T}{V_T} = \overline{X}_a = \overline{X}_{g1} \exp\left(0.5 \ln^2 s_{g1}\right) = \overline{X}_{g2} \exp\left(0.5 \ln^2 s_{g2}\right) \tag{2}$$

Subscript 1 refers to sample volume elements of set 1 which are (uniform and) smaller than volume elements of set 2 (subscript 2).

From the central limit theorem, one should expect $s_{g2} < s_{g1}$. Precisely, if the distribution is log-normal, Equation 3 applies

$$\ln^2 s_{g2} = \frac{\ln^2 s_{g1}}{V_2/V_1} \tag{3}$$

[Equation 3 can be derived by considering $\ln s_g$ to be a standard error of the mean (var $\overline{X}$)$^{1/2}$ as in

$$\ln^2 s_g = \text{var}\,(\overline{\ln X}) = \frac{\sigma^2}{n}$$

where σ^2 is the variance for fundamental units of medium (volume = v) and n is the number of those units involved in

estimating $(\overline{\ln X})$; that is, $n = V/v$. Equation 3 involves the case where volumes in sets 1 and 2 are larger than the fundamental volume v. Thus,

$$\text{var } (\overline{\ln X_1}) = \frac{\sigma^2}{V_1/v} \text{ and var } (\overline{\ln X_2}) = \frac{\sigma^2}{V_2/v}$$

The small fundamental volume v and the corresponding variance σ^2 cancel when establishing the ratio in Equation 3.] In Equation 3 V_1 and V_2 represent the volumes of individual samples in sets 1 and 2. A consequence of Equations 2 and 3 is that $\overline{X}_{g1} < \overline{X}_{g2}$. That $\overline{X}_{g1} < \overline{X}_{g2}$ also is apparent considering (for log-normal distributions) that $\overline{X}_g < \overline{X}_a$, together with results expected due to compositing all samples of a set prior to analysis. Compositing yields the arithmetic average concentration for the set. The single value obtained from a composited sample (ideally) should be identical to the result of applying Equation 2 to a log-normal distribution of values from a number of smaller samples. Thus, by extension, the distribution of results from a set of larger volume samples tends to show greater geometric average concentrations than a set of smaller volume samples from the same media.

The relationship can be quantified by substituting Equation 3 into Equation 2, which yields Equation 4:

$$\frac{\overline{X}_{g2}}{\overline{X}_{g1}} = \frac{\exp 0.5 \, (\ln S_{g1})^2}{\exp 0.5 \, \dfrac{(\ln S_{g1})^2}{V_2/V_1}} \tag{4}$$

Equation 4 relates the ratio of geometric average concentrations (determined empirically) to the ratio of volumes used in the sampling.

A map of Equation 4 (Figure 1) shows ratios of geometric average concentrations plotted as a function of volume ratio and standard geometric deviation. The concentration discrepancy is not very severe, i.e., less than 10% mismatch exists if the standard geometric deviation is smaller than about 1.5. [For standard geometric deviations smaller than about 1.3, there is little advantage in treating data as log-normal; they may be treated as Gaussian (6).] However, for standard geometric deviations greater than 2.0, discrepancies greater than 20% mismatch can be expected. A few ultratrace materials show standard geometric deviations greater than 6 (the author has observed standard geometric deviations as large as 14 for $^{238}\text{PuO}_2$ in certain stream sediments, for example), and for these, discrepancies in average concentration approaching an order of magnitude could be expected between different samplings solely due to choosing to take dissimilar volumes in the samples.

In practice, large standard geometric deviations can be reduced somewhat by increasing sample size according to Equation 3. For example, if samples of volume V_1 gave $S_{g1} = 4$, a more tractable value of $S_{g2} = 2$ might be obtained by increasing sample volume by a factor of 4 as indicated by Equation 5.

$$V_2/V_1 = \left[\frac{\ln S_{g1}}{\ln S_{g2}}\right]^2 = \left[\frac{1.39}{0.69}\right]^2 = 4 \tag{5}$$

There is a limit to this application obviously, because practical volumes are those which equipment and personnel can handle with suitable economy. The flattening of all curves in the right side of Figure 1 shows the diminishing effect of increasing sample volumes.

Scale of Heterogeneity

The steep slope of curves in Figure 1 close to the ordinate corresponds to severe heterogeneity on a small dimensional scale. "How small is small" depends on the overall concentration of the contaminant. For example, if PuO_2 particulates in air have a population density of 1 particle/50 m^3, then vol-

umes on the order of several cubic meters should be considered small. In terms of sample-to-sample variability, successive samples of 100 m^3, for example, would have significant probabilities of holding 0, 1, 2, or 3 particles, indicating a broad range of concentration, i.e., large standard deviation. (In this case, the probabilities are, respectively, 0.14, 0.27, 0.27, and 0.19.) Because the Pu particles are (hypothesized here to be) scarce, the scale of heterogeneity is said to be large compared to a sample volume of 100 m^3. This phenomenon is purely one of scales which can be visualized in another way. For example, consider measuring the composition of the atmosphere by taking samples which contain only 10 molecules each. On such a scale the atmosphere would appear grossly heterogeneous. In this kind of situation, concepts of concentration, which are philosophically concerned with homogeneous distributions, are maladapted to describing the reality of particulate distributions.

When one wishes to describe the abundance of a contaminant, usually in terms of concentration, a certain emphasis is given to reproducibility of results from sample to sample. The problem of sampling scarce particulates is partly one of obtaining samples large enough so that replicate samples have a statistical chance of holding the same numbers of particles, within some preselected precision. For contaminants like PuO_2 particles in air, this strategy leads to uncommonly large volumes per sample. The example below illustrates the point.

In the vicinity of a nuclear facility, the Pu in air is of two origins. Residuum from weapons fallout is a low-level background due to particulates with diameters on the order of tens of nanometers. The effect of the nuclear facility is to add particulates having a size distribution characteristic of the plant but with average particle size distinctly larger than fallout, perhaps on the order of hundreds of nanometers.

A nominal background may be taken as 30 attocuries per cubic meter of air (30 aCi/m^3) which is due to a PuO_2 particle abundance on the order of 30 fallout particles per cubic meter. [A PuO_2 fallout particle 10 nm across has a nominal activity of 1 aCi (10^{-18} Ci).] PuO_2 particles from our hypothetical operation have about 1000 times the activity per particle compared to fallout because their tenfold greater diameters involve a thousandfold greater mass per particle. If effluent were to double the gross PuO_2 content of background air, the effluent particle abundance would be only $1/1000$ the particle abundance of fallout, or 30 particles/1000 m^3 (1 particle/33 m^3). Obtaining representative numbers of these effluent particles is a sampling problem.

If replicate samples are expected to agree within ±10% in terms of the numbers of PuO_2 effluent particles they contain, then the required number of effluent particles per sample and its volume can be calculated, based on statistical considerations.

An appropriate model is based on Poisson statistics, since the collection of a PuO_2 effluent particle is a relatively rare event (7). Figure 2 shows how the number of particles in a (Poisson) sample may differ from the overall average. (Tabular counterparts of Figure 2 appear in several statistics texts up to 50 events, for example, see ref. 7, page 160. Extension beyond 50 events was calculated according to a Gaussian approximation to the Poisson as described in ref. 8, page 181.) The upper and lower limits are for a 95% confidence level. That is, 5% of the samples would lie beyond one limit or the other. Note that the number of particles collected in a sample will be reliably (95% of the time) within 10% of the true value only when the sample contains more than about 400 particles. Thus, one can calculate that at a concentration of one effluent particle per 33 m^3, samples should involve about 13 000 m^3 if it is intended that they be representative within 10% of the true (twice background) concentration of our example. (This
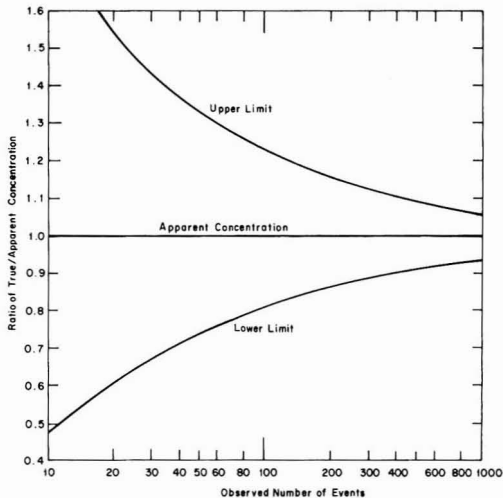
Figure 2. Uncertainty in apparent concentrations

Apparent concentration due to observed number of items (photons, decays, etc.) could have been due to statistical fluctuations about true concentration. Relative range of true concentrations which could yield an apparent concentration is indicated by limit lines. Confidence level is 95%

example does not consider other factors which cause the final analytical result to be at variance with the true concentration. For example, volumes of air pumped during sampling are seldom known within ±10%, the representivity of the sampling location may be questionable, and the analysis contains a host of circumstances which affect accuracy.)

Conclusions

Poor reproducibility of results between replicate samplings for dilute environmental contaminants may partly be a consequence of the sample volume being relatively small. An additional effect, manifested as differences in geometric average concentrations between sets of samples from the same environment, is related to the different volumes (that may have been) taken in the sampling, as, for example, when government agencies and industry have independent programs for monitoring effluents in the same space. This effect can be quantified by considering the relationship between arithmetic and geometric averages for a data set. The effect can be substantial when standard geometric deviations are greater than 2 and the ratio of sample volumes is greater than 5 (or less than 0.2).

For sampling to collect enough particles to be representative of the average abundance (within 10% of the true value 95% of the time), about 400 particles of the target substance must be included in the sample. For certain scarce particulates, such a particle number requirement implies uncommonly large sample volumes. Note that the collective mass (or radioactivity) of the target substance collected in sampling may be less important to sample-sample reproducibility than the number of particles involved with that mass.

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INDUSTRY TRENDS

Reynolds Aluminum Recycling Co. (Richmond, VA) has established a toll-free phone number for persons wanting to know the nearest Reynolds recycling collection point. It is (800) 243–6000, or, in Connecticut (800) 882–6500.

Southern California Edison Co. is "pleased" that ERDA chose Edison's Barstow, CA, site to build the world's first electric generating station powered directly by solar energy.

American Air Filter Co., Inc., has developed a new recirculating air cleaning system that permits indoor firing ranges to comply with NIOSH standards. It meets standards of 0.1 mg of lead, and removes 99+% of particulate matter from range environmental air.

Super Products (Milwaukee, WI) has appointed Wajax Ltd. as exclusive distributor for Canada. Super products is marketing a vacuum loader that removes many air pollutants to well within EPA standards.

Owens-Corning Fiberglas (Toledo, OH) foresees a market for 132 million yd^2 of fiber glass over the next decade, brought about by needs for filter bags for pollution control, and has prepared a report on the subject.

Public Service Co. of New Hampshire announced that construction activities on the Seabrook Nuclear Project will continue "at substantially reduced levels," but is not being "scrubbed."

UOP Inc. announced that two electrostatic precipitators that it recently installed at Central Electric Power Cooperative (Chamois, MO) are on stream, and are being performance-tested.

Culligan International Co. is now marketing "DB Deionizers" to provide high-quality water for industrial and institutional uses, and to treat certain types of wastewater.

RECON Systems, Inc. (Princeton, NJ) has a 1-y renewable ERDA contract to stack-test liquid and vapor waste incineration at the Synthane coal gasification pilot plant (Bruceton, PA), being operated by Lummus Corp.

Dames & Moore (Los Angeles, CA) is doing feasibility studies for an underground coal mine near Rock Springs, WY, for Sunoco Energy Development Co., and Rocky Mountain Energy Co. Focus is on environmental and groundwater engineering studies.

Action Instruments Co., Inc. (San Diego, CA), which, among its products, offers monitoring and control instruments, has formed Action Electronic Instruments Ltd., at Mississauga, ON, Canada.

Enpo-Cornell Pump Co., (Piqua, OH), a division of Roper Industries, Inc., has purchased the pump business of Construction Machinery Co. (Waterloo, IA). Among pumps made by the acquired firm are self-priming pumps used for handling wastewater.

Engineering-Science (Arcadia, CA) said that a wastewater treatment plant it has designed for California-Hawaiian Sugar at Crockett, CA, is being constructed on schedule. A May startup is expected.

Grumman Corp. (Bethpage, NY) plans to build a $45 million pilot plant to turn 1500 tpd of garbage from Jefferson County, KY, to steam.

Combustion Engineering, Inc. will provide two air quality control systems, valued at over $16 million, to the Cooperative Power Association (Minneapolis, MN), and United Power Association (Elk River, MN).

Radian Corp. (Austin, TX), which offers professional services in energy, environment, and chemical processing, is opening a Washington Regional Office at McLean, VA.

Air Products and Chemicals, Inc., announced that construction has been completed on OASES pure-oxygen wastewater treatment systems at Dubuque, IA, and Hollywood, FL.

Titan Group, Inc. (Paramus, NJ) has a $14.3 million contract to construct sewage treatment facilities for the Township of Hamilton, NJ.

Lab Safety Supply Co., has been organized at Janesville, WI, to offer a full line of laboratory safety products, including products for personnel safety, and treatment/disposal of chemical spills.

United McGill Corp. (Columbus, OH) has received a turn-key contract worth $5 million for an air pollution control system for C.F. & I. Steel Corp., of Pueblo, CO, including particulate removal from basic oxygen furnaces.

United Nuclear Corp. (Falls Church, VA) has been awarded a $39 million ERDA contract for production of nuclear components.

Environmental Elements Corp. (Baltimore, MD) will supply $7 million worth of gas turbine air filtration and silencing systems to Cooper-Bessemer U.K., which will install them in gas compressor modules on gas pipelines in the U.S.S.R.

The Du Pont Co. has denounced allegations by the Natural Resources Defense Council that the Philadelphia "Legionnaires' Disease" may have been caused by fluorocarbon refrigerant leaks as "unfounded and irresponsible."

Georgia-Pacific is drafting an approximately $5 million environmental project to double its present 35 million gal wastewater treatment facilities at its Toledo, OH, pulp and paper mill.

Union Carbide Corp. proposed to offer $12 million in 30-year pollution control revenue bonds to be issued by the State of Ohio through the Ohio Water Development Authority, to finance pollution control at Union Carbide's ferroalloy plants.

Zimpro Inc. will furnish 200-gpm units to sterilize sewage solids and convert them to dewaterable material at the 42-mgd plant at Cedar Rapids, IA. Contract value: $11.5 million.

Kaiser Steel Corp. (Oakland, CA) said that it is prepared to spend an additional $7.8 million over the next 2 years to achieve coke oven emission control equivalent to the strictest in the U.S. today.

Freeport Minerals Co. (New York, NY) is proceeding with a $32 million project to recover uranium oxide as a by-product from phosphate rock processed into fertilizer material by Freeport at Uncle Sam, LA.

Colt Industries (Beloit, WI) will provide 15 ENVIROVAC vacuum sewage collection systems to be used on U.S. Coast Guard cutters, for $440 000. They are listed as USCG zero-discharge sanitation devices.

Research-Cottrell, Inc. announced that its financial dispute with Calgary Power has been amicably resolved, and was given effect in R-C's earnings statement for fiscal 1976, which were a record $6.3 million.

Nippon Kokan (Japan) has opened a unique $3.3 billion, 5.5 million m^2 integrated steel plant on a reclaimed island in Tokyo Bay. Over $300 million was spent for antipollution and environmental protection.

Combustion Equipment Associates (CEA) opened a temporary transfer station for solid waste at Stratford, CT. CEA and Occidental Petroleum Corp. are building transfer stations where solid waste can be converted to useful products and energy.

Peabody Air Resources Equipment Co. (Princeton, NJ) is providing the world's largest single pocket filter installation to control metallic oxide emissions from a machine tool foundry (400 000 cfm) at Koluszki, Poland.

Dorr-Oliver Inc. will develop and supply a pressurized fluid-bed reactor for a pilot power plant using high-sulfur coal. The plant will produce 13 MW, and operate at 7 atm, and 1400 – 1700 °F.

The **Institute of Scrap Iron and Steel, Inc.** (Washington, DC) warned that total iron and steel scrap demand for 1976 could come to less than the very depressed levels of 1975.

Guardian Chemical Corp. (Hauppauge, NY) stands ready to supply its Polycomplex A-11 to clean up any oil spill damage from the tanker *Argo Merchant,* that may hurt beaches or bird and animal life.

Camp Dresser & McKee has been selected to conduct a major operations and maintenance project for the Detroit (MI) Water and Sewerage Dept., to ensure that its systems meet all standards.

General Electric, along with three consultants, is designing an electric car with the possibility of twice the performance of commercially available ones—"from the ground up."

Hydranautics (Santa Barbara, CA) shipped a 175 000-gpd reverse osmosis water desalination system to a major oil company for use at a housing complex in eastern Saudi Arabia.

Michael Baker, Jr., Inc. (Beaver, PA) and Radian Corp. are part of a team commissioned by the Electric Power Research Institute (Palo Alto, CA) to work on ways to control contaminants from the coal-burning process.

Flack & Kurtz (New York, NY) won honorable mention in the institutional category of Owens-Corning Fiberglas Corp.'s fifth annual Energy Conservation Awards Program for design of a solar energy heating system at the Madeira School, Greenway, VA.

Waste Resources Corp. (Philadelphia, PA) expects to merge into Warner Co., a firm engaged in industrial minerals, real estate, and building and construction materials and products.

NEW PRODUCTS

Non-clogging air diffuser
The cone-shaped diffuser does not allow sewage to plug the diffusion system because the sewage cannot enter the lines. This non-clogging feature saves maintenance labor, parts costs and reduces plant downtime, according to the manufacturer. Jet Aeration **101**

Incremental cassette recorder
This bit-by-bit incremental recorder features low power usage and rapid on/off capability. Up to 2.2 million bits may be recorded on a single 300 ft cassette, using the dual track complementary method. The unit may be purchased as a transport only or as a complete system. Datel Systems **102**

Oil/water separator system
Oily wastes are collected in a lagoon and sufficient time is allowed to elapse for the oil to separate and float to the top. A floating weir with a tube-type oil skimmer picks up the floating oil into one compartment. A second compartment connected to a syphon pump allows the passage of oil-free water to existing polishing pack for final clarification. Environetics **103**

Radioactive waste disposal
The compactor is designed to dispose of low-level radioactive waste materials. The 3000-lb compaction force crushes 55-gal drum down to 4-in. steel pancakes. Several different compactor sizes are available. S&G Enterprises **104**

Turbidimeter
This portable instrument measures a range of turbidities from 0–400 NTU (nephelometric turbidity units) without the need to dilute water samples. Accuracy is ±2% over the entire range. LaMotte Chemical **105**

Portable air sampler
This sequential air quality sampling system can be programmed to fill any size bag over any hour of a 24-h period, or over a 4-day period. The bags are sealed and returned to the laboratory for analysis. Environmental Measurements **106**

Tracer gas monitor
The unit is an electron capture gas chromatograph especially designed for field use. Gases such as sulfur hexafluoride and selected halocarbons can be detected. Systems, Science and Software **107**

Dichotomous impactor
Samples and fractionates suspended ambient particles into two sizes—greater and less than 3.5 μ. The larger particle fraction impacts into a void rather than on a surface, thus permitting longer sampling times. Both size fractions are collected on 37-mm membrane filter media. Sierra Instruments **108**

Water filter
The machine, consisting of 34 sheets, has a total filtering area of 120 ft^2. The perforated screen plate design permits flow rates in excess of four times those of cast waffle-grid filters. Using a divider plate for two-stage operation, the machine removes all bacterial, cellular debris and fibers—including asbestos fibers—down to 0.1 μ. Star Tank & Filter **109**

Composite water sampler
Designed for continuous monitoring of effluent flows, the sampling is accomplished by driving a peristaltic pump via the rotation of a paddle wheel suspended in a moving stream. The sample is pumped to a remote collection bottle. Enviren Co. **110**

Test meter for gases
This meter finds application in flue gas analysis and pollution control measurements. Meters cannot be used with oxygen, acetylene or corrosive gases. Accuracy of the unit is 0.5% throughout the range from about 5–100% capacity of 160 cfh of air. Sprague-Textron **111**

Centrifugal pump
This ejector pump is designed for use with vacuum-type oil skimmers. It operates over a pressure range of 20–30 psig, is capable of a 10-ft lift and a discharge head up to 25 ft. Flow rates from 8–50 gpm can be obtained. Skim, Inc. **112**
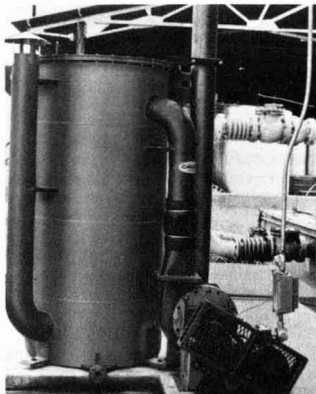
Modular adsorption system
These units are granular-activated-carbon for control of organic and sulfur odors. Modular units are available in sizes from 500–12 000 cfm. Calgon **113**

Wet scrubber
Scrubber operates without filters, screens or strainers to remove dust particles and aerosol mists of all sizes down to the sub-micron level. Ecar Products **114**

Fluid level sensor
The sensor discriminates between fluids of differing characteristics; it responds in fuel/air, water/air and fuel/water interfaces. An indicating or control signal is either created or interrupted when the sensed fluid changes. Liquidometer **115**
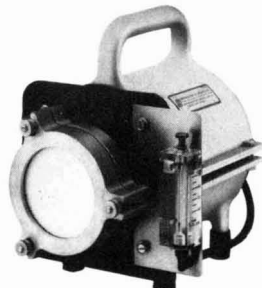
High-volume air sampler
The 13.5-lb sampler collects and measures ambient particulate matter, as small as 0.01 microns, by monitoring large volumes of air. It is designed primarily for in-plant use. General Metal Works **116**

Air velocity meter
This portable anemometer has a full-scale range of 0–30 m/s. The thermister probes are interchangeable. A 0–2 V full-scale recorder output is provided. Aikenwood
117

Event count & time totalizer
Gathers data from machines, networks or experimental setups on up to 248 channels, programmed through an on-board keyboard. The event count & time totalizer key sets input, channel functions, timing, data output times, counter intervals and outputs to display and recording, or prints out a listing by channel of total performance for the last minute, hour, 8 hours or month. Esterline Angus
118

Mobile tire shredder
Tire dealers and municipalities can have tires shredded anywhere in two sizes suitable for landfill disposal. The shredder is mounted on the bed of a 10-ton truck. Kleco Shredder Systems
119

Image-shearing eyepiece
To be used with most microscopes, this eyepiece permits the measurement of small particles rapidly and accurately, according to the manufacturer. The device can be used in dust control programs, and features direct digital readout. Hacker Instruments
120
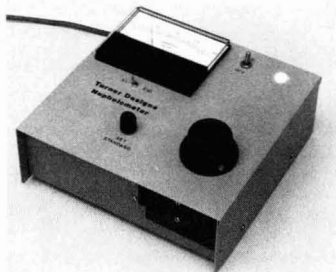
Nephelometer
Features of this unit include rapid warmup period; capped sample cells to minimize sample contamination and facilitate removal of bubbles; and terminals for connection to an external recorder. The unit is unaffected by variations in temperature or voltage, and can be converted to an instrument suitable for field use. Turner Designs
121

Ultrafiltration system
This hollow-fiber system is capable of processing from 200–30 000 gal/day of oil/water emulsions. It reduces the volume of soluble oil waste by 95%. The effluent is free of oils, bacteria and suspended solids, and the concentrated oil waste can be reused or disposed of. Romicon
122

Multiple dropsonde system
The system continuously samples wind speed, direction, temperature, humidity and pressure from an aircraft altitude of 30 000 ft down to sea level. The free-falling dropsondes are released at 5-min intervals from an aircraft flying over the weather front. Beukers Laboratories
123

Air purifier
This three-stage filtration unit removes ambient dust and lint in the first stage, odors in the second and all particles 3.9 $\times$ 10^{-5}-in. or larger in the third. The second stage uses activated charcoal, the third HEPA filters. Texas Dynamics
124

Iron/manganese remover
The patented microbiological process reduces the iron and manganese content of well waters in the ground before pumping. This process is claimed to reduce iron and manganese concentrations to below EPA standards without the construction of filtration plants and the resultant sludge formation. Layne New York Co.
125

Bar screen cleaner
The mechanical cleaning device is designed for the operating conditions of water and wastewater treatment plants. The drive unit operates in one direction only, and all moving parts remain above the water line. Infilco Degremont
126

Mass flow meter
The portable unit finds application in process control, air pollution and flow research; it calibrates particle analyzers, gas analyzers, and samplers. Sierra Instruments
127

Oil/water separator
The separator removes oil particles as small as 50 μ and produces an effluent containing less than 10 mg/L of free oil. The heart of the system is a matrix of vertical, perforated polypropylene tubes. AFL Industries
128

Shelter
The one-piece, double-door, fiberglass shelter is ruggedly constructed, leak-proof, corrosion-resistant and maintenance-free. It is suitable for chlorination equipment, field-mounted instruments or sewage disposal plant usage. Warminster Fiberglass
129

Disposable filters
The polypropylene-pleated filters contain no resin binders or other extraneous materials. These cartridge filters are capable of withstanding 75 psi differential pressure at 70 °F in normal outside-to-inside flow direction. Pall Corp.
130

Air/gas sampling bags, systems
A forwarding pump, tubing and gas sampling bag make up the complete system. The system operates on batteries for 42–46 h, automatically collecting integrated samples. Calibrated Instruments
131

Flow measuring instrument
The unit can be used to measure flow rates of gases and liquids. It is designed with three tubes of graduated size to accommodate a range of flows with the switch of a stopcock. Flow ranges for air are 3–68 200 mL/min; for water, 0.043–2070 mL/min. Manostat
132

Digital pH meter
The unit is claimed to be accurate to 0.03 pH units and to offer 0.05 pH resolution. It operates off of 1.5 V batteries, or with an adaptor, off ac. Extech International
133

Tipping plate regulator
Limits the flow of sewage from a combined sewer to an interceptor. The unit requires no external actuator and has only one moving part. It is available in opening widths of 12, 24 and 36 in. Rodney Hunt Co.
134

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.

NEW LITERATURE

Filtration. Brochure 4803 details line of UHR filtration systems for treatment of industrial wastewater. De Laval Turbine Inc. **151**

Wastewater processing. Brochure describes available techniques and equipment for upgrading wastewater processes. Techniques include use of ozone. TII Corp. **152**

Solvent analysis. CIRA Circular (Issue No. 5, November 1976) describes analysis of solvents and solvent systems with the CIRA 101 chromatographic infrared analyzer. Sadtler Research Laboratories, Inc. **153**

Ultrafiltration. Literature tells engineers how to evaluate economically benefits of hollow-fiber ultrafiltration with standard industrial cartridges. Romicon, Inc. **154**

Filters. Bulletin provides detailed description of filter plates, tubes, and media. Filtration ratings 2–140 μ. Michigan Dynamics **155**

Biochemicals. Winter 1977 catalog provides a list of biochemicals and analytical supplies to meet many needs. ICN Pharmaceuticals, Inc. **156**

Pumps. Bulletin 307 describes flow and application capabilities of a series of horizontal and vertical pumps made of stainless steel and hastelloy. Sethco Mfg. Corp. **157**

Gas sampling. Bulletin 77-22 is a fact sheet on air/gas sampling bags now available. Odor and vapor collection are also possible. Calibrated Instruments, Inc. **158**

Fuel cost reduction. Brochure describes proven fuel-saving techniques developed from over 40 years of experience with boilers, burners, and heaters. A. B. Wolle & Co. **159**

Level sensors. Bulletin describes easy-to-install level sensors for sewer, pond, well, stream, cavern, or other applications. Metritape, Inc. **160**

Sulfur recovery. Bulletin E1.1421-AB describes use of heat-radiation pyrometer for temperature measurement in sulfur-recovery units in gas processing plants. Leeds & Northrup Co. **161**

Heavy metal removal. Paper, "Heavy Metal Removal with Sphagnum Peat," describes process that meets EPA requirements. Actual operating systems for chromium treatment are also covered. Hussong-Walker-Davis Co. **162**

Gas adsorption. Bulletin W-117 describes activated carbon products developed for gas-phase adsorption applications. Internal surface area and pore structure are given. Witco Chemical Corp. **163**

Pinch valves. Technical packet describes pinch valves for piping systems. They are especially useful to systems in which abrasive slurries are being transported. Red Valve Co., Inc. **164**

Shut-off valves. Bulletin Series 1100/1100HP/1200 covers improved solenoid shut-off valves for handling fuel gases, fuel oils, steam, and the like, to pressures up to 1440 psi. R. G. Laurence Co., Inc. **165**

Sludge conditioning. Brochure describes conditioning sludge, including raw sewage, rags, paper, wood, plastics, and hard materials, so that sludge becomes free flowing, with no need for an open pit. Franklin Miller, Inc. **166**

Well castings. Brochure gives detailed information on corrosion-resistant well casings for potable water, irrigation water, and waste disposal wells. Amoco Reinforced Plastics Co. **167**

Sewer regulator. Data sheet describes completely automatic Tipping Plate Regulator that limits sewage flow from a combined sewer to an interceptor. Rodney Hunt Co. **168**

Air handling. Catalog spotlights company's line of institutional air handling systems for supply or exhaust. OSHA requirements are taken into account. United McGill Corp. **169**

Sulfur analyzer. Technical report describes a sulfur analyzer, good for any solid or liquid, that can detect 0.003–9.999 wt % with better than 0.01% accuracy. Applications to oil and coal. Horiba Instruments, Inc. **170**

Silencers. Brochure, "Silencing Systems for Gas Turbines," describes methods of suppressing noise from such equipment. Environmental Elements Corp. **171**

Adsorption service. Bulletin 27-24 describes granular-activated carbon adsorption service for sewage treatment plants, with carbon exchange, or reactivation service only, as desired, for a monthly fee. Calgon Corp. **172**

Density gauges. Bulletin No. SDBD-7977 explains uses of density gauges in sewage and waste treatment plants, and contains a guide and reference for engineers and technicians. The Ohmart Corp. **173**

Waste management. Leaflet describes waste management information bureau, and company expertise in the field of hazardous and toxic wastes and materials. Harwell **174**

Filter. Bulletin KSB-509 describes horizontal belt filter for waste treatment, mining, dyestuffs, chemicals, and other applications. Controlled cake thickness 2–100 mm. Komline-Sanderson **175**

Facilities and environment. Brochure helps managers deal with odor problem solving. Brochure also helps managers deal with odor problems in existing or proposed facilities, and proposes plans for action. TRC **176**

Vertical turbines. Bulletin describes vertical industrial turbine (VIT) pump for cooling towers, effluent disposal, raw water, and other uses. Up to 29 000 gpm; heads to 3500 ft. Goulds Pumps, Inc. **177**

Sample preparation. Application Notes ANG C 5-76 and 6-76 tell about sample preparation and automatic analysis of volatile organics in water. Hewlett-Packard **178**

Environment books. 1977 catalog lists books on environment, energy, and other scientific and technical subjects. Ann Arbor Science Publishers, Inc. **179**

Instrument lease. Literature describes lease plan for analytical instruments used in research and development laboratories. V. G. Leasing Associates **180**

Contaminant monitoring. Guide lists sampling procedures for over 140 hazardous gases, vapors, and dusts. OSHA and NIOSH information is given. National Environmental Instruments, Inc. **181**

Soil testing. Catalog features expanded section on soil testing equipment. Soiltest, Inc. **182**

Gas chromatography. Brochures describe equipment and supplies for gas chromatography and gas chromatography/mass spectrometry. LKB Instruments, Inc. **183**

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Fabric filter. Brochure describes Norblo ES fabric filter for efficient removal of fine particulates from gas streams. Applications in foundries, chemical plants, and elsewhere. Buell, Envirotech Corp. **184**

Waste treatment. Catalog D-751 describes method for high-efficiency aeration in lagoons, extended aeration, aerobic digestion, and activated sludge systems. Highest oxygenation efficiency. Ralph B. Carter Co. **185**

Slurry Trenches. Brochure details possible uses of slurry trenches and slurry walls in construction; for instance, where water table cannot be lowered. BENCOR Corp. of America **186**

Atomizer. Booklet describes IL 555 controlled-temperature furnace atomizer for use with AA spectrophotometers. Analytical sensitivity is improved 100–1000 times. Instrumentation Laboratory, Inc. **187**

Water flow control. Brochure describes sluice gates, valves, and other equipment used in flow control for sewage, waste and power facilities, and flood control. Rodney Hunt Co. **188**

Energy saving. Brochure No. H6 sets forth a systems approach to energy conservation in any industrial process where heat is used. AER Corp. **189**

Ion exchange. Brochure describes new design of continuous ion exchange process with regeneration. Iconex Systems, Inc. **190**

Hearing protection. Film, "It's Up to You," shows how improper use of hearing protection can cause serious, and even irreversible, hearing damage. E-A-R Corp. **191**

Weather data. Bulletin No. 131 describes equipment for simulating temperature, humidity, altitude, and the space environment. Tenney Engineering, Inc. **192**

Air hazard detection. Data Sheet 07-00-01 describes continuous surveillance instruments that detect the presence of combustible and toxic gases and vapors in the air. Mine Safety Appliances Co. **193**

Protective coatings. Guide explains protective coatings designed specifically for municipal and industrial water/wastewater treatment plants. Advanced technology is included. Carboline Co. **194**

Gas scrubbers. Brochure, "Gas Scrubbers," examines a complete line of gas scrubbers available for air pollution control and gas treatment applications. Peabody Air Resources Equipment Co. **195**

Aerosol behavior. Technical paper, "How Particles Behave," defines behavior of aerosols and hydrosols. Gases and smog particles are among the topics discussed. Climet Instruments Co. **196**

Industrial gas scrubbers. Bulletin 7W106 describes company's full line of gas scrubbers or "wet collectors" for efficient removal of fine solid or liquid particles. Emtrol Corp. **197**

Vapor recovery. Literature describes gasoline vapor recovery systems to meet EPA regulations. Also applicable to other petrochemicals. Tenney Engineering, Inc. **198**

Air pollution control. Brochure tells about systems, equipment, and technology that not only control air pollution, but help to recover energy. Utility and iron and steel applications featured. Envirotech/Chemico Air Pollution Control **199**

1977 Gas Mileage Guide. Gas mileage listed for cars and trucks; separate version for California. Fuel Economy, Pueblo, CO 81009, or Fuel Economy, Federal Energy Administration, DPM Room 6500, Washington, DC 20461 (write direct).

Land use and water. Report is entitled "Land Use Water Quality Relationship." William C. Lienesch, Division of Water Planning (WH-554), U.S. EPA, Washington, DC 20460 (write direct).

Environment/energy balance. Brochure, "Striking the Balance: Energy/Environment," highlights company's programs for environmental protection and power production. Niagara Mohawk Power Corp., 300 Erie Blvd. West, Syracuse, NY 13202 (write direct).

Pollutant attenuation in landfills. Environmental Geology Notes 78 explains attenuation of pollutants in municipal landfill leachate by clay minerals through column leaching. Illinois State Geological Survey, Urbana, IL 61801 (write direct).

Land disposal. November 1976 newsletter probes comparative costs of land disposal of wastewater. Institute for Research on Land and Water Resources, Land and Water Research Bldg., University Park, Pa 16802 (write direct).

Resource recovery/Europe. Fall issue of NCRR Bulletin tells of resource recovery efforts in five European countries. National Center for Resource Recovery, 1211 Connecticut Ave., N.W., Washington, DC 20036 (write direct).

Laboratory set-up. Catalog tells how to furnish complete laboratories for wastewater treatment and pollution control. United Industries, Inc., Dept. Labtime, P.O. Box 1058, Wichita, KS 67201 (write direct).

Energy challenge. Free-loan 16-mm, 28½-min color film looks at problems and options of less abundant, more expensive energy to come. ERDA Film Library, P.O. Box 62, Oak Ridge, TN 37830 (write direct).

BOOKS

Enzymatic Conversation of Cellulosic Materials: Technology and Applications. Elmer L. Gaden, Jr., et al., Eds. vi + 316 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1976. Paper.

One approach to tackling the problem of cellulosic wastes is by treating them with cellulose-consuming fungi that produce glucose. The glucose is then usable as such, as feedstocks for other materials. This book discusses such cellulose breakdown, which was the subject of a symposium held at Newton, MA, in September 1975. It is part of a symposium series for which the subscription price is $100/year.

Actinides in the Environment. Arnold M. Friedman, Ed. ix + 107 pages. American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. 1976. $14.25, hard cover.

What happens to actinides, especially plutonium and americium, when they get out into the environment? This book offers the latest current knowledge on the subject, presented by experts from nuclear laboratories in the U.S., and West Germany. It is part of the ACS Symposium Series.

ERTS-1 A New Window On Our Planet. Geological Survey Professional Paper 929. xix + 362 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. Stock No. 024-001-02757-7. $13, paper.

If one wants rational management of earth resources, and correct evaluation of man's impact on the environment, one needs "the big picture." This paper offers many ERTS Satellite pictures along these lines, which present amazingly clear detail. Most pictures are in color, and were taken by the most advanced methods of photography.

The Energy Explosion. S. T. Butler, Robert Raymond. 84 pages. Publicity Dept., Doubleday & Co., Inc., 245 Park Ave., New York, NY 10017. 1976. $2.95, paper.

This volume of the Frontiers of Science series looks at energy available, the energy crisis, and what new and better sources of energy may be in the future. Aimed at younger people, it presents this material in pictorial form.

Environmental Economics. D. W. Pearce. ix + 202 pages. Longman Inc., 19 W. 44th St., New York, NY 10036. 1976. $16.50, hard cover.

Here is a text on economics of environmental problems from the standpoint of pollution (including noise) and natural resource depletion. The name of the game is to conserve natural resources and avoid the ravages of unconstrained economic growth. This book provides some approaches to that "game," and an idea of the catastrophe that can occur if the present situation continues.

Hydrogen Technology for Energy. David A. Mathis. xi + 285 pages. Noyes Data Corp., Mill Road at Grand Ave., Park Ridge, NJ 07656. 1976. $32, hard cover.

This ninth volume of the Energy Technology Review Series looks at a clean, plentiful energy source. It examines hydrogen production, storage, hazards, and safe use, as well as transmission systems for a possible "hydrogen economy." Non-technical aspects are also covered, and a list of 263 experts, with their affiliations, addresses, and backgrounds are given.

Mathematical Bioeconomics: The Optimal Management of Renewable Resources. Colin W. Clark. xi + 352 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1976. $21.95, hard cover.

Much has been said about renewable resources, particularly from the standpoint of biological conservation. Yet a sound theoretical basis, quantified, has not heretofore been evolved. Thus, the author looks at this subject from a solid mathematical point of view, and presents equations, many of which define the economics involved.

Environmental Data Management. Carl H. Oppenheimer, et al., Eds. xvi + 244 pages. Plenum Publishing Co., 227 W. 17th St., New York, NY 10011. 1976. $25, hard cover.

Environmental data serve best when they are properly managed. The contributors to this work explain how to utilize existing technology for an environmental data pool on a worldwide basis, and look at data transferability; statistical theory; computer capabilities; and unifying concepts.

The Conservation Response. Lloyd J. Dumas. xvii + 289 pages. Lexington Books, D. C. Heath and Company, 125 Spring St., Lexington, MA 02173. 1976. $14, hard cover.

There is only one "quick-fix" approach to the energy crisis, and that is conservation. Also, conservation is fully compatible with conservation of other natural resources, and pollution reduction. The author provides conservation strategies, and stresses the urgency of getting the point across that plentiful, inexpensive energy cannot be regarded as an American birthright.

Handbook of Ventilation for Contaminant Control. Henry J. McDermott. viii + 368 pages. Ann Arbor Science Publishers Inc., P.O. Box 1425, Ann Arbor, MI 48106. 1976. $29.50, hard cover.

Requirements for safety in the workplace are becoming ever stiffer. This includes the air the working people must breathe. Written by an industrial hygienist, this book explains principles of ventilation; how to design ventilation to meet OSHA requirements; instructions for handling toxic materials, and many other pertinent topics.

Atmospheric Chemistry. Julian Heicklen. xiv + 406 pages. Academic Press, Inc., 111 Fifth Ave., New York, NY 10003. 1976. $38, hard cover.

This book discusses the chemistry of the upper and lower atmospheres in a comprehensive manner. It also covers pollutants in urban areas, rates, concentrations effects, and influences of emissions, and control methods.

Pesticide Index. Fifth Edition. William J. Wiswesser, Ed. viii + 328 pages. Entomological Society of America, 4603 Calvert Rd., College Park, MD 20740. 1976. $12, paper.

This book provides a list of chemicals used against insects, rats, fungi, and unwanted plants, as well as other pests. Chemical characteristics are given, and structural formulae are included wherever possible.

History of Ocean Dumping in the Gulf of Mexico. Roy W. Hann, Jr. et al. Publication No. TAMU-SG-77-201. Sea Grant Program, Center for Marine Resources, Texas A&M University, College Station, TX 77843. 1976. $4.

Past and present dumping practices are discussed. Economic importance of dumping is also covered, and a full discussion of the nature of the Gulf is presented. Also dealt with are permitting programs of the EPA and the U.S. Army Corps of Engineers.

Chlorination of Wastewater. 120 pages. Water Pollution Control Federation, 2626 Pennsylvania Ave., N.W., Washington, DC

20037, 1976. $4 for WPCF members; $8 for others.

This Manual of Practice (MOP) covers topics from early uses of chlorine to technical discussions of the properties of chemicals used for chlorination. Reactions involved, effects on microorganisms, and safety aspects are discussed.

North Marin's Little Compendium of Water Saving Ideas. John Olaf Nelson. 200+ pages. North Marin County Water District, P.O. Box 146, Novato, CA 94947. 1976. $7.

Last year, North Marin County, near San Francisco, had a very severe drought. Thus, water saving methods had to be developed. Here are some suggestions applicable to all areas, as presented by the general manager of the North Marin County Water District.

Water and Wastewater Engineering Treatment. Edward D. Schroeder. 544 pages. McGraw-Hill Book Co., Attn: Peter R. Karsten, College Division, 27, Dept. BISA 1234, 1221 Avenue of the Americas, New York, NY 10020. 1977. $19.50.

This book presents a thoroughly up-to-date treatment of physical-chemical and biological aspects of water/wastewater treatment. It emphasizes conceptual and theoretical development rather than design procedures.

Operation and Maintenance of Wastewater Collection Systems. Kenneth D. Kerri, California State University, 6000 Jay St., Sacramento, CA 95819. 1976. Book, $30; as part of course, $55.

This book is really meant to be part of a home study course in O&M of wastewater collection systems. It covers construction, inspection, sulfide control, testing, repairs safety, and many other applicable subjects.

The Liquid and Solid Waste Treatment Markets in Europe. 300 pages. Frost & Sullivan, Inc., 106 Fulton St., New York, NY 10038. 1976. $700.

This report (No. E198) presents forecasts of what this market will be through 1985. It is based on information very carefully compiled and analyzed.

World Environmental Directory. Business Publishers Inc., P.O. Box 1067, Silver Spring, MD 20910. 1977. $39.

This Directory provides current information on control equipment manufacturers, engineers, Washington representatives for an industry, EPA and other federal personnel, and environmental libraries, just to name a few headings. Foreign environmental agencies, public interest organizations, universities offering environmental studies, and many other such listings are furnished.

How to Identify and Control Water Weeds and Algae. 64 pages. Applied Biochemists, Inc., P.O. Box 25, Mequon, WI 53092. 1976. $3.95, paper.

This book is a full guide to water weed and algae control, understandable by scientist and layman, alike. It presents recommended control methods, rates, and equipment. The publisher has 50 years of experience in this field.

The Toxic Substances Control Act. Ray M. Druley and Girard L. Ordway. 430 pages. BNA Books, The Bureau of National Affairs, Inc., 1231 25th St., N.W., Washington, DC 20037. 1976. $15.

The Act became effective on January 1. What this law means to the private and public sectors, and its key provisions, are fully discussed in this book. Judicial and enforcement matters are also covered.

Solid Waste Technology Assessment Study. 350 pages. Patricia Nellis, Technology Marketing Operation, General Electric Co., One River Road, Schenectady, NY 12345. 1976. $26.50, U.S. and Canada; $25, other.

This report provides hard facts on solid waste management. It assesses disposal technology, material reclamation, pyrolysis, and fuel recovery. Also covered are sanitary landfills, baling, hybrid systems, capital/operating cost estimates, and other pertinent topics.

MEETING GUIDE

March 20–25 New Orleans, La.
173rd American Chemical Society National Meeting. American Chemical Society
Write: A. T. Winstead, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036

March 20–25 Nashville, Tenn.
Seminar on Development of Design Criteria for Wastewater Treatment Processes. Vanderbilt University
Write: Dr. W. Wesley Eckenfelder, Jr., Vanderbilt University, Box 6222, Station B, Nashville, Tenn. 37235

March 21–25 Omaha, Neb.
Land Use: Tough Choices in Today's World. Soil Conservation Society of America
Write: Soil Conservation Society of America, 7515 Northeast Ankeny Rd., Ankeny, Iowa 50021

March 22–24 New Orleans, La.
1977 Annual Ocean Thermal Energy Conversion Conference. U.S. ERDA and the University of New Orleans
Write: Dr. David F. Mayer, conference coordinator, OTEC Conference, Dept. of Mathematics, University of New Orleans, New Orleans, La. 70122

March 22–24 Chicago, Ill.
Seminar on Packaging of Hazardous Materials for Transportation. Hazardous Materials Advisory Committee
Write: W. W. Bixby, Hazardous Materials Advisory Committee, 1100 17th St., N.W., Suite 1107, Washington, D.C. 20036

March 23–25 Seattle, Wash.
Man's Impact on the Waters of Puget Sound and Coastal Washington. Washington Sea Grant Program, U.S. EPA and others
Write: Puget Sound Symposium, Division of Marine Resources, HG-30, University of Washington, Seattle, Wash. 98105

March 24–25 Oakland, Calif.
Women in the Workplace. American Industrial Hygiene Association
Write: Greta Raymond, Stanford Research Institute, 333 Ravens Woods Ave., Menlo Park, Calif. 94025

March 27–30 Kansas City, Mo.
2nd National Energy/Environment Conference & Exhibits. American Defense Preparedness Association
Write: American Defense Preparedness Association, P.O. Box 17413, Dulles International Airport, Washington, D.C. 20041

March 27–30 New Orleans, La.
INFO 77: Nuclear Power and the Public. Atomic Industrial Forum, Inc.
Write: Conference Office, Atomic Industrial Forum, Inc., 7101 Wisconsin Ave., N.W., Washington, D.C. 20014

CLASSIFIED SECTION ■ POSITIONS OPEN

March 28–30 San Diego, Calif.
Energy Facts for Hospitals. HEW's Health Resource Administration (HRA), American Hospital Association and others
Solar energy, and new energy laws will be discussed. *Write:* HRA Energy Action Staff, Room 10A-41, 5600 Fishers Lane, Rockville, Md. 20857

March 29 Paramus, N.J.
7th Annual Industrial Air Pollution Control Seminar. American Institute of Plant Engineers and Rossnagel & Associates
Write: William L. Smedley, Box 8045, Route 8, Browns Mills, N.J. 08015

March 30–April 1 Seattle, Wash.
Eighth National Symposium on Food Processing Wastes. U.S. Environmental Protection Agency and others
Write: Kenneth Dostal, Environmental Protection Agency, Food and Wood Products Branch, 200 S.W. 35th St., Corvallis, Ore. 97330

April 7–8 Tucson, Ariz.
International Symposium on Controlled Environment Agriculture. University of Arizona's Environmental Research Laboratory
Write: International Symposium on CEA, Environmental Research Laboratory, Tucson International Airport, Tucson, Ariz. 85706

April 11–13 Washington, D.C.
Academy Forum on Coal. National Academy of Sciences
Coal as a future energy source will be discussed. *Write:* National Academy of Sciences, 2101 Constitution Ave., N.W., Washington, D.C. 20418

April 13–16 Blacksburg, Va.
Public Policy for Ground Water Protection. Engineering Foundation
Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

Courses

March 19–23 Atlanta, Ga.
Solar Heating & Cooling Workshop and Product Exhibition. Solar Energy Industries Association
Fee: $125 (members); $175 (nonmembers). *Write:* Solar Energy Industries Association, 1001 Connecticut Ave., N.W., Suite 632, Washington, D.C. 20036

March 27–April 1 Pacific Grove, Calif.
The Influence of Limited Resources on Housing Production and Delivery. Engineering Association
Questions of environmental protection and energy will be addressed. Fee: $220. *Write:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

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MEETING GUIDE (continued)

March 29–30 Madison, Wis.
Industrial Plant Boilers: Measuring and Improving Efficiency. University of Wisconsin–Extension

Environmental and energy topics will be discussed. Fee: $145. *Write:* Charles E. Dorgan, program director, Dept. of Engineering, University of Wisconsin–Extension, 432 N. Lake St., Madison, Wis. 53706

March 30–31 Denver, Colo.
Visible Emissions Recertification, Course No. 471. Air Pollution Training Institute (APTI)

Fee: $88. *Write:* Registrar, APTI, MD 20, National Environmental Research Center, Research Triangle Park, N.C. 27711

March 31–April 1 Chicago, Ill.
Microscopical Identification of Asbestos, Course No. 508. McCrone Research Institute

Fee: $200. *Write:* Registrar, McCrone Research Institute, 2508 S. Michigan Ave., Chicago, Ill. 60616

April 5–6 Newark, N.J.
Energy from Solid Wastes. New Jersey Institute of Technology

Fee: $235. *Write:* Division of Continuing Education, New Jersey Institute of Technology, 323 High St., Newark, N.J. 07102

April 5–7 Champaign, Ill.
19th Annual Public Water Supply Engineers Conference: Water Treatment, Part II. University of Illinois, Illinois EPA and American Water Works Association

Fee: $55. *Write:* Dr. Michael Semmens, University of Illinois, Dept. of Civil Engineering, Urbana, Ill. 61801

April 5–9 Research Triangle Park, N.C.
Continuous Monitoring for Source Emissions, Course No. 474. Air Pollution Training Institute

Fee: $175. *Write:* Registrar, Air Pollution Training Institute, MD-20, National Environmental Research Center, Research Triangle Park, N.C. 27711

April 11–15 Research Triangle Park, N.C.
Air Pollution Microscopy, Course No. 420. Air Pollution Training Institute

Fee: $157.50. *Write:* Registrar, Air Pollution Training Institute, MD-20, National Environmental Research Center, Research Triangle Park, N.C. 27711

April 11–15 Cincinnati, Ohio
Orientation to Wastewater Treatment Operation, Course No. 173. U.S. EPA

Fee: $110. *Write:* Registrar, National Training and Operational Technology Center, MOTD, OWPO, WHM, U.S. EPA, Cincinnati, Ohio 45268

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April 12–15 Chicago, Ill.
Control of Particulate Emissions, Course No. 413. Air Pollution Training Institute
Fee: $88. *Write:* Registrar, Air Pollution Training Institute, MD-20, National Environmental Research Center, Research Triangle Park, N.C. 27711

International

March 22–25 Middlesex, England
29th Technical Exhibition of Oil and Colour Chemists' Association. Oil and Colour Chemists' Association (OCCA)
Write: R. H. Hamblin, Priory House, 967 Harrow Rd., Wembley, Middlesex, England

May 4–6 Paris, France
3rd International Symposium and World Congress on Ozone Technology. International Ozone Institute
Write: International Ozone Institute, European Committee Secretariat, 52, Rue d'Anjou, 75384 CEDEX 08 Paris, France

May 16–20 London, England and Stockholm, Sweden
IAWPR Workshop: Instrumentation and Control for Water and Wastewater Treatment and Transport Systems. International Association of Water Pollution Research (IAWPR)
The first 3½ days will be held in London, the last 1½ in Stockholm. *Write:* R. A. R. Drake, U.K. Workshop Chairman, Thames Water Authority, 50-64 Broadway Buildings, Broadway, London SW 1, England

May 17–21 Bucharest, Romania
VIIIth World Congress on the Prevention of Occupational Accidents and Diseases. Ministry of Labor of Romania and others
Write: National Organizing Committee, VIIIth World Congress on the Prevention of Occupational Accidents and Diseases, Ministry of Labor, 1-3 Strada Scaune, Bucharest, Romania

May 29–June 2 Montreal, Que.
Advanced Methods for Water Treatment. Division of Environmental Chemistry, American Chemical Society
Write: I. J. Wilk, P.O. 5006, Stanford, Calif. 94305

June 14–18 Basel, Switzerland
7th International Exhibition and Technical Meetings for Environmental Sanitation. Pro Aqua Ltd. and the Swiss Industries Fair
Theme is Pro Aqua-Pro Vita. *Write:* Secretariat Pro Aqua-Pro Vita, c/o Swiss Industries Fair, P.O. Box CH-4021, Basel, Switzerland

Call for Papers

April 15 deadline
Fourth Annual UMR-MEC Conference on Energy. University of Missouri–Rolla and the Missouri Energy Council
Conference will be held October 11–13 at Rolla, Missouri. *Write:* Dr. J. Derald Morgan, conference director, 108 Electrical Engineering Dept., University of Missouri–Rolla, Rolla, Mo. 65401
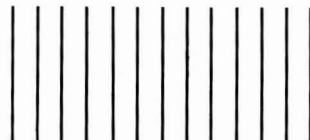
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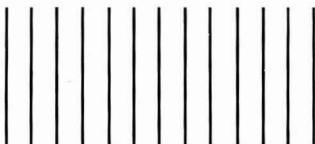
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29	30	31	32	33	34	35	36	37	38	39	40	41	42
43	44	45	46	47	48	49	50	51	52	53	54	55	56
57	58	59	60	61	62	63	64	65	66	67	68	69	70
71	72	73	74	75	76	77	78	79	80	81	82	83	84

NEW PRODUCTS, NEW LITERATURE:

101	102	103	104	105	106	107	108	109	110	111	112	113	114
115	116	117	118	119	120	121	122	123	124	125	126	127	128
129	130	131	132	133	134	135	136	137	138	139	140	141	142
143	144	145	146	147	148	149	150	151	152	153	154	155	156
157	158	159	160	161	162	163	164	165	166	167	168	169	170
171	172	173	174	175	176	177	178	179	180	181	182	183	184
185	186	187	188	189	190	191	192	193	194	195	196	197	198

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201	202	203	204	205	206	207	208	209	210	211	212	213	214

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