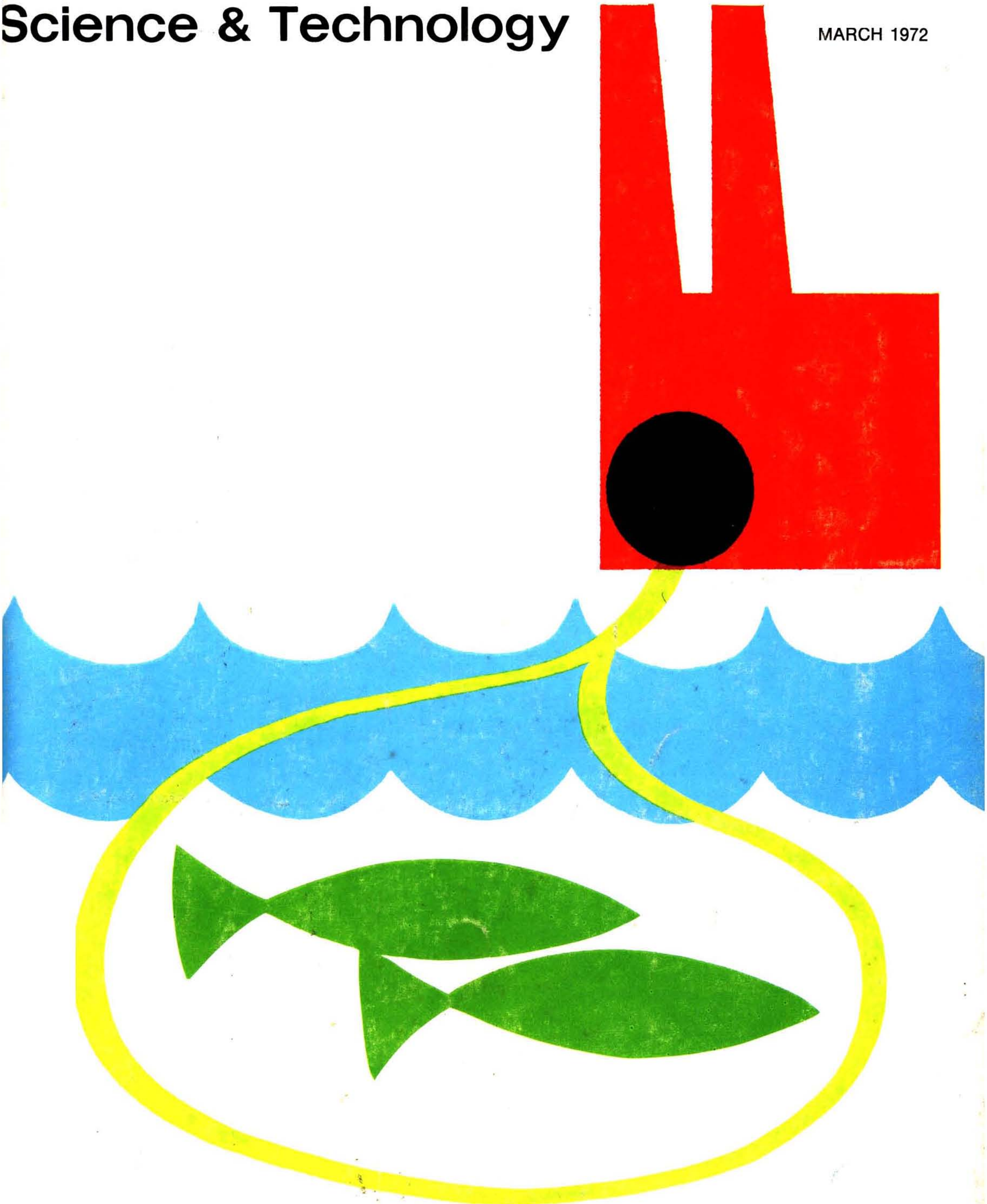
Environmental Science & Technology

MARCH 1972



Thermal pollution 224

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Environmental
Science & Technology

Volume 6, Number 3
March 1972
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ห้องสมุด กรมวิทยาศาสตร์
16 พ.ค. 2515

Current research

Effect of lead on oxidation activity of copper oxide–alumina catalyst 239

L. L. C. Sorensen and K. Nobe

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A. Zirino and M. L. Healy

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Quantitative separation of nitric oxide from nitrogen dioxide at atmospheric concentration ranges 250

D. A. Levaggi, W. Siu, M. Feldstein, and E. L. Kothny

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Effects of hydrocarbon and nitrogen oxides on photochemical smog formation 253

B. Dimitriades

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J. M. Smith, A. N. Masse, W. A. Feige, and L. J. Kamphake

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R. E. Cranston and D. E. Buckley

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Communication

Solubilization of lead in lake and reservoir sediments by NTA 278

C. D. Gregor

Lead emanating from automobile fuel exhausts (an appreciable lead fallout occurs from traffic near and around water reservoirs) can be solubilized rather rapidly by NTA present at relatively low concentration. As little as 2 ppm of NTA can raise the lead up to and exceeding the Public Health Service drinking water standard of 0.05 ppm. A concentration of 20 ppm of NTA raised the level of soluble lead to approximately 0.6 ppm in one situation.

Correspondence

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G. V. Levin and J. Shapiro
D. I. Jenkins

While earlier data showing that phosphate removal by activated sludge due to chemical precipitation are impressive, the authors caution that these earlier data are not universal in application. The last author points out that bubbling with CO_2-free gas is significant for removing soluble phosphate from activated sludge.

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letters

Strip mining control

DEAR SIR:

Many thanks for your comprehensive article on coal strip mining (ES&T, January 1972, p 27) and your mention of Conservation Foundation testimony presented by Malcolm Baldwin of our staff before congressional committees.

I want to correct your reference to the Conservation Foundation as an environmental lobby similar to the Sierra Club, however. This does not accurately describe our tax status. The Foundation is a tax-deductible, tax-exempt organization which, unlike the Sierra Club, cannot in any substantial way seek to influence legislation. Our testimony before Congress was by committee invitation.

I might also note, in a substantive vein, that our position differs from that of the Sierra Club, in that we advocate abolition of contour stripping only, and stringent regulation, but not necessarily abolition, of flatland or area stripping. In that respect, we differ with several other environmental groups.

Sydney Howe, President
The Conservation Foundation
Washington, DC 20036

Sewers and groundwater

DEAR SIR:

Your criticism of the government's simplistic approaches to the funding of water pollution control (November 1971, editorial) is both well taken and timely. It is particularly pertinent to the situation in Long Island's Nassau and Suffolk Counties, where sanitation officials have opted for environmentally and economically disastrous sewer and sewage treatment plant construction programs, without a comprehensive consideration of alternative approaches.

Sewers and sewage treatment plants serve a useful function in densely populated metropolitan areas which draw their supplies from and discharge their effluent into surface waterways. However, Long Island is entirely dependent on groundwater for its supplies, while its coastal waters support a rich ecosystem that is very sensitive to changes in salinity and other environmental parameters. Thus, the indiscriminate replacement of septic tanks by sewers and sewage treatment plants that dump their effluents into the bays poses a major threat to Long Island's water supplies and to its coastal ecosystem. To add insult to injury, the cost of the program

(Continued on p 194)

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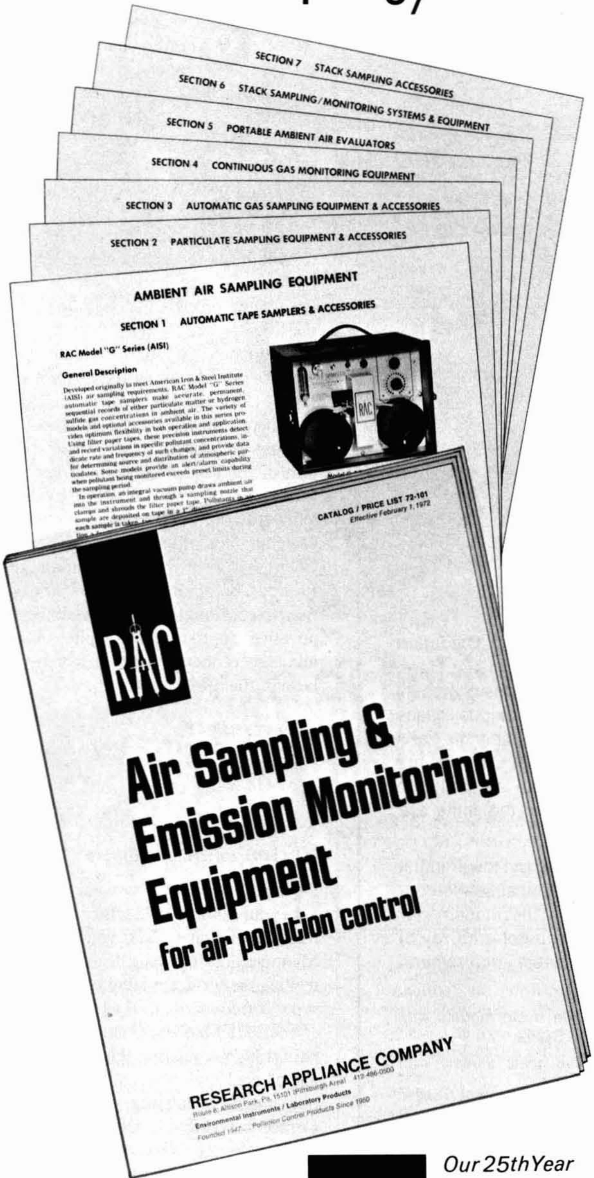

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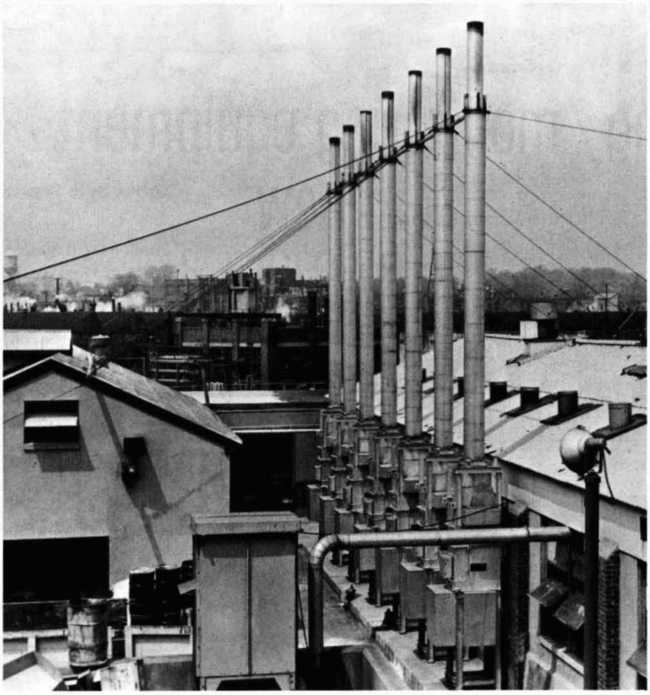

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to the average homeowner is expected to rival the price of his house!

The primary justification for sewers lies in preventing the contamination of groundwater supplies by nitrates from human toilet wastes. (Incidentally, sewers do nothing to curtail nitrate contamination by fertilizers, which are estimated to contribute about half of the loading in Suffolk County.) Other water-borne wastes are either degraded or filtered out in the soil (e.g., organic matter, phosphates), or banned (e.g., surfactants). Thus, if separate disposition could be provided for toilet wastes, which constitute less than 1% of an average household's waste load, the remaining waste water could be recycled through the purifying mechanisms of the soil to replenish groundwater supplies.

Fortunately, modern technology is able to provide for such separate disposal by thermal, chemical, or biological treatment. Several manufacturers are offering such systems at a small fraction of the cost of sewers and none of their adverse environmental effects. Why then have these innovations not been adopted in Nassau and Suffolk Counties? The rhetoric is long and tortuous, but it all boils down to the fact that most sanitation officials abhor innovative approaches, in spite of the immense economic and environmental benefits that would accrue.

Alex Hershaft
Environmental Technology Seminar
Bethpage, NY 11714

Missouri controls strippers

DEAR SIR:

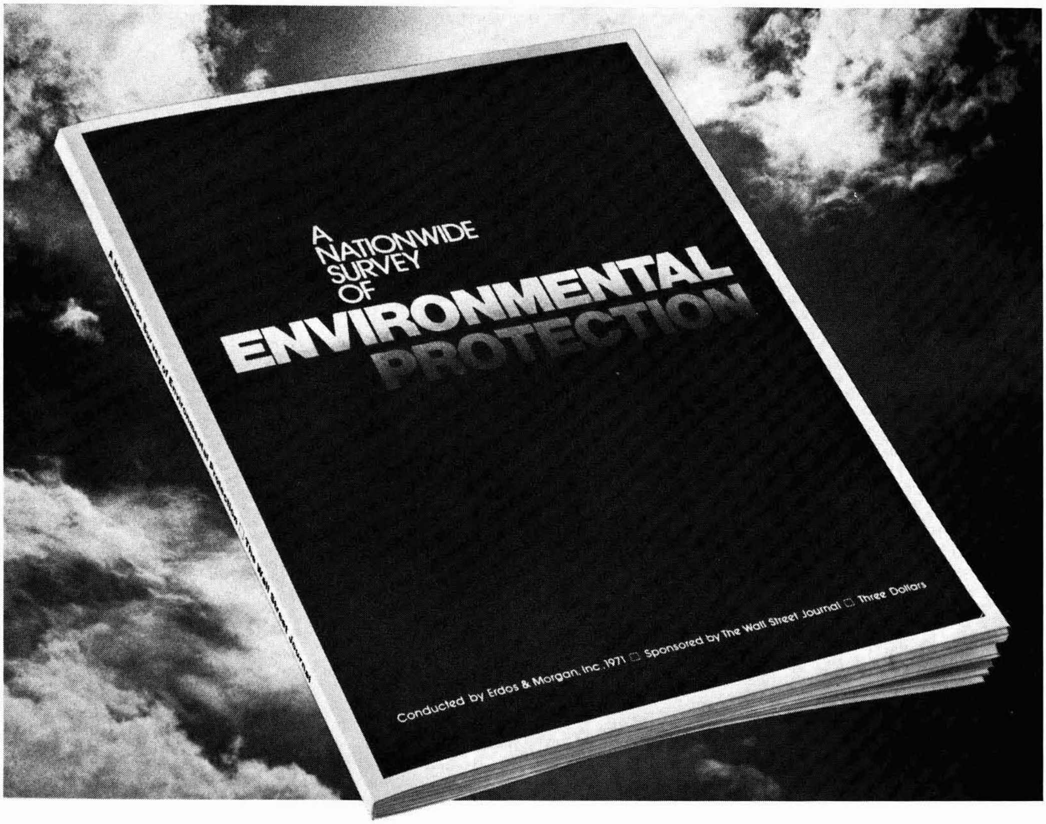
In your January 1972 article on surface mine legislation (p 27), you state that Missouri does not have legislation controlling the surface mining of coal. This is not correct.

The 1971 Missouri General Assembly passed bills regulating the surface mining of coal and other minerals. These bills impose a bonding requirement on surface miners that is designed to ensure that the affected land is reclaimed.

This legislation can be found in Chapter 444 of the Revised Statutes of Missouri, 1971 Supplement.

Peter H. Ruger
Assistant Attorney General
State of Missouri
Jefferson City, MO 65101

- *We regret the error—Ed.*



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The guys in the white hats

No one profession can claim all the expertise needed to clean up; what we need now is interdisciplinary teamwork

This year is of course an election year, and it will be no great surprise if a good part of the race is devoted to seeing who can most effectively claim credentials as the number one "Mr. Clean" in the nation. While such shenanigans are pretty much what the rest of us have learned to expect from politicians, it is well to point out that a somewhat similar sort of game of one-upmanship has been going on in the scientific and engineering professions at the same time. At stake, presumably, is the honor of being the most vital discipline in the environmental field.

Traditionally, very few professions have been engaged in working on what are today regarded as environmental problems. For many years, sanitary engineers, industrial hygienists, toxicologists, and others toiled away, largely unknown and certainly unsung. Those were the years when an ecologist was someone who was to be found happily working away on the forest floor studying the relationships between insects, or wading in a quiet pond, trying to discover which aquatic creature swallowed which. In these days when an ecologist, according to the media, is anyone with an opinion that is generally "pro-environment," just who has the expertise to solve the nation's environmental ills seems to be up for grabs.

The public impatience with the past lack of progress in curbing pollution has probably not really been directed at any one group, but many technical people feel nevertheless that they have been asked to shoulder too much of the blame. Hence, sanitary engineers, for instance, believe that it has been no fault of theirs that the nation is so far behind its needs in building sewage treatment facilities. "Society," they say, "just didn't care to spend the money." Obviously, there is a great deal of justification in the engineers' attitude.

Where interdisciplinary rivalry comes into the picture is intimately bound up with employment. If there's any money to be spent for environmental improvement, other groups, too, want a slice of the pie, whether or not their past expertise has been in any way environmental. The current fate of aerospace engineers is a case in point. Virtual collapse of the aerospace industry of the sixties has forced highly trained engineers to seek employment in pollution control positions. But, say critics—spearheaded by those already ensconced in pollution control jobs—where is the evidence that aerospace engineers can turn their hands and minds to environmental problems?

Such criticism has a point, but may be excessively defensive. In our opinion, there is no good reason why any properly trained scientist or engineer could not, perhaps with some retraining, contribute to an environmental project. And recently trained technical graduates have generally taken courses heavily laced with environmental applications.

The answer, of course, lies not in interprofessional rivalry, but in interdisciplinary teamwork. The different attitudes, backgrounds, and ways of approaching problems which biologists, sociologists, chemical engineers and all the rest can together bring to bear is the greatest assurance that progress will, in fact, be made. But before that can happen, those professionals who have spent years in the environmental field must swallow their pride and start encouraging other professionals to join them. And many would-be environmental scientists and technologists, for their part, had best forget about their past, so often rooted in the tradition of science for science's sake. For environment is a problem-oriented field. That is both its intellectual attraction and the reason why society seems cautiously ready to fund it with monies that all professions covet.

D. H. Michael Bowen

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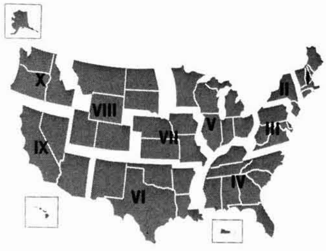
environmental currents

WASHINGTON

Environmental message calls for year of enactment

In his third environmental message to the Congress, President Nixon pointed to 18 items in need of legislative attention involving three areas—pollution control, land use management, and protection of natural heritage. Some of the major thrusts include proposals for • land disposal of wastes • control of sediments from construction activities • SO_x emission charges • land use measure in which states, if they did not come up with land use plans by 1975, would loose their federal eligibility for 7% airport funds, 7% highway funds, and 7% water resource funds. He also called for establishment of a voluntary fund of $100 million over a five-year period for projects stemming from the UN Conference on Human Environment this June.



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EPA: Implementation plans, lead additives, and radiation

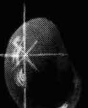
By the deadline (January 30) EPA has received 49 state implementation plans that were required by the Clean Air Amendments of 1970 and word that four other plans, (VA, CT, KY, MT) would be in by the end of February. As we move into March, Alaska is the only remaining state to submit its plan due to the fact that the public hearing was scheduled for the last of February and first of March. No approval announcement to any plan will be made until the state involved is notified. However, summaries of the most significant features of state plans will be provided by the EPA. The effects of lead additives in gasoline on emissions control systems, a report by the Aerospace Corp. is now available. EPA also announced award of study of radiation effects on newborn children of parents living in Mesa County, CO where uranium mill tailings have been used in construction of some 3000 homes from 1953–66.

USGS stores water underground and later recovers it

For the first time on the East Coast, hydrologists of the U.S. Geological Survey have injected water into aquifers (water-bearing subsurface rocks) underlying the Norfolk, VA area and recovered it. In the first experiment 200,000 gal of water were injected into a cavity about 900 ft below the surface, left in the cavity for 16 hr. More than 75% (some 168,000 gal) of water was recovered which met USPHS drinking water standards. The native water is 60 times more salty than the injected water. At press time, a second experiment called for the injection of 2 million gallons, leaving it in the cavity for 3 or 4 days and then back pumping. Ultimately, the goal is injection of several hundred million gallons of water for withdrawal several years later, for example, in cases of draught. (For more on injection wells, see ES&T, February 1972, p 120.)

PPB has fizzled, and a replacement is needed

"The planning, programming, and budgeting system (PPB), which was devised in the Defense Department and adopted governmentwide with great fanfare in 1965, was terminated, almost without notice, with the fiscal year 1972 budget cycle," says Sen. Henry Jackson (D.-WA). The failure of PPB is documented to some degree by the agency goals and objectives included in a recent publication of the Senate Committee on Interior and Insular Affairs, "Goals and Objectives of Federal Agencies in Fuels and Energy," a so-called background document for the National Fuels and Energy Study. (For application of PPB to the water pollution effort, see ES&T, October 1968, p 759).



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environmental currents

STATES

IL outlaws defoliant incineration, sets regulations

Illinois EPA will not permit incineration of the U.S. Air Force chemical defoliant "Orange." Air Force officials had considered disposing of 2.3 million gallons of Orange at Monsanto Chemical Co.'s incineration facilities in Sauget, IL. "We do not feel that Illinois citizens should be subjected to the risks of potential accidents," emphasized IL EPA Director William Blaser. The Illinois Pollution Control Board is warning all industries that they must obtain state permits before installing air pollution control devices in compliance with a 1970 law (exceptions had been made previously). The board also adopted effluent standards as part of revised water quality standards and established statewide asbestos regulations.

DE receives hurricane funds; geese poisoned by lead

The U.S. Coast Guard has tentatively agreed to reimburse the state of Delaware for costs of cleaning up beaches contaminated by oil as a result of hurricane Ginger. The state Department of Natural Resources and Environmental Control was notified that $9885 will be available under Section 11 of the Federal Water Pollution Control Act. Canadian geese are dying of lead poisoning in the Middletown, DE area. The birds are poisoned by ingesting lead shot as they gather gravel to aid digestion. Part of their intestinal tracts become paralyzed which prevents food digestion. Current estimates by the U.S. Dept. of Interior's Fish and Wildlife Service indicate that 2–3% of the total waterfowl population in the U.S. dies annually from ingested lead shot.

NY, IN take new tacks on sewage

New York City is testing on-site generation of sodium hypochlorite for disinfecting sewage treatment plant effluents to protect bathers using city beaches. New York pays about $1.3 million annually for 8 million gallons of 15% hypochlorite solution and could save as much as $1 million/year by on-site generation. Allied Chemical Corp. tested phosphate removal using aluminum sulfate (alum) and ferric chloride at the aeration chamber in the secondary stage; the chemicals cut phosphate content by 80%. Costs run from $11.45 to $14.60 per million gallons of wastes treated. Also, officials discovered that adding polyelectrolytes reduces BOD and suspended solids substantially.

Scientists form environmental consortium

Twelve universities (one in Japan) have established the Interuniversity Consortium for Environmental Studies (ICES) for collaborative research investigating environmental problems, mainly involving mercury and other trace metals, DDT, and PCB's. Supported by funds contributed by individuals, foundations, industries, and trade associations, ICES' functions range from congressional testimony to supporting research projects in distress. For example, one Wisconsin laboratory, working with limited funds, found that algae will detoxify several organic mercury compounds including notorious methyl mercury chloride, and ICES is raising funds to keep the project going. ICES headquarters are presently at Duke University under the auspices of Leonard Goldwater.

ICES participants

Columbia University
Duke University
Kurume University (Japan)
Michigan State University
North Carolina State University
Tulane University
Vanderbilt University
University of California (Berkeley)
University of Michigan
University of North Carolina
University of Rochester
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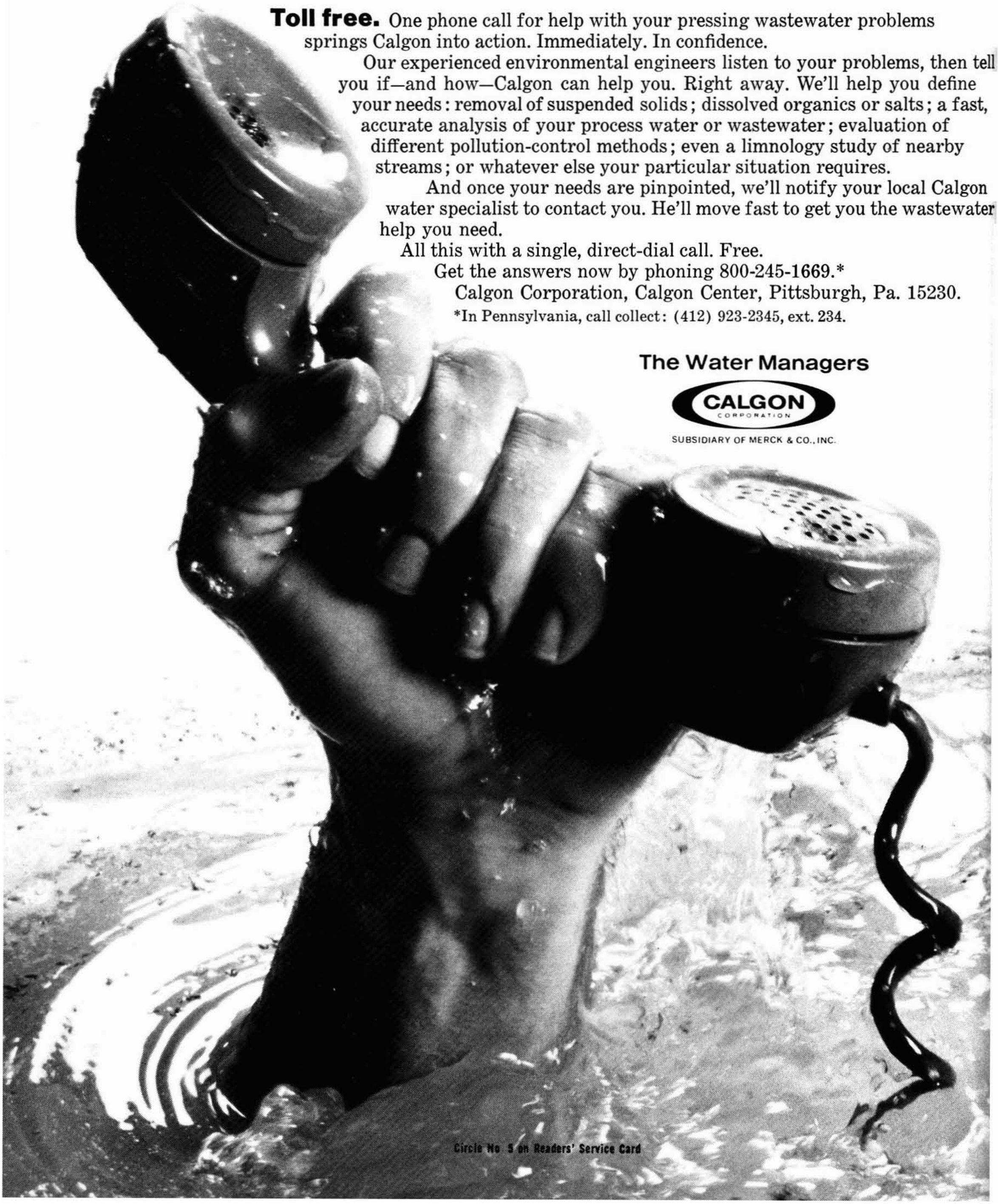

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environmental currents

TECHNOLOGY

Pyrolysis plus oxygen reduce solid wastes

Linde Division's (Union Carbide Corp.) Oxygen Refuse Generator System employs pyrolysis to convert organic wastes, such as paper and garbage, to fuel gas. Oxygen is added for high temperatures needed for both this step and to melt and fuse inorganic solid wastes, such as metals and glass. The system reduces waste volume by 95–98% and has been tested for nine months at Linde's Tarrytown, NY laboratories; however, Mount Vernon, NY is requesting construction funds from the federal EPA to construct a 150-ton/day unit to demonstrate benefits.

Conversion of waste sludge to landfill with chemicals

Chemfix Corp. (Pittsburgh, PA) changes waste sludge into a dirt-like material within 24–72 hr that can be used safely as landfill. Solid and liquid chemicals are mixed with sludge in a trailer. The chemicals (which Chemfix won't reveal) react with polyvalent metal ions to produce a stable, insoluble, inorganic compound, according to Chemfix. Monovalent cations, many organic compounds, anions, water, and colloidal material that may not enter into the reaction are physically trapped in the resulting structure of the landfill material. Prices range from 2–10¢/gal for high-solids wastes.

Controlled spraying of herbicides reduces pollution

"An automatic control device cuts sprayed herbicide volumes by some 60%," Floyd Fulgham, an engineer with the USDA Agricultural Research Service told the Southern Weed Science Society earlier this year. The control device, consisting of a plant sensor and solenoid valve set to "monitor" two rows of cotton, sprays short bursts of herbicide at the base of the cotton plants as the sensor "sees" the plants and triggers the solenoid valve. By such spot spraying, a farmer not only would need less herbicide for weed control but also would reduce herbicide drift.

Grooming future detergent builders

Benzopolycarboxylic acids (BCPA's) have a lot going for them as detergent builders. Eldib Engineering & Research (Newark, NJ) has been evaluating the properties of nine BCPA's, and Proctor & Gamble has a patent on penta- and hexa-benzocarboxylic acids in Belgium. Points on BCPA's side include • high sequestering power • good cleaning ability • high biodegradability • fairly low price and • pH range comparable to most detergents. Toxicological testing results thus far are favorable, but marketers are waiting for complete test results.

William Lear and bus

Lear unwraps steam turbine vehicle

Industrialist William P. Lear has unveiled his much-heralded steam-powered vehicle—a 50 passenger GM coach with a steam-raising, Rankine-cycle power plant. The engine, developed at a cost of more than $11 million of Lear's personal fortune, represents "the first new engine in 40 years," according to the Reno, NV inventor. The diesel-powered bus has emissions as low as 1% of the proposed 1975 California standards for heavy-duty deisel vehicles. A passenger car powered by a similar engine will go on display next month at the New York Auto Show.

The Cairox® Method clears up odorous and toxic industrial exhaust problems. Inexpensively.

When you use the CAIROX® Method you simply add a small amount of CAIROX® potassium permanganate ($KMnO_4$) to the water in a wet scrubber. The resulting solution has an oxidizing action that *destroys* the odorous or toxic qualities of gaseous industrial discharges – or converts them to an acceptable state.

It's more efficient and more economical than other methods. It works on aldehydes, amines, hydrogen sulfide, mercaptans, sulfur dioxide, ketones and phenol – as well as cooking and animal odors. It's in use now at chemical processing plants, breweries, rendering plants, textile mills, sewage plants, and asphalt plants, among others.

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INDUSTRY

Automobile imports must meet federal U.S. standards

Foreign car makers will have to comply with whatever federal air pollution standard is applicable in the year the vehicle was built. Under the 1970 Clean Air Amendments, any imported vehicle must be covered by a certificate of conformity, whether the vehicle is new or used or whether imported for personal use or sale. Under previous regulations, autos imported solely for private use were exempt from the emissions standards. Now, however, vehicles not meeting the standards will be denied final admission by the Bureau of Customs, which means the importer will have to deliver the vehicle for export or other disposition by customs, and faces a possible $10,000 fine. Among foreign car makers, Volvo is the only one yet to file asking for a one-year extension of 1975 emission standards.

NR chief raps Muskie bill, calls for impact study


Willard Rockwell, Jr.

North American Rockwell Corp. (NR) Chief Executive Willard F. Rockwell, Jr. says there are limits to how far and how fast pollution abatement can proceed without jeopardizing the national economy. Rockwell says that the cost of projected controls for the steel industry alone is about $4.5 billion—a sum greater than the combined profits of the American Steel industry for the past five years. Similarly, the paper industry is reportedly investing one sixth of its capital expenditures in pollution control. If the zero discharge concept embodied in the Muskie bill becomes law, Rockwell warns, the precentage would increase to 30 or 50%, resulting in an increase for paper from 25 to 65%. Although the aims of the zero discharge provision are good, Rockwell says, "the lack of realism is appalling."

Model correlates water quality and recreational use . . .

Envirogenics Corp. (El Monte, CA) has a computer technique for charting the specific risk to humans when exposed to nine water pollutants including bacterial and chemical contamination. With its computer program, public health officials can establish definite percentage of risks in relation to the kind and amount of pollution found in any body of water. The information can be used as a scientific basis for deciding when people should, or should not, use recreational waters for swimming and other sports, according to systems engineer Kenneth Hekimian. The technique was developed under a two-year contract with the Environmental Protection Agency.

. . . another will predict national energy data

Decision Sciences Corp. (Jenkintown, PA), an international computer technology firm that specializes in the application of technology to the decision-making process, will develop a computer-based national energy model for the American Gas Assoc. Under contract from AGA, Decision Sciences will develop the model so that AGA member companies can evaluate the role of natural gas in the U.S. energy industries. The model TERA (Total Energy Resources Analysis) should be particularly valuable to help the natural gas industry overcome the shortage of clean-burning fuel, says AGA President F. D. Hart. Complete development, implementation, and operation of the TERA model is expected by the end of this year.

The Chiyoda THOROUGHBRED 101 Flue Gas Desulfurization Process...best of the breed

Now there's a simpler way to keep the air free of sulfur and other pollutants from power plants, steel works, refineries, sulfur plants and even smelters. A more economical, more effective way. It's the Chiyoda THOROUGHBRED 101 Flue Gas Desulfurization Process. We tested it and proved it in 150 days of continuous operation. The first commercial plant employing this new process is to be installed at Nippon Mining Company's Mizushima Refinery to treat 35,000 Nm^3/hr of tail gas from a sulfur recovery plant.

Here's what the Chiyoda THOROUGHBRED 101 offers:

- * Continuously stable operation—no slurry is used in the absorber, so there's no clogging.
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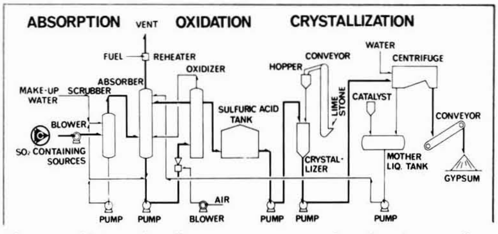
- * High efficiency—approximately 97% desulfurization rate is obtained.
- * Allows use of low grade fuels—the process is so effective it can treat such low grade fuels as vacuum residue.
- * Usable end product—nothing comes out of the system except the treated gas and commercially usable gypsum. There is no waste stream.
- * Process flexibility—the crystallizer can operate semi-independently of the absorber-oxidizer section. It can be installed in a separate place. One crystallizer can serve several absorber-oxidizer sections.

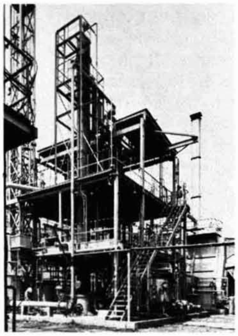
The Chiyoda THOROUGHBRED 101 Flue Gas Desulfurization Process is just the first in a series of pollution control processes being developed by Chiyoda's environmental research task forces.



After scrubbing, the flue gas goes into the absorber. Dilute sulfuric acid absorbs SO_2 from the gas.

The acid goes to the oxidizer. The oxidizing catalyst is an inexpensive, non-poisonous compound that is soluble in the acid.

Part of the acid goes from the oxidizer back to the absorber, the rest goes to the crystallizer to be mixed with limestone to form gypsum. The mother liquor and wash water are recycled to the absorber. There is no effluent.



This 1000 Nm^3/hr pilot plant operated continuously for 150 days desulfurizing flue gas.

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Federal Report

Government backs environment

EXECUTIVE OFFICE OF THE PRESIDENT OF THE UNITED STATES
OFFICE OF MANAGEMENT AND BUDGET

Executive, legislative, and judicial branches act on environmental matters; President's budget request calls for a leveling-off in environmental spending at $6.6 billion

Federal environmental programs once again are the subject of a special analysis in the Official Budget of the U.S. Government, for fiscal year 1973 (which begins this July 1). With the exception of the sewer and waters program, the three activities are the same as those designated in last year's special analysis plus one new item:

- Pollution control and abatement ($3.419 billion)
- Selected environmental protection and enhancement activities ($0.962 billion)
- Understanding, describing, and predicting the environment ($1.101 billion).
- Environmental research and development activities ($1.142 billion).

Summing it up, the total proposed by the President is $6.624 billion.

The new 1973 budget authority for pollution control and abatement activities, a central theme for environmental quality in the federal government, is $3.4 billion, slightly more than last year's figure of $3.3 billion. The Environmental Protection Agency, the lead agency in the activity, has a budget authority of $2.5 billion. In light of the fact that fiscal 1973 will be another year of deficit spending, in which the federal government will spend more than it receives, the EPA has fared rather well and Administrator William Ruckelshaus, at a press briefing on the budget, said, "We are satisfied."

After doubling last year, the EPA budget has reached the seemingly stable level of $2.5 billion. Over all, there is a $34 million increase in this year's request over last year's—$2.481 billion for fiscal '73 compared with $2.447 billion for fiscal '72 (which included two supplemental requests for funds made during fiscal 1972). The sharp increases were reflected in last year's budget request (ES&T, March 1971, p 200) which contained $45.5 million worth of nonrecurring items. One of the larger nonrecurring items ($28 million) was for the National Research Laboratory at Cincinnati.

Internal shifts

Within this year's request, there are a number of significant new directions. By medium, the largest single increase ($28 million) goes to the air program. It certainly seems justified considering the fact that annual air pollution damages are estimated to be $16 billion—including damage to health, vegetation, materials, and property values. Other increases are shown for the water program (up $10.9 million), radiation program (up $600,000), and noise program (up $30,000). An interdisciplinary item calls for a $6 million increase for operation of the Toxicological Research Center (Pine Bluff, AR) bringing the '73 level to $8.3 million.

The pesticides program remains at the same level as in 1972 ($11.5 million); but there are decreases in certain water and solid waste elements (see box). The federal solid waste program will be reoriented away from the development and demonstration of technology. The new thrust will be directed toward the application of today's equipment and hardware in the best systems management approach that is economical.

Construction grant funds for waste water treatment facilities, the largest share of the EPA request, remain at the same level as last year's request ($2 billion). But during fiscal year 1973, outlays will double over two years ago ($1.1 billion in fiscal '73 from $478 million in fiscal '71). Largely because of a construction backlog, there currently is about $7 billion worth of waste treatment facilities for which federal assistance has been committed and for which construction is incomplete or not yet under contract.

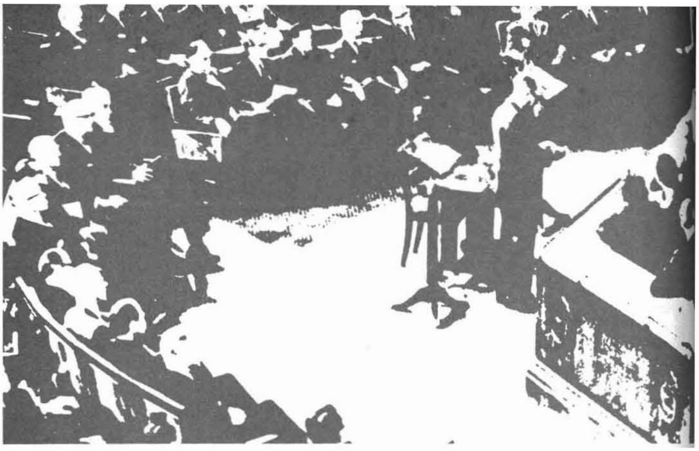
EPA: New directions

	Changes (from 1972) (million of dollars)	'73 Request (million of dollars)
Research, development, and demonstration		
AIR		
control technology	+5	30.6
regional studies	+5	5
health effects	+5	11.8
WATER		
eutrophication research	+4	6.2
effluent guidelines	+2	3.5
new methods for waste water treatment	−5.4	25.3
SOLID WASTE	−15.1	10.9
Abatement and control		
AIR		
assistant to control agencies	+8.6	51.5
compliance and surveillance program	+3.3	8.5
WATER		
assistant to control agencies	+5	20
TRAINING PROGRAM	−3	7.4
Enforcement		
AIR		
enforcing standards	+1.1	2.3
WATER		
permit program	+3.5	9.2
compliance with water quality standards and permit program	+2.8	12.1
Program support		
economic studies	+3.5	4.3

ห้องสมุด กรมวิทยาศาสตร์

Other new starts include user charges for pesticide registrations and training activities. EPA estimates that these charges annually cost the agency $3 million for its pesticides registration program and $3.1 for the training program. Users, including industries, must now pay for each of these services.

Nevertheless, there is some leeway for the future; in the budget request is an additional item of $35 million for several new pieces of legislation which are pending before the Congress, such as the new pesticides legislation and the ocean-dumping proposal.



Congress faces record backlog of proposals

Clean water amendments and others vie for attention before legislators hit the campaign trails this election year

After the President poses, Congress disposes. The budget request next comes before the appropriations committees of the House and of the Senate for their annual reviews. These committees control the government's spending; they can approve spending at the level requested or they can approve spending at some lower level.

At the same time, other pending legislation courses its way through various committees, subcommittees, and the two houses of Congress. New legislation, for example, could specify increased expenditures of funds by the federal government for programs deserving national priority. An obvious example is the funding level for construction of water pollution control facilities, the largest item in the EPA budget. Indeed, the present mood of Congress favors a $27 billion expenditure over the next five years for the nation's water quality effort—$20 million for construction and $7 million for research and planning.

When the second session of the 92nd Congress opened on January 18, it was faced with 90 pieces of unfinished administration legislative proposals, 15 of which were environmental bills (see box). Understandably, the environmental issues will probably take a back seat to pressing national issues such as inflation, unemployment, and the winding down of the war in Southeast Asia.

But environment may be the sleeper issue this election year. The environmental issue certainly is still alive politically, but it probably will lose much of its luster soon after new water pollution control legislation is enacted. If the proposal doesn't run aground on a House-Senate conference snag, the measure hopefully will be on the President's desk before May 1.

Coupled with the Clean Air Amendments of 1970, the nation then will have adequate blueprints for both water and air pollution control efforts through the first half of this environmental decade. The legislators can then sit back and give the measures a chance to take hold. During this time, however, massive doses of science and technology must be applied to protect and to begin to roll back pollution of our environment.

How important?

When ES&T asked legislators how important will the environmental issue be this election year, here is a sample of what we heard:

Sen. Howard Baker (R.-TN) says, "Generally I believe that environmental quality will continue to be a matter of genuine concern to the electorate and thus to elected officials and candidates for office. . . ."

Rep. John Dingell (D.-MI) tells ES&T, "The environmental issue can be expected to warm up as the voters come to realize that there is a tremendous gap between the words of the Nixon administration and its performance." On the other political side, Sen Bob Dole (R.-KS) counters with, "While President Nixon's record in the environmental area will be an issue in the campaign, other issues, including his successful policy in winding down the Vietnam war, strengthening our economy, and the leadership he is providing in foreign and domestic policies, will be more important."

Rep. Bella Abzug (D.-NY) says that the environmental issues will be "more important than a lot of politicians seem to think. It may be the sleeper issue of the campaign since the voters have not forgotten about it, no matter who else has."

Unfinished business

The first session of the 92nd Congress produced no new, major environmental law. The only major environmental achievement of the first session was the Senate passage of its version of the Clean Water Amendments (S. 2770) by a unanimous vote of 86-0. Nevertheless, the House public works committee was on the brink of passing its version when the first session adjourned.

This session, only those legislative proposals that receive early attention will make it through the congressional maze. Legislators will be in a rush to hit the campaign trails early this election year.

Amending the water pollution control act is undoubtedly the number one item of congressional business. Without any reservations, it can be predicted that the amended version will come out this session. But then, of course, there are 15 other separate pieces of administration business in various stages of legislative development.

Land use, the most important environmental issue remaining substantially unaddressed as a matter of national policy, will most likely not be settled this session. The jurisdictional disputes between the administration's and Sen. Jackson's proposals have not, as yet, been ironed out. Unresolved are the differences regarding which federal agencies get the major slice of the action.

Power plant siting legislation will be the major environmental matter in the House Interstate and Foreign Commerce committee. In addition, Sen. Bob Dole, a member of the Senate Public Works Committee, says that this committee will be involved with "oversight" hearings on air pollution, which began last month, and hearings on noise pollution.

Even after the bills and authorizations have been agreed to, they must go through the appropriations process. The Senate Appropriations Committee began its hearings last month. The chairman of the committee, Sen. Allen Ellender (D.-LA) says that the full committee is taking a look at the overall spending authority to see if national and domestic priorities are "properly in line."

On the House side, the annual funding requests of both EPA and CEQ go to the Environmental and Consumer Protection Activities subcommittee of the House Appropriations committee, which is chaired by Rep. Jamie Whitten (D.-MS). On environmental issues, Rep. Whitten says, "I hope that those of us who have been trying to do something to improve the environment and rectify ravages of the past will be able to harness present enthusiasm to make still greater progress in pollution control and in protecting and improving the environment before many of them go off on other subjects. One of our great problems is that those who are extreme in their views seem to be against all change in the environment, though such change may be for the overall betterment according to the objective viewers. We must avoid all excesses so that we can proceed to make the maximum progress in protecting and restoring the environment."

Last session

In spite of the fact that no major new legislation was enacted, two administration environmental proposals did in fact become public laws. These include the Vessel Bridge-to-Bridge Radiotelephone Act (P.L. 92-63) which would prove useful as a preventive measure for spills of oil or other hazardous materials into the nation's waters; and the expanded HUD appropriations for open space programs (P.L. 92-213).

A piece of legislation that passed both Houses is the ocean-dumping bill. Identified as a national as well as an international priority item, final enactment of this measure is imminent. The U.S. law can and probably will be used as a showpiece at the forthcoming UN Conference on the Human Environment in Stockholm, along with the amended air and water bills' specific deadlines for mid decade which will be complete before the opening of the Conference on June 6. Other showpiece items will include the U.S. moves to help solve the oil spill problem. The Senate ratified the IMCO intervention convention on September 20, 1971, along with amendments to the 1954 Oil Spill Convention.

Lead agencies

When asked whether legislators were satisfied with the initiative and progress that the two federal environmental agencies—EPA and CEQ—were making, the consensus was that each is doing a commendable job, all things considered. Qualitatively, however, legislators feel that EPA has an edge on CEQ.

Unfinished environmental business

- water amendments
- ocean dumping
- pesticides
- national land use policy
- power plant sitings
- toxic substances controls
- resource land management
- noise regulations
- environmental protection of mined areas
- land and water conservation fund amendments
- environmental financing authority
- ports and waterways safety act
- surplus property amendments
- expenses for relocation of federal facilities
- national housing amendments

Sen. Baker says, "EPA and CEQ are doing a commendable job, particularly when left to their own devices."

Rep. Dingell says, "In view of opposing pressures from within the Nixon administration, I feel that both the EPA and CEQ have done rather well in carrying out their responsibilities. However, I do feel that having a President who was truly devoted to the concepts of environmental quality would make these agencies much more responsive to the public interest."

Sen. Dole mentions that "EPA has had difficulty in organizing its various functional agencies, but it appears to have made remarkable progress. CEQ is providing a valuable overview in the environmental area."

But all legislators' comments were not so laudatory. Rep. Abzug says, "The efforts of EPA have been stymied at every turn by inadequate backing from the White House and by the recalcitrance and power of the large business interest it is supposed to be controlling. A more effective use of enforcement power is obviously mandatory. CEQ has been generally ineffective."

So, the races are on—the race to early adjournment, the race to the primaries, and race to the White House. But the environmental issue should fare rather well.

Courts say NEPA is a law for all people

Recent decisions force federal decision-makers to weigh alternatives in their environmental projects or else

After Congress has enacted new laws and authorized new beginnings, the courts must decide when the new laws are complied with and when they are not. When new laws are upheld, progress is made. One of the nation's newest environmental laws, the National Environmental Policy Act (NEPA) is being upheld. Certainly, most people have not forgotten about the environmental issue, and the extent to which NEPA has been invoked attests to that fact.

On January 1, 1972, NEPA was two years old. Hailed as the most important and far-reaching conservation-environmental measure ever cleared by any Congress, NEPA was signed by President Nixon on the first day of 1970—at the beginning of the environmental decade—(ES&T, February 1970, p 103).

At the outset, no one knew what impact, if any, the law would have. But now, two years later, everyone agrees that NEPA is causing a quiet revolution in the federal decision-making process.

Federal Report

The law has been embraced by all—the public, the lawyers, the courts, and federal decision-makers. It has caused a complete turnabout in the way the federal government conducts its business.

Prior to NEPA, federal agencies performed their missions and if environmental damage or harm resulted, then court cases were filed, and awards were made, after the fact. Now, before any agency can take any major action, it must weigh and balance the impact it will have on the environment before that action is taken. NEPA provides a new layer of information which is placed on an equal footing with cost benefit analyses and engineering feasibility studies.

In the past, any citizen group interested in blocking federal projects faced an enormous problem of developing evidence. NEPA shifted the burden of proof, placed the onus of actions affecting the environment on the federal decision-makers, and made them responsible for their federal decisions. NEPA is an open disclosure act. It has been likened to the Securities and Exchange Act which required that certain financial information be made available to the public before the company could take actions, such as issuance of stock certificates. Similarly, NEPA requires that federal agencies disclose in their impact statements detailed information prior to the decision-making process on matters affecting the environment.

A beginning

One of the major responsibilities required by NEPA is the preparation of impact statements—technically called 102(2)(C) statements after the relevant subsection of NEPA, but often just called 102 statements. The statement requires five basic elements (see box); it must be prepared by the federal agency that plans to take action. The agency prepares a "draft" statement, circulates it to other federal, state, and local agencies for comments, and makes it available to the public for comments on the proposed actions. After comments on the "draft" statement are taken into consideration, the agency prepares a "final" statement which is then filed with the Council on Environmental Quality (CEQ). According to CEQ guidelines, a draft statement must be available for 90 days before any action is taken, and a final statement must be filed 30 days before action is taken. So much for the mechanics.

For a while, it was perhaps safe to say that, with a few exceptions, agencies were confused about the preparation of statements. That may in fact still be true. Nevertheless, the tally shows that 24 federal agencies had filed a total of 2264 statements with CEQ by the first of this year—1240 "draft" and 1024 "final" statements.

The real test

Until now, not one statement has measured up to the test of a court case. By NEPA's second anniversary at the beginning of this year, there had been 66 decisions involving NEPA—15 Courts of Appeals decisions, 48 District Court opinions, and 3 discussions in Supreme Court dissents. Two third of the cases simply reflected that the 102 statement had not been prepared at all. The remaining one third of the cases, as a general rule, involves an agency's ongoing "pet" project which may have been well along in the planning and management stage for years and got caught up, so to speak, when NEPA was enacted. These include, for example, Interior's Trans-Alaskan Pipeline System (TAPS) and the Corps of Engineers' Tennessee-Tombigbee waterway project.

These projects were and are still being whipsawed by the new law. In effect, the federal agencies tried to retrofit an impact statement for a project that was well along in the agency's planning and management process. In most cases it hasn't worked, at least in the courts.

Environmental Defense Fund (EDF), a coalition of lawyers and scientists, is one of the leading organizations whose proddings and pressures have resulted in some of the federal turnabout that we have seen up to this time. EDF's Ed Chaney says that they have nine cases in the courts today, running the gamut of environmental protection—cases against Interior over power at the Four Corners area, and over the Trans-Alaska Pipeline System (TAPS); cases against the Corps on five projects including the Cross Florida Barge Canal and Tennessee-Tombigbee waterway project; cases against TVA on the Tellico Dam.

But EDF, of course, is not the only organization that has brought pressure on agencies. In fact, the first case that hit the Court of Appeals attacking the whole regulatory structure of the Atomic Energy Commission (AEC) was brought by the National Wildlife Federation, the Sierra Club, and the Calvert Cliffs' Coordinating Committee. The Calvert Cliffs' decision of July 23, which called a halt to construction of a nuclear power station at Calvert Cliffs, MD and shook the AEC to the core, was the result. Then, late last December, the Natural Resources Defense Council, another organization, won a preliminary injunction against Interior's off-shore leasing sales in the Gulf of Mexico.

Basically, the courts have held NEPA to be a procedural act. The decisions rendered up to this time, have in general been restraining orders—in legal terms, preliminary injunctions. The court decision has stopped an agency from proceeding with the project, such as the Tenn-Tom project, until the agency goes back and complies with NEPA. In most cases, the agency has been ordered to give more adequate consideration to possible alternatives, the third item required in the statement (see box).

Clarification

Requested by Rep. John Dingell (D.-MI), two ongoing studies will provide additional insight for NEPA operations. The Congressional Research Service of the Library of Congress, for example, has been busy gathering information on how an agency handles its statement-generating responsibility. Some federal agencies contracted for help in developing manuals on environmental analyses; the Transportation Department hired A. D. Little, and the Bureau of Reclamation in the Interior Department hired Battelle-Northwest to

tell the agency how to go about preparing the statement.

The Government Accounting Office (GAO) undertook a management orientation study of five agencies—HUD, DOT, Interior, Corps of Engineers, and Agriculture. The GAO study aimed at assessing whether the agency has adequate personnel, interdisciplinary teams, and manuals as standard operating procedures to prepare impact statements. GAO also was interested in knowing whether the procedures and manuals were available.

The findings of these two studies will certainly be of interest to the House Committee on Merchant Marine and Fisheries, the House committee with responsibility for overseeing the administration of NEPA. Rep. John Dingell, chairman of its subcommittee on Fisheries and Wildlife Conservation opened his oversight hearings last month; findings of both studies will be available soon.

It is not too early to speculate that most agencies by now have gone through a turnabout and are gearing up to prepare adequate impact statements, or to guess that no agency is really ready to comment on the statements from other agencies. One outstanding deficiency is that neither of the federal environmental agencies—EPA nor CEQ—has explicit comments, procedures, or guidelines for commenting on other agencies' statements.

Of course, whether or not these statements are adequate must not only await the challenge of a test case in the courts but in addition, the test of time. As yet, no court has decided that a federal agency has prepared an exemplary statement, and no judge has concurred with the decision to take the action specified in the statement.

One pitfall of the act was that it had no "feathering-in" procedures for retrofitting an agency's "pet" project which was in the system when the act was signed. For these projects, it is and will continue to be a catch-up ball game.

Teams

By now, federal agencies have put together interdisciplinary teams for follow-through on NEPA. Bruce Blanchard, Interior's director of environmental project review, who reports directly to the assistant secretary for program policy, says that Interior filed 18 "finals" in 1970 and 21 in 1971. He also says 83 "drafts" are outstanding. In 1972, Interior will probably file more than 200 statements.

Rep. John Dingell
. . . overseeing NEPA administration

Interior is in a unique situation; it is both the developer, the enhancer, and protector of the environment. Commenting on other departments' statements as well as on those of agencies within Interior heavily burdens the department. Blanchard says that Interior expects to comment on 2000–3000 statements this year. One dilemma facing this Interior official is the problem of alternatives. "How far do you go?" Blanchard asks. "Broad national policy statements do not belong in 102 statements on specific projects." Of necessity, these must be balanced before Interior prepares its draft statement.

Some agencies, including AEC and the Corps of Engineers have also put together interdisciplinary teams. In fact, 280 Corps personnel in its offices about the U.S. are now spending 25% or more of their time in the preparation and coordination of environmental statements.

Lester Rogers, director of AEC's division of radiological and environmental protection, says AEC now has about 55 people involved with the preparation of draft statements on its headquarters team. There are also approximately 100 people at the three AEC national labs—Oak Ridge, Battelle Pacific Northwest, and Argonne—working on statements.

Prior to NEPA, AEC responsibility was limited to the safety and hazards of the plant from a radiological point of view. "We would not ask an applicant to consider alternative power sources, nor would we ask him to consider the thermal and chemical effects of the proposal," Rogers explains.

Post NEPA and post Calvert Cliffs, the utility applicant must submit detailed environmental reports, including information on site selection, impact on the environment including thermal and chemical effects, and cost-benefit considerations. Two "draft" AEC statements have been published since the Calvert Cliffs' decision. In fact, several more will be issued soon. "Overall, our prime concern has been to minimize the delay of plants scheduled to come online consistent with full consideration of all environmental effects," Rogers concludes.

George Marienthal of the EPA Office of federal activities tells ES&T that pursuant to Section 309 of the Clean Air Amendments, EPA filed 129 sets of comments on 102 statements in the Federal Register during the past month. Section 309 requires EPA to make public its comments on any major federal action to which a 102 applies, on any proposed legislation or regulations, and on any newly authorized construction project, all of which must reflect environmental impact relating to the duties and responsibilities of the administrator.

To satisfy this requirement, EPA developed numerical ratings from one to four on the various statements. The ratings are: 1—general agreement, lack of objection; 2—inadequate information; 3—disagree, minor revisions needed; 4—disagree as written, need major change. The majority of EPA's comments were on DOT highway statements and ratings for the majority were either one or two.

What's ahead

Whether 1972 will be the year in which a court decision will uphold both the adequacy of a statement and the decision of the federal agency resulting therefrom is moot. Nevertheless, the unofficial goal for 1972 is preparation of statements that will withstand not only the procedural test of a court challenge but also a test of the project on its merits.

Whether that happens in 1972 is really not all that important. Truly, we are seeing a new beginning in the way the federal government handles its environmental business. There is still a lot to be done, and the more public discussion and clarification in the upcoming hearings will benefit all. SSM

Elements required in statements

- environmental impact of the proposed action
- any unavoidable adverse effects
- alternatives
- relationship of short-term uses and long-term productivity
- any irreversible and irretrievable commitment of resources

WATER AND WASTE CONTROL NEWS

Practicing the Automation we preach!

Honeywell was paying its Fort Washington (Pa.) industrial park landlord \$88,700/year to treat water and sewage from its 857,000 sq. ft. plant. At this time it was standard procedure to let water run uncontrolled through air compressors, degreasers, and plating rinse tanks, 28 of which consumed 106,700 gal./day.

TWO-FISTED COST FIGHTER! Two-pen ElectroniK *111 in Honeywell plant waste treatment facility records pH and Conductivity in plating department neutralizing tank. pH signal comes directly from flow-through electrode holder assembly with sensor-mounted pre-amplifier. For information on* ElectroniK *pH controllers write for Specification Sheets S540-2a and S546-1.*

Installation of conductivity controllers on each rinse tank to measure the concentration of metallic salts so water input could be controlled, brought a 66% reduction in rinse water, to 36,260 gal./day, saving \$23,000 per year. Temperature and flow controls on the water circuit of the air compressors cut usage by \$3,000 per year. Temperature controllers to cut flow of trichloroethylene solvent cooling water saved another \$3,000 per year.

In the past three years the plant has saved one full year's water and waste treatment costs by applying the principles of good plant water management.

"Problem-Solver" pH Electrode Better Three Ways

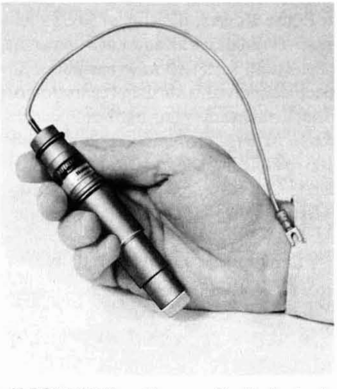
Solving three electrode problems common to process pH measurement is easy with the new Honeywell "Zero Flow" pH reference electrode.

First problem is high solution contact resistance; second is capillary clogging; and the third is "poisoning" of the silver chloride reference material by the intrusion of process fluid.

The new design develops low enough resistance to assure good contact and minimize stray effects. Large diffusion paths minimize clogging. Design licks the third problem, "poisoning", with a double-membrane, "pressure-lock" construction which places two diffusion time-constants between the process fluid and the silver chloride.

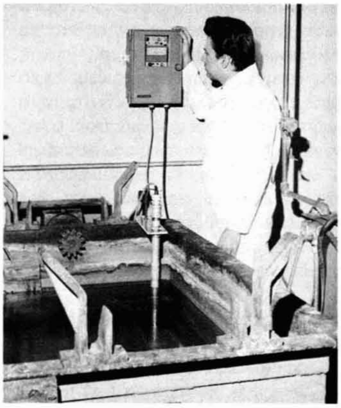
Rugged construction assures high resistance to physical and thermal shock. Ambient temperature range is –5 to 120° C. Because of its "Zero Flow" design, there's no need for accessory electrolyte reservoirs, air supplies, or pressure regulators

For further information, write for Specification Sheet S546-1.



pH POWER! New Honeywell pH electrode is designed to develop low solution contact resistance, with minimum susceptibility to clogging and "poisoning".

NEW WATER MANAGER! Honeywell conductivity analyzer is shown wall-mounted controlling a plating rinse tank to conserve make-up water. The submersible sensor is in the far corner of the tank. The identical equipment also is applicable to cooling tower blow-down control. Enclosures are weather-proof for hard industrial service. Also available in this line of analyzers are pH, ORP, and Dissolved Oxygen. Outputs available for ElectroniK *and* VutroniK *recorder-controllers. For further information on analyzer transmitters write for Specification Sheets S542-1, -2, -3, and S546-1 and -2.*



Cut Costs of Plant Water Usage

"Analyzing Factors For Lower Cost Plant Water Management", a paper by Christopher P. Blakeley, develops detailed cost considerations affecting the economics of industrial plant process water usage. Blakeley, Market Manager for Honeywell Water Management Markets, presented the paper at the April 1971 meeting of the Industrial Management Center's conference on Environmental Management for Industry and Government held at Sterling Institute, Washington, D.C.

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After many years of apathy and indifference, private citizens, industry, and government are now advocating national policies for . . .

Groundwater pollution and conservation

Remember the days when a man hired a dowser or water witch before digging a new well? The dowser would point a forked witch hazel twig toward the ground and be mysteriously drawn to the spot where the well should be dug. His chances of predicting where water could be found were quite good, for "groundwater" can be found almost anywhere beneath the earth's surface at varying depths (see map). In fact, over 97% of fresh water in the U.S. is underground.

Most people are unaware of or oblivious to groundwater, since you can't water ski on it, fish or swim in it, or gaze across it to watch a sunset. Actually, surface water at one point may be groundwater at another, and then emerge again at a third point as surface water.

To understand groundwater and its role in the environment, its characteristics must be explained. Groundwater is water beneath the earth's surface in a geological formation that supplies wells and springs. Groundwater moves through and is stored in an aquifer—the porous geological formation containing water. The best aquifers are layers of gravel, sand, sandstone, limestone, or even nonlayered rock that has sizeable and interconnected openings such as some lava rocks. Clay, shale, and crystalline rocks are usually poor water carriers but may yield at least enough water for domestic and stock uses in areas where there are no better aquifers.

Aquifers may be a few feet to hundreds of feet thick and may underlie a few acres or many square miles. Most aquifers are local in extent; however, the Dakota Sandstone, for instance, (in the West) carries water across several states.

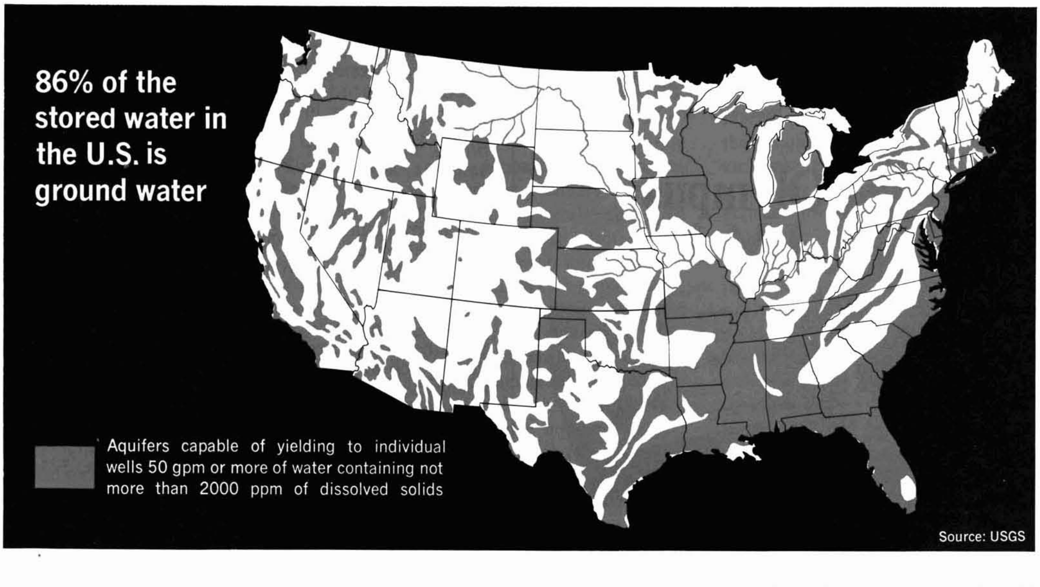
The water table is the top level of groundwater or the zone of saturation—the area in which all pore spaces in the rocks are saturated with water. Between the land surface and the water table is an area which hydrologists call the zone of aeration where water moves downward from the land surface to the water table. This zone may contain a little water, but it cannot be obtained through wells and is held to soil particles and rock by capillary action.

Groundwater moves through permeable rock and around or in between impermeable ones. Just like surface water, it takes the path of least resistance down as far as it can go. This downward flow can be stopped by solid rock, clay, or a denser fluid. If held between two such impermeable layers, groundwater may be under enough pressure to create artesian flow when opened by a well. Groundwater movement is quite slow and is measured in ft/year as contrasted with streams measured in ft/sec.

Importance of groundwater

Groundwater discharges into springs, streams, rivers, lakes, swamp areas, geysers, and wells. Water flow can range from a few gal/hr to thousands of gal/min. Man taps these groundwater sources for a variety of urban, industrial, and rural uses.

Aquifers can be recharged naturally or artificially. Under natural conditions, aquifers are recharged with water moving from regions higher than the discharge area by the means of rain, snow, streams, etc. After the zone of aeration is saturated, the aquifer itself is recharged.



86% of the stored water in the U.S. is ground water

▨ Aquifers capable of yielding to individual wells 50 gpm or more of water containing not more than 2000 ppm of dissolved solids

Source: USGS

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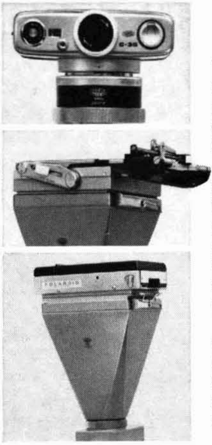

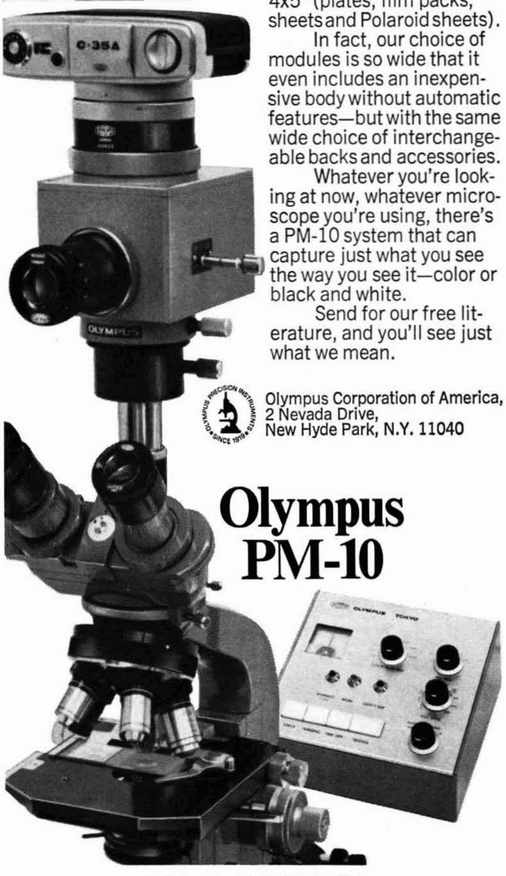

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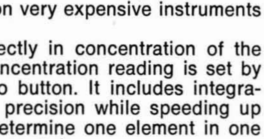

AA spectrophotometry is increasingly used to determine metallic elements in waters, effluents, brines, impinged air samples, and other materials that can be dissolved or suspended.

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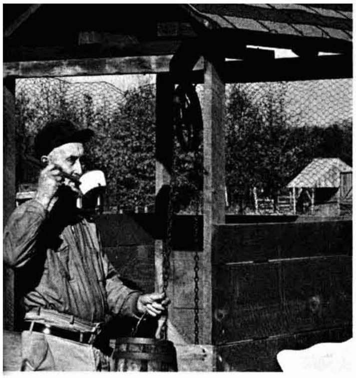

Wells. *Groundwater supplies 95% of domestic water used in rural areas*

Artificial recharging is a valuable conservation tool and is used to counteract excessive water withdrawal from an aquifer. Sometimes wells are drilled just for recharging; in other areas, irrigation helps to recharge the groundwater aquifer.

On Long Island (NY) and in the Los Angeles area, aquifers are being recharged to protect against intrusion of salt water. The Hanover Canning Co. (Hanover, PA) and other food processors use spray irrigation to dispose of liquid wastes; this contributes to crop nourishment and groundwater recharge. Storm water runoff is used for recharging in Orlando, FL and Fresno, CA. A number of recharging projects are under way in the arid and semiarid regions of the U.S.

Why is groundwater so important and such care taken to recharge it? Groundwater supplies 20% of the fresh water used in the U.S. (61 billion gal/day). Of the nation's 100 largest cities, 20 depend entirely on groundwater for their public water supply, and 13 use both groundwater and surface water. Twelve states obtain more than 50% of their statewide public water supplies from groundwater.

Furthermore, industry uses 7.7 billion gpd, rural areas use 45.2 billion gpd, and urban areas use 8.1 billion gpd. In fact, more than 95% of the rural population in the U.S. uses groundwater for its domestic water supply. The arid and semiarid Southwest is almost entirely dependent on groundwater.

In the West and Southwest, groundwater depletion is a problem. There, as in most states, more water is being withdrawn than is being recharged into the aquifer; in hydrologic language, the water is being "mined." Because of natural recharging, groundwater is a renewable resource; but when it's being steadily mined, water is used on a deficit basis.

In areas of Texas, New Mexico, Kansas, Colorado, Arizona, and California, "it is being mined at an alarming rate," says Bob Aitken, EPA's International, Interagency, and Intermedia Standards Coordinator. Because of this, some farms and ranches have been abandoned in Texas and New Mexico. Years ago, water was found 10–30 ft below land surface and, in some cases, even flowed above land surface. But as the water table lowered, wells had to be dug deeper and deeper until water lifting costs outweighed profits derived from the land.

Contamination

Constant withdrawal of groundwater is not the only problem. Groundwater pollution is increasing, even though groundwater has always been considered insulated against contamination.

Groundwater, purer and cleaner than surface water, is protected naturally by an excellent filtering system—soil, clays, rock particles, etc.—that removes suspended solids, bacteria, and, to a large extent, viruses. If that filtering system is overloaded or bypassed, the aquifer itself may become polluted.

"Pollution of groundwater has always been with us, like all other water pollution problems," continues EPA's Aitken, but the result is different. If a stream is polluted and then that contaminating source is removed, the stream can be flushed in about a week, more or less (although reversing pollution effects is not that simple). For a large freshwater lake, the retention time is about 100 years. When an underground aquifer is polluted, however, the waste is retained for 200 to 10,000 years. U.S. Geological Survey officials say that water supplies for future generations could be jeopardized by groundwater pollution.

Surface disposal of domestic and industrial waste, seepage from septic tanks, mine drainage, feedlot wastes, deep-well disposal, sanitary landfills, and agricultural chemicals—the same type of pollutants that affect surface water—have a greater impact and a more prolonged effect on groundwater. In some areas, groundwater aquifers are quite sensitive to pollutants, while in others, due to soil and geological conditions, contamination is limited.

Industrial waste disposal into surface waters can pollute aquifers fed by streams. For example, phenol wastes discharged into the Caloosahatchie River made it necessary to abandon wells near Ft. Myer, FL. On Long Island, nitrates—from fertilizers, rain picking up nitrates from the air, and septic tanks—were detected in groundwater.

Regulation

Nationwide, groundwater charting and investigation is presently under the auspices of the U.S Geological Survey in the Department of the Interior. However, there is only limited federal control over groundwater regulation; the USGS merely advises and supplies information on groundwater resources. By and large, control is left up to states and municipalities which, unfortunately, usually attempt regulation only when there is a shortage of water, according to USGS officials. A number of basin management programs are presently in the making.

One major groundwater management problem is the question of riparian right and local, state, or federal control. In some areas (appropriation states), if a beneficial use for groundwater is established, then no subsequent user can deprive the original user of his prior water rights. In other areas, permits are required before drilling of any kind, yet other regions have no regulation at all. These are some of the inconsistencies that EPA would like to eliminate by promulgating a national policy for groundwater protection.

The Water Pollution Control Act Amendments of 1970 apply to navigable streams and mention groundwater only once, but S. 2770 and H. 11896 (the controversial bills now in Congress) are a huge step forward from the point of protecting the subsurface environment in general and groundwater in particular.

The major flaw, environmentalists point out, has to do with deep-well injection (usually for disposal purposes). At press time, both bills give the EPA administrator responsibility and authority to administer waste inputs in the ground with the exception of oil and gas injection wells. The debate centers around the bills' language that excludes, through definition, oil, gas, or water injection associated with the word pollutant. (For more on deep-well disposal, see ES&T, February 1972, p 120.)

The groundwater issue is still undecided. Although groundwater has been considered a separate species of water, it is not isolated. It has direct communication with atmospheric water, lakes, rivers, and oceans. Many streams, at their high input stages, recharge groundwater, and when streams are at low flow, the entire water source may be groundwater. Groundwater is important. CKL

A new breed of manager is on the industrial scene—tangible evidence of the growing corporate commitment to a cleaner environment

Pollution control's man in the middle

ENVIRONMENTAL COORDINATOR

* * * * * *

Medium size midwestern chemical company has immediate opening for experienced administrator as Corporate Director of Environmental Affairs

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CornChem Corp.

No doubt there are some well-qualified people who could respond in all honesty to the fictitious help-wanted ad above. But it wouldn't be because they planned their careers accordingly. The environmental coordinator slot is a relatively new addition to the corporate organization chart. But it's a job that looms more and more important.

A 1970 study by the Conference Board, a New York-based nonprofit business research organization, showed that out of 174 firms in pollution-prone industries surveyed in North America, 89 companies give special organizational emphasis to pollution control. In many of these companies, there is a top corporate manager in charge, with direct access to the President or Chairman of the Board. Formal job descriptions vary widely, but in virtually all cases, the environmental managers follow a single, unwritten mandate: reconcile the need for environmental protection with an equally real need for his company to make money.

What they do

ES&T talked with several environmental coordinators to see how they viewed their jobs, among them A. J. von Frank, director of Environmental Control for Allied Chemical Corp.

Allied has some 150 production plants organized into eight domestic operating divisions, in addition to Canadian and International Divisions. Each division now has at least one person at division headquarters—and usually more than one—responsible for environmental matters. Technical people at each of the plants report to divisional managers of environmental affiairs who in turn report to von Frank.

Allied's von Frank is a registered professional engineer who's been around the company a long time. In 1947 he was put in charge of environmental matters in Allied's Plastics division. At this time there were only two other divisions in the company with counterpart environmental positions.

At first, his job was largely a technical one. But the pressures and problems of environmental matters were already creeping into the executive suite at that early date. Allied's then largest division—industrial chemicals—had a well-organized pollution control group in 1947, but it had no real corporate function. Over the years, von Frank says, "there was a progressive realization that the divisional structure was needed to coordinate policy."

So, in 1964, Allied tapped von Frank to be the company's first corporate director of Air and Water Pollution Control. "It was my choice of titles," von Frank notes, "because I didn't want the word 'environmental' in it." The reason, he explains, was that he didn't want to become enmeshed with occupational health and safety, noise, toxicology, and the like.

In 1964, about half of Allied's operating divisions had working pollution control groups. "One of the first things I did was to establish groups in the remaining smaller divisions where the presidents would say 'What do I need this group for?' " von Frank recalls. By 1969, things had broadened out more to include those areas which von Frank skirted when he took over.

What he does today could be described as a combination of economics, diplomacy, technology, law, public relations, and management. His advice carries a lot of weight at the top. "I don't think top staff positions are ever exclusively advisory," he says. "We're not just giving trivial advice to people who are running their own games. We get into some pretty hot arguments."

Von Frank sees his job as one of piecing together a solution from seemingly irreconcilable parts. "It's not a matter of slick political compromising," he says. "There has to be more rational input—mostly technical and economic. There's always an answer when you have all the facts."

Hooker

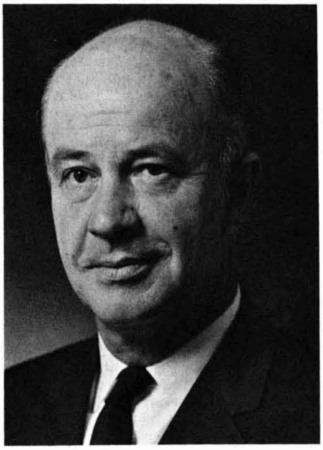
Another jack-of-all-trades and master of all is Jerome Wilkenfeld, Director of Environmental Health for Hooker Chemical Co. Wilkenfeld is a chemical engineer with many years of experience behind him. He started with the company's Niagara Falls (Buffalo, NY) chemical plant in 1943, working in process engineering. He moved more directly into pollution control in the early 50's.

Hooker's structuring of pollution control activities is different from that of most major companies that have reorganized to fight pollution. There are no special groups or committees. That arrangement is "very deliberate," says Wilkenfeld. Pollution control is the responsibility of the plant manager, and is really not different from product safety, cost control, or a host of other crosses a plant manager has to bear, Wilkenfeld argues. "The idea of 'it's their responsibility' is very effective," Wilkenfeld says. So, with information supplied by technical people throughout the company, the plant manager has to see to it that he runs a clean as well as profitable operation.

Wilkenfeld's job is largely one of coordinating corporate policy, anticipating problems at the "precrisis stage," consulting with control agencies to set forth the industry position, working for "effective legislation," and educating plant managers so that they know what's required of them. "My general charge is to do all that's necessary to see that we're in compliance," Wilkenfeld says.

Officially, Wilkenfeld reports to a group vice-president but he frequently goes straight to the top when the situation calls for it. He serves as an information broker—offering legal and technical advice to his plant managers—and as a lobbyist within the executive suite, going to bat for plant managers to get the money they need for pollution control.

He is active in industry trade groups and frequently testifies before congressional committees on pollution matters. He often lectures at nearby colleges and was chairman of New York State's Air Pollution Control Board. Although Hooker is located in Stamford, CT, Wilkenfeld prefers to live in New York State to continue his work with environmental groups there. HMM



Allied's von Frank
Some pretty hot arguments

Hooker's Wilkenfeld
It's their responsibility

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Waste heat recovery makes sense

Small incinerator economics looks much better
when heat from stack gases can be recovered and put to use

Sometimes "new technology" is simply a matter of applying old technology to new situations. Take steam-raising incinerators for instance. While using waste heat generated from burning municipal refuse is not really old hat, it's been done successfully for years in Europe and the idea is beginning to catch on in North America as well (see "Plants burn garbage, produce steam," ES&T, March 1971, p 207). All of which raises a question: If waste heat recovery makes economic sense for municipal incinerators, why wouldn't it be advantageous to trap some of the heat that goes up the chimneys in smaller units, say those in apartment complexes or commercial buildings?

A. W. Hindenlang, vice-president for engineering at Ecology Industries, Inc. (S. Plainfield, NJ) says it would make sense. Ecology Industries is marketing a modular solid waste handling and disposal system—aimed primarily at hospitals—which includes a boiler for trapping heat that can be used in-house for producing heat or hot water.

Although the system could work in apartment houses or virtually any reasonably sized commercial building, says Ecology Industry's President William Carey, hospitals provide an especially favorable proving ground for the concept because of the high volumes of waste generated. Only a few years ago, an average figure for hospital waste production cited by the Incineration Institute of America was 8 lb/person/day. That figure was recently revised upward to 15 lb/person/day. Because the use of disposables in hospitals continues to grow at a phenomenal rate, Hindenlang says, the figure could reach 25 lb/person/day within the next five years.

Hindenlang argues the economic case for on-site disposal and heat recovery this way: A hypothetical 800-bed hospital with clinical and laboratory facilities could be expected to generate about 15,000 lb of wastes per day. That much waste could easily cost $75 per day just to cart away.

Hospital waste has an average heat content of about 7624 Btu/lb—or a total of 114.3 million Btu per day at the 800-bed hospital. If the waste were to be burned and the heat recovered down to an exit gas temperature of 600°F, the total dry gas, moisture, and radiation loss would be about 1600 Btu/lb. That means a net heat energy of 6025 Btu/lb or a total of 90.3 million Btu/day can be recuperated.

If that energy were converted for use in the hospital, the fuel bill reduction (assuming a 60-cent per million Btu fuel cost) would be $54.14 per day. That figure added to the savings resulting from elimination of hauling the waste away yields a gross savings of $129.18 per day or better than $47,000 annually.

These figures ignore contributions to overall community air pollution problems and the benefit of reducing demand on the national energy supply because return to the individual institution is intangible. "However," Hindenlang says, "we feel that widespread adoption of such a process would contribute greatly to both these areas."

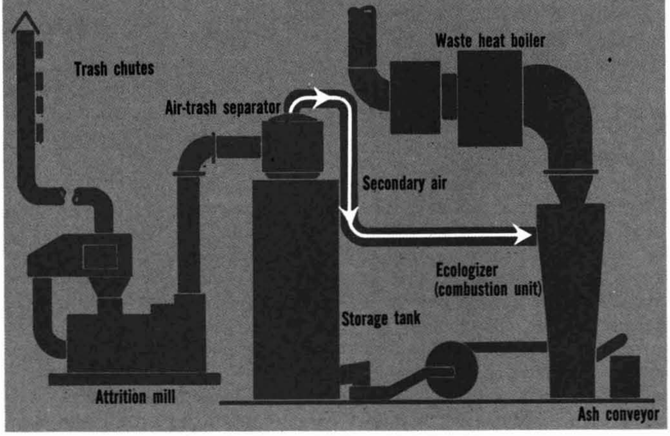
Total package

Ecology Industries' system is a modular collection and disposal package that allows a hospital to take as much or as little as it needs. The complete package begins with a collection system and ends up with the boiler. Waste is deposited in a central collection chute where it drops into an attrition mill that grinds unsorted materials and reduces total volume by as much as 80%. Once through the mill, ground refuse goes to a storage unit, intended to provide a uniform flow of material to the burner.

The heart of the system is the combustion unit, dubbed an "Ecologizer." Ground waste is injected pneumatically at the bottom through a burner flame. Combustibles are consumed during their upward trek through the unit by introduction of preheated secondary air. The whirling motion produced by the tangential air injection mixes fuel and air and separates particulate matter at the top of the unit. Ash falls into quenching water at the bottom of the combustion chamber and is conveyed to an outside conveyor. Hot gases fire the boiler atop the unit and, at the same time, are cooled to the point where remaining particulate matter can be removed by a precipitator.

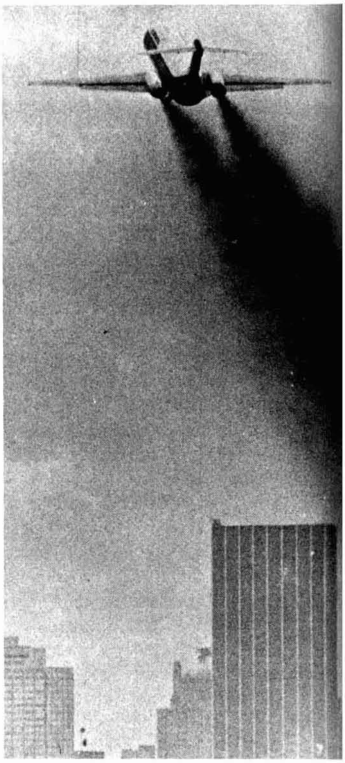
Although Ecology Industries has not yet tested a completed installation, the first system complete with a waste heat recovery unit is scheduled to go into operation in a Chicago hospital later this month. Several units without waste heat recovery have been installed and are working fine. HMM

Total package includes waste heat recovery



Next federal cleanup target: aircraft noise and emissions

Airplanes are cleaner and quieter than they used to be, but EPA thinks there's still room for improvement



The airplane is one of man's most ingenious inventions and represents a giant technological step forward in time and travel. As air traffic and operations increased, people living or working near airports began complaining about noise, and more recently, air pollution. As a result, the aircraft industries are under fire to produce quieter planes with few or no emissions.

Noise is difficult to picture, describe, or define, but it has become an environmental hazard, a pollutant to be reckoned with. Some serious health effects have been correlated with prolonged exposure to noise. The medical opinion is that noise levels above 85 decibels [dB(A)] over an extended period of time pose a serious threat to human hearing and the rest of the body. Besides obvious hearing effects on the ears, the heart, blood vessels, hormone output by glands, acid secretion by the stomach, and the ability of eyes to focus can be adversely affected by sudden exposure to noise (for more on noise, see ES&T, February 1972, p 124).

British studies show that families living near an airport may have a higher incidence of mental illness. Of course, these are extreme effects, and lesser exposure to noise may only be annoying and cause irritability. However, noise complaints about aircraft have been continually increasing as airports become bigger and busier and cities expand and build closer to airport operations. In fact, over the next 10 years, domestic air traffic is expected to grow 8.9%/yr.

In discussing aircraft noise, it's necessary to describe aircraft and engines. Two generations of aircraft are in commercial service today. The old generation encompasses almost the total of today's present commercial fleet of turbofan-powered aircraft (similar to jet engine although some of the air passing through bypasses the engine combustion system): four-engine Boeing 707 and 720, the McDonnell-Douglas DC8, and the Convair 880 and 890; the three-engine Boeing 727; and the twin-engine Boeing 737 and McDonnell-Douglas DC9. Turbofan engines are responsible for 85% of flights in the U.S.

The Pratt & Whitney JT8D gas turbine engine is used in the 727, 737, and DC9 planes and accounts for 55% of the 3000 commercial aircraft in use. The JT3D gas turbine engine is used in the old-generation longer range aircraft. Both types of engines are noisy and smoky. The jet exhaust (roar) and the fan (scream) are the two major noise sources in an engine.

The new "jumbo jets," the Boeing 747, Douglas DC-10, and Lockheed L1011 (Tristar) represent a new generation of aircraft and, in fact, meet the present Federal Aviation Administration (FAA) noise certification standards. The engines in these aircraft (with reduced noise and smoke emission characteristics and more fuel consumption efficiency) are classified as "high bypass" turbofan engines, in contrast to low bypass engines of the older planes. In other words, for the amount of thrust generated in a high bypass engine, the amount of noise does not increase proportionately. The high bypass engine moves air at a lower velocity through the jet exhaust; low bypass engines compress air and force it through, and produce more "whine."

FAA, the U.S. government agency which certifies aircraft and maintains strict control over safety, promulgated in 1969 Federal Air Regulation 36 (FAR 36) which sets noise limits for commercial aircraft. FAR 36 was established after Congress passed the Aircraft Noise Abatement Act directing FAA to regulate noise and sonic boom generated by aircraft.

FAA uses the international Effective Perceived Noise Decibel (EPNdB) in measuring noise levels. EPNdB includes tone levels as well as duration of noise and varies from −10 to +5 difference from dB(A) for the same sound. The FAA noise limits for takeoff and landing are 108 EPNdB for aircraft with maximum load. Measurements for FAR 36 are taken 3.5 nautical miles from brake release or beginning of takeoff roll, 0.35 nautical mile from the center line when the plane is halfway down the runway, and underneath the plane after takeoff. For landing, measurements are taken one nautical mile from touchdown and at the same side and overhead locations as in takeoff.

The DC-10, for example, with a 98 EPNdB takeoff measurement and an approach rating of 106 EPNdB, exemplifies the new aircraft that meet FAA noise regulations. Even though these new planes meet FAA standards, many citizens believe noise levels to still be too high and still capable of being annoying or injurious to health (see p 222).

Reducing noise

As for retrofitting (aircraft or engine modification) old-generation aircraft to reduce noise, R. P. Skully, director of FAA's Environmental Quality Office, says retrofitting methodology has not yet been proved airworthy and safe (the projection is five years) and that it would cost about $1 million to retrofit a four-engine plane for noise reduction.

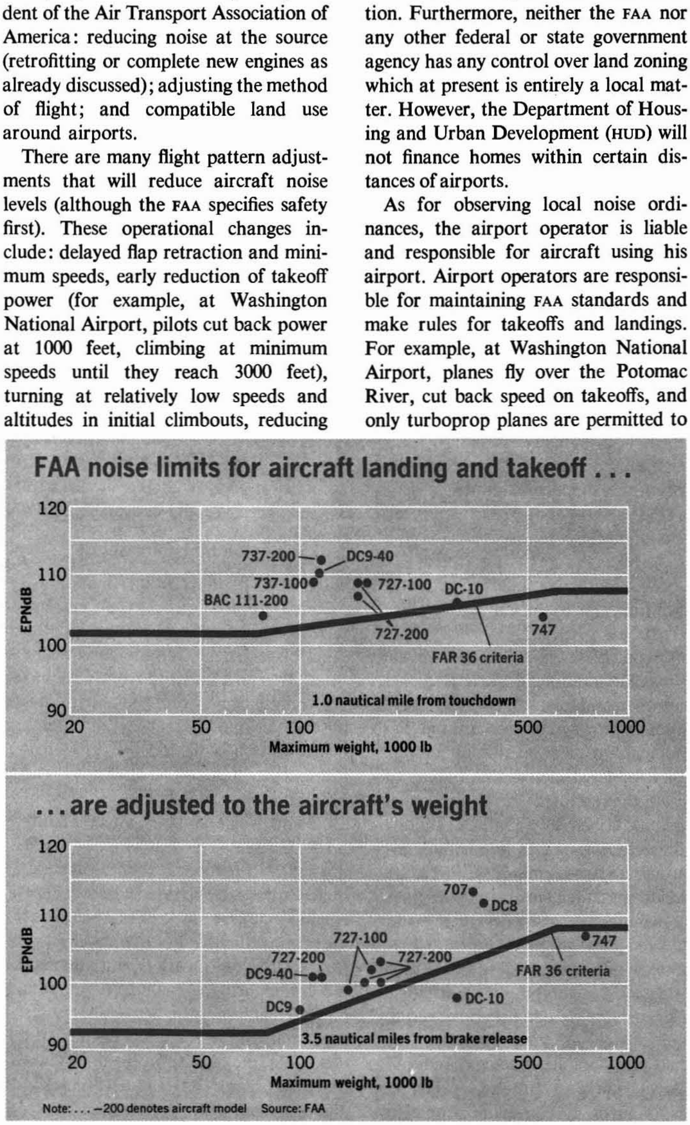
By revamping present JT8D or JT3D engines and by using different operational procedures, FAA is aiming to reduce noise to 108 EPNdB for takeoff and 104 EPNdB for landing for the older planes. However, FAA and aircraft industries argue that if costly changes reduce noise only a couple of decibels, people cannot tell the difference, and the action taken is not justifiable.

Other measures can reduce aircraft noise, says William Becker, vice-president of the Air Transport Association of America: reducing noise at the source (retrofitting or complete new engines as already discussed); adjusting the method of flight; and compatible land use around airports.

There are many flight pattern adjustments that will reduce aircraft noise levels (although the FAA specifies safety first). These operational changes include: delayed flap retraction and minimum speeds, early reduction of takeoff power (for example, at Washington National Airport, pilots cut back power at 1000 feet, climbing at minimum speeds until they reach 3000 feet), turning at relatively low speeds and altitudes in initial climbouts, reducing overall climbout speed, extending time spent in initial climbout, using preferential runways with crosswinds up to 15 knots and 90° to runway heading (rather than always landing into the wind regardless of runway location), using air tracks over seas, rivers, and unpopulated areas, approaching airports at 1500 feet or above for as long as possible before descending, and rescheduling flights or reducing flights (tremendous economic problems occur here).

Compatible land use is hindered by unscrupulous developers who build and sell homes to buyers who may not be aware of the potential noise situation. Furthermore, neither the FAA nor any other federal or state government agency has any control over land zoning which at present is entirely a local matter. However, the Department of Housing and Urban Development (HUD) will not finance homes within certain distances of airports.

As for observing local noise ordinances, the airport operator is liable and responsible for aircraft using his airport. Airport operators are responsible for maintaining FAA standards and make rules for takeoffs and landings. For example, at Washington National Airport, planes fly over the Potomac River, cut back speed on takeoffs, and only turboprop planes are permitted to use airport facilities between 11 P.M. and 6 A.M.



Note: . . . —200 denotes aircraft model Source: FAA

FAA and Boeing Co. are collaborating in engine noise reduction programs by designing acoustical treatment techniques for the Pratt & Whitney JT8D and JT3D engines. Aircraft industries themselves are actively working for quieter planes by redesigning both air frames and engines.

Enforcement

Proposed state laws in California, New York, Maryland, and Connecticut would, according to Franklin Kolk, vice-president of Development Engineering, American Airlines, "although primarily directed at SST's, sharply restrict—if not ban completely—all existing commercial jet aircraft from these states." California's regulations have been suspended for a year. No state has yet actively enforced noise control regulations.

Present legislation in Congress may reduce FAA's power in noise control and place enforcement action under the aegis of the federal Environmental Protection Agency (EPA). The noise act introduced by the administration and approved by the Senate provides that: EPA would coordinate all activities in the federal government relating to noise; all federal departments and agencies would incorporate into their programs the same requirements that apply to the rest of the country (except in some cases of national defense); EPA would approve any noise standards issued by the FAA; the EPA administrator would publish criteria on the effects of noise and then set standards for transportation equipment and construction equipment with internal combustion engines; and no state could establish standards different than those set by the federal government (although they could establish zoning restrictions).

The House has changed some portions of the bill; in particular, the House version says that EPA would only be a consultant to FAA, rather than having veto authority over FAA noise regulations. With the extensive public interest in the matter, EPA officials hope that the legislation will be passed this year.

Emissions

Aircraft emissions are presenting more problems for the aircraft industries. Since the Clean Air Act of 1970 empowered EPA to set emission standards for air pollutant sources, EPA officials

Common noise levels

Sound quality	Decibels	Sound source
Threshold of feeling/ pain	120	Rocket engine Ram jet Turbojet; 7000 lb thrust
Deafening	110 100	Propeller aircraft Boiler factory Nearby riveter Thunder Subway and elevated trains
Very loud	90 80	Woodsaw Loud street noises Noisy factory Pneumatic drill Police whistle
Loud	70 60	Noisy office Average traffic Normal radio Average factory
Moderate	50 40	Noisy home Average office Ordinary conversation Quiet radio
Faint	30 20	Quiet home Private office Average auditorium Quiet conversation
Very faint—threshold of audibility	10 0	Rustle of leaves Whisper

Source: AMF Beaird, Inc.

Aircraft engine emissions[a]

(thousands of tons/year)

Type of contaminant	All civil aircraft in U.S.
Carbon monoxide	924
Hydrocarbons	152
Nitrogen oxides	16
Particulate matter	11

[a] Based on 1967 average annual emissions.
Source: HEW

Aircraft emissions are decreasing

(During Takeoff and Landing)

	Total emissions, lb/engine	Particulate matter, lb
Piston engines	111.6	0.20
Jet engines 1958	55.2	0.52
Fan jets 1961	49.1	0.20
JT8D standard 1964	25.0	0.42
JT8D smoke fixed 1970	19.1	0.19
JT9D engines 1970	33.5	0.15

Source: Air Quality Emission Group, HEW.

are casting scrutinizing eyes toward aircraft. Although FAA officials formally refuse to list or discuss any air pollution from aircraft (pending release of EPA proposed standards), commercial planes do in fact emit carbon monoxide, unburned and partially oxidized hydrocarbons, nitrogen oxides, and particulate matter. Sulfur dioxide is emitted from aircraft in miniscule amounts, say EPA officials and are not included in proposed standards; however, odors are another complaint, but are difficult to quantify since a sensitive mechanical analyzer does not yet exist. "We would like to control odors from aircraft operations, but we don't know how to do it yet," says George Kittredge, EPA's chief, Mobile Sources Emissions Characterization and Control.

When aircraft emissions are placed alongside other air pollution sources or compared on nationwide basis, the percentage is indeed small. For example, aircraft emissions represent 3.3% of all sources, and that emitted by the air carriers represents 1.2% (the remainder being military and private aviation). However, these figures can be misleading, and EPA is concerned with excessive pollutant concentrations in localized areas around airports, which are not reflected by nationwide figures.

EPA officials contend that aircraft emissions in the airport area exceed ambient air quality standards—although FAA disputes this. EPA aircraft emission measurements and traffic density studies show that 32,661 tons/year of pollutants are released around the Los Angeles Airport, 4176 tons/year from Washington National Airport, and 29,542 tons/year in the Chicago O'Hare International Airport area. These emissions contribute significantly to air quality deterioration in those localized areas, EPA maintains.

About a year ago, EPA began studying the impact of air operations on air quality for large metropolitan areas to indicate the feasibility of reducing such emissions either by handling aircraft in different ways or by mechanical alterations. Private laboratories made emission measurements on new engines that manufacturers are developing and in-use engines through the cooperation of United, American, and Trans World Airlines, and military installations. Northern Research & Engineering Corp. looked at such questions as: Would emissions be effectively reduced by towing aircraft with tugs while on the ground or by conveying people to the aircraft (as at Dulles International Airport)? Would it be helpful to operate fewer than the full number of engines on the ground, at more efficient power settings? Would these methods be more effective than expensive modifications to engines themselves? How soon could this be done? How much would this cost?

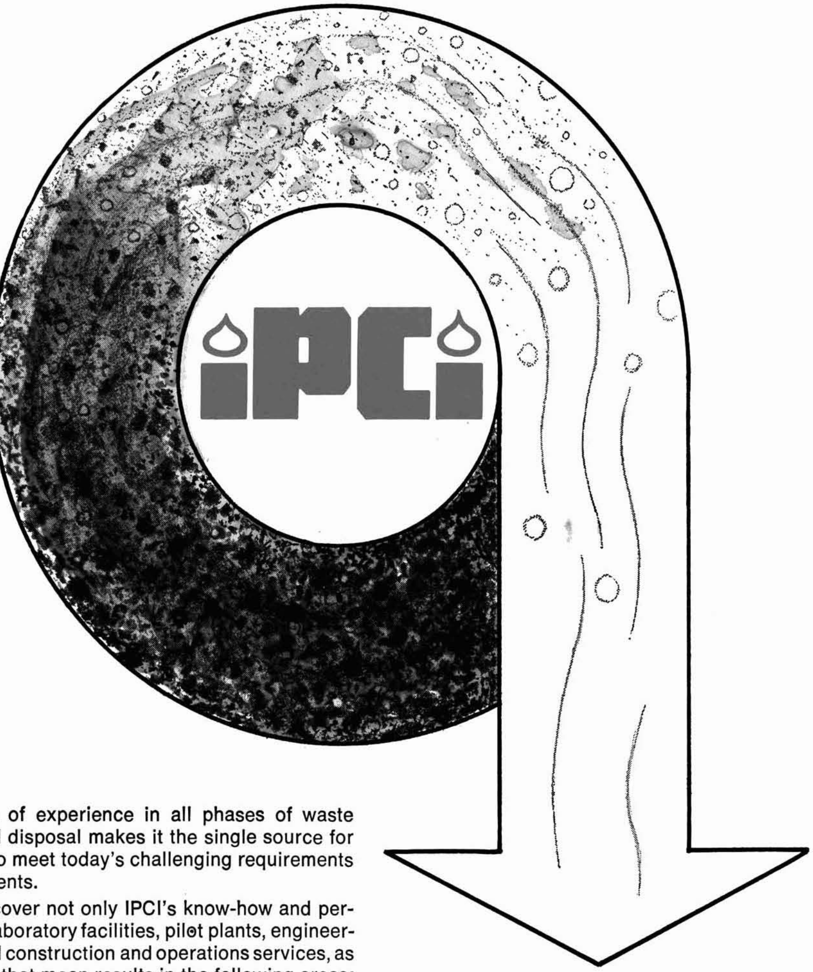
Northern also modeled the patterns of air movements around several major air terminals (New York, Chicago, and Los Angeles) to identify the relationship between pollutants emitted and characteristics of the area (frequency of operation, prevailing weather conditions, and surface transportation and stationary emission sources in the area).

Proposed emission standards for aircraft, submitted internally in EPA last September, are designed to be implemented into the existing framework of FAA certification procedures. At press time, EPA proposed standards were receiving final scrutiny before being publicly released. Officials recognize that varying amounts of time are necessary for different approaches to emission control. "The package of standards considered this sort of thing," emphasized Kittredge.

The aircraft industry has been working on smoke control from exhaust for several years. FAA, Pratt & Whitney, McDonnell-Douglas, and Boeing joined together in a smoke retrofit program for the JT8D engine. This engine is used in the 727, 737, and DC-9 planes which account for 55% of the engines in use. These planes are the short-to-medium range fleet but have a 4-1 operation ratio (takeoffs and landings) when compared with longer range planes.

This retrofitting process concentrates on the burner cans where combustion takes place. There are nine burner cans in each engine, and the front part has been redesigned for more complete combustion of fuel to reduce the smoky, black carbon emissions. This retrofitting costs about $5000/engine. The program will be completed by the end of 1972 and will eventually affect 31 airlines. Incidentally, this smoke retrofit process also reduces carbon monoxide, hydrocarbons, and particulate matter emissions. Nitrogen oxides remain at the same or slightly increased levels.

According to Pratt & Whitney, one of the leading engine manufacturers, the bigger engines and higher temperatures encountered in new aircraft engines will make NO_x the biggest problem. Engines of the future may have to be completely different from those presently in use to control NO_x. CKL



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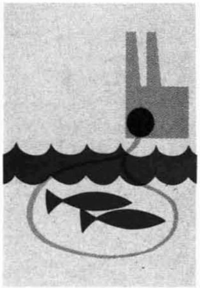


Thermal discharges: ecological effects

Degradation to aquatic ecosystems from cooling water discharges hasn't occurred at some power plants; however, future expansion will make waste management more difficult

During the past several years, public interest in environmental quality as it relates to central-station power generation has intensified. The continued dominant role of thermal power plants to meet expanding electrical demands has focused attention on the effects of power plant–heated effluents on aquatic life.

Thus, one of the most important questions being asked today is, "What are the environmental effects resulting from waste heat additions to rivers, lakes, estuaries, and oceans?" Possible thermal effects are of concern to sports and commercial fishermen who want game and commercial species of fish available for their enjoyment and livelihood; conservationists who want the ecosystem preserved in its "natural" state; government regulatory agencies that set water temperature criteria and standards; and various users of water for cooling purposes who must discharge heated water within certain criteria and standards.

Water use

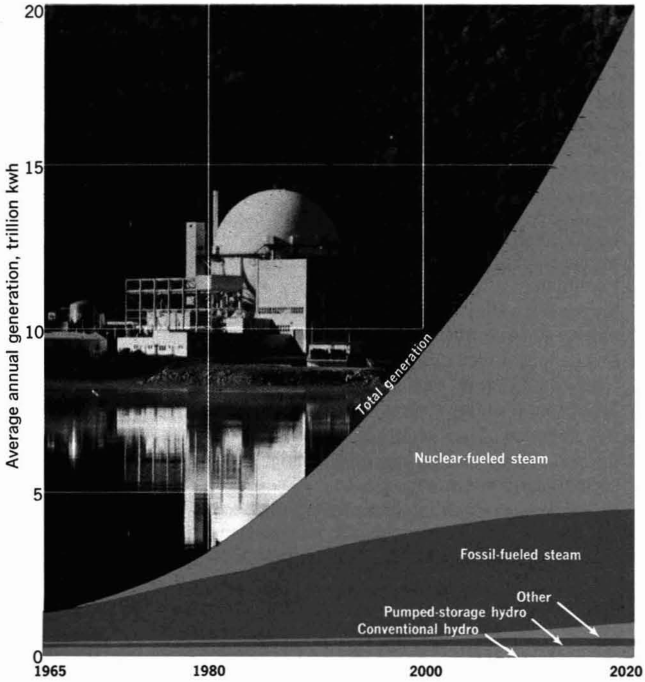
Estimated projections indicate that future electric power requirements in the U.S. are expected to double approximately every 10 years. Even though hydroelectric power generation is expected to increase, steam-electric power (including both fossil- and nuclear-fueled plants) is expected to supply over 90% of the requirements in 2020 (Figure 1). By the year 2000, nuclear power will supply over 50% of the energy produced.

Of utmost importance to the steam-electric power industry is available water for condenser cooling. Estimated water use and projected requirements, by purpose, for the U.S. was forecasted in the 1968 report of the Water Resources Council (Table I). In 1965, the steam-electric power industry used approximately 33% of the total water withdrawals. In 1980, the electric power industry will use about 44% of the total water withdrawals, and the forecast for water withdrawal for the year 2020 will be 67% of the total. Projected consumptive use (nonreusable) of the total water withdrawal is about 23%, while projected consumptive use for water withdrawal for steam-electric power is only slightly greater than 1%.

Waste heat rejected to cooling water will be a function of the thermal ef-

Figure 1

Nuclear power to supply majority of electricity



Arthur A. Levin, Thomas J. Birch, Robert E. Hillman, and Gilbert E. Raines

Battelle Memorial Institute
Columbus Laboratories
Columbus, Ohio 43201

feature

TABLE I. Estimated water withdrawals in the U.S.

(Million gallons daily)

Type of use	Used 1965	Projected requirements 1980	2000	2020
Rural domestic	2,351	2,474	2,852	3,334
Municipal (public-supplied)	23,745	33,596	50,724	74,256
Industrial (self-supplied)	46,405	75,026	127,365	210,767
Steam-electric power:				
Fresh	62,738	133,963	259,208	410,553
Saline	21,800	59,340	211,240	503,540
Agriculture:				
Irrigation	110,852	135,852	149,824	160,978
Livestock	1,726	2,375	3,397	4,660
Total	**269,617**	**442,626**	**804,610**	**1,368,088**

Source: U.S. Water Resources Council

ficiency of the particular steam-electric plant. With the steam temperatures currently in use in large fossil-fueled plants, the maximum theoretical thermal efficiency is slightly above 60%. The thermal efficiency of the best operating fossil-fueled plants is presently about 40%.

Because of a lower thermal efficiency for nuclear plants (about 33%), cooling water requirements are presently greater than for fossil-fueled plants of the same electrical generation capacity. Approximately 10% of the gross waste heat is dissipated directly to the atmosphere through the stack in the fossil-fueled plant, while none is dissipated in this manner for the nuclear-fueled plant. Thus, about 50% more waste heat is rejected to the condenser cooling water from the nuclear plant.

Any method of reducing waste heat discharged into aquatic ecosystems would be useful where a temperature rise in receiving waters is unacceptable. Several options can reduce waste heat discharged from steam-electric plants into the aquatic ecosystem. Although thermal efficiencies from fossil-fueled steam plants have reached a plateau, molten salt breeder reactors and high-temperature gas reactors should increase thermal efficiencies for nuclear plants almost to 45%. However, these improvements will probably not be available for at least a decade. Since a dramatic increase in thermal efficiency for steam-electric plants is not forecast for the immediate future, recycling or retaining condenser cooling water may be necessary to reduce waste heat effects on aquatic ecosystems.

By utilizing projections of both fossil- and nuclear-fueled electrical generation capacity, data on thermal efficiencies of steam-electric plants, and water withdrawal forecasts, the quantity of waste heat that will be dissipated into the condenser cooling waters of steam-electric plants can be determined. The total quantity of waste heat discharged to condenser cooling waters by the electric utility industry will more than double from the year 1967 to the year 1980. The contribution of heated effluents from nuclear-fueled power plants in this time period increases from 1% to 45%, while contribution of heated effluents from fossil-fueled power plants decreases from 99% to 55%.

These waste heat values should be placed in proper perspective. For example, the total quantity of water used for steam-electric power for 1980 (assuming once-through cooling water) is estimated to be 193 million gallons per day, while the estimated annual heat rejection for steam-cycle systems for the same year is 11,700 trillion Btu's. This quantity of heat, assuming a once-through cooling cycle, will raise the temperature of the cooling water approximately 20°F. Temperature increase in the condenser cooling water for condensers installed in the past ranges between 10° and 30°F. Thus, the estimated 20°F rise in once-through condenser cooling water seems to be a reasonable estimate although this will vary according to each specific site location.

Site Studies

Most studies directly concerning the effects of heated effluents on aquatic biota at the site of electrical power generating stations are relatively recent, and few results have been published to date. Most field investigations are presently in progress.

Continuing studies of the ecological effects of thermal discharges have been conducted at the Hanford Nuclear Complex on the Columbia River (Wash.). These studies conducted over the last 25 years were mainly oriented toward the salmonid fishes because of their high value to the Columbia River commercial and sports fisheries. Although the temperature of the undiluted reactor effluent would be lethal to the fish, waste heat discharged by the Hanford reactors to the Columbia adds only a relatively small heat increment to the widely variable seasonal river temperature (less than 40°F to greater than 65°F). Also, because of the hydraulic characteristics at the outfall and the swimming behavior of the fish, many seaward migrant salmonids may be swept to cooler waters and not actually experience the direct effluent plume.

Laboratory and field studies concerning biological effects of Hanford waste heat on salmonids shows no demonstrable evidence of damage to the salmonid resources. There simply has not been any evidence to indicate kills or unreasonable risks despite a long history of heated discharges from the Hanford reactors. However, direct extrapolation of Hanford's results to another site, even in the Columbia River system, must be made only with due consideration for the uniqueness of each ecosystem as the snow-fed Columbia River is a large, cool river and not typical of many U.S. river systems.

The Chalk Point fossil-fueled steam generating plant on the Patuxent River (Md.) has been studied since 1963. Two 335-MW units use estuary water for condenser cooling with a once-through cooling system. The condenser cooling water temperature increase is designed to be 23°F under winter operating conditions and 11.5°F during summer conditions. While no major detrimental effects of thermal additions have been noted, changes have occurred in various populations which may be attributed to heated cooling water discharges. Epifaunal populations in the intake and effluent canals of the Chalk Point plant provide a number of interesting results. Among them was: • a higher rate of production was found in the effluent canal than in the intake canal during all months studied • average production in the effluent canal was nearly three times as great as production in the intake • an increase in the maximum size of the barnacle, *Balanus*, was noted in the intake and effluent canals over those in the Patuxent River itself. During July and August, the warmest months, there was a decline in the number of species in the effluent canal and the anemone, *Sagartia*, and, the tunicate, *Molgula*, were not noted in the effluent canal, although both were in abundance just outside the effluent canal.

The power plant has not added enough heat to the Patuxent River to exceed the thermal tolerance of the zooplankton species studied. On the other hand, phytoplankton destruction and productivity suppression have been reported in the cooling water supply of the Chalk Point plant, although chlorination may be partly responsible for the mortality. Also, oysters in the Patuxent River have high copper levels. The rate of copper uptake in the oysters could have been enhanced by the water temperature increase, or copper concentrations in the water may have increased due to operation of the Chalk Point plant. However, no major effects on growth, condition, or gonad development were shown by oysters on natural bars near the plant.

At the Contra Costa Power Plant (1298 MW) on the San Joaquin River, (Calif.), studies showed that passing young salmon and striped bass through cooling condensers was far less hazardous than screening them at the intake. At the same plant, young salmon could tolerate an instantaneous temperature increase to 25°F for 10 min with no mortality.

At the Morro Bay Power Plant (1030 MW) (Calif.) on the Pacific Ocean, healthy populations of the pismo clam, *Tivela stultorum*, have been maintained over the full 13 years that the plant has been in operation.

The Humboldt Bay Nuclear Plant (172 MW) in California is the first nuclear plant in the U.S. utilizing estuarine waters for cooling and is located on the Pacific Ocean about five miles from an important shellfish area. Studies at Humboldt Bay showed that the elevated temperature regime of the discharge canal was favorable for the natural setting of native oysters (*Ostrea lurida*), cockles (*Cardium corbis*), littleneck clams (*Protothaca staminae*), butter clams (*Saxidomus giganteus*), gaper clams (*Tresus nuttalli*), and a half dozen other bivalves (even though some passed through the plant's condenser system).

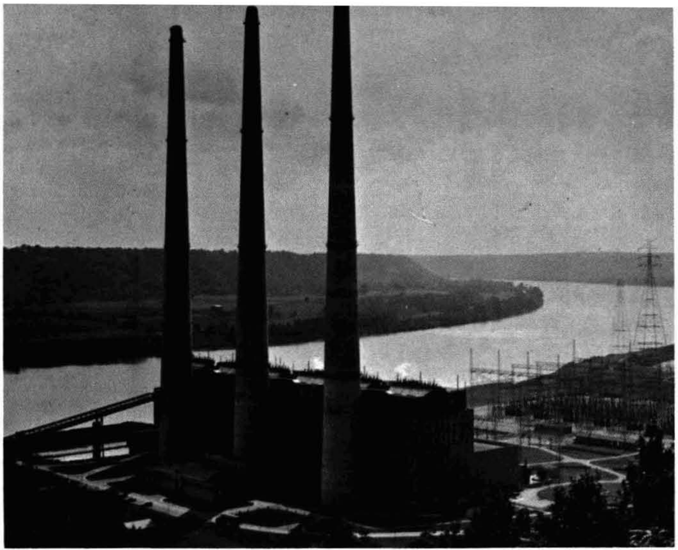
The effects of heated discharges from the Connecticut Yankee Nuclear Plant into the Connecticut River (Conn.) are examples of a well-documented study started in 1965, about 2$^1/_2$ years before the plant began operation. The plant was designed to produce 562 MW with a temperature rise of 20°F in the condenser cooling water. The major thermal study areas were fish studies; benthic organisms studies; bacteriology, microbiology, and algae studies; hydrology studies; and temperature distribution predictions and measurements.

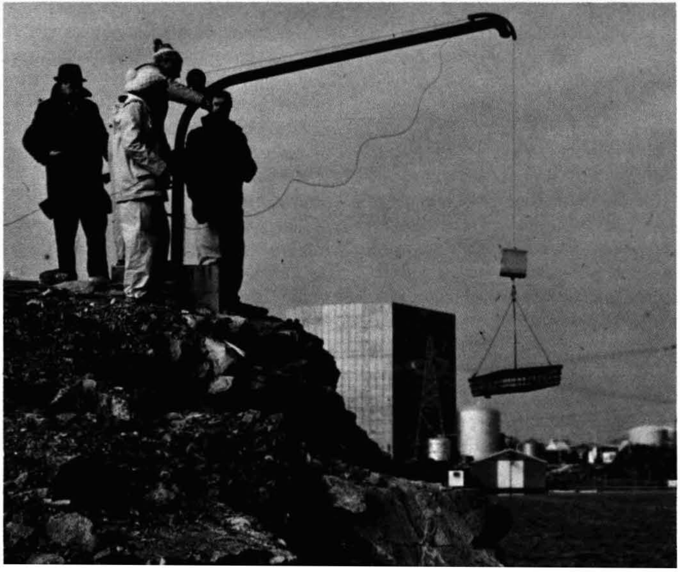
The Connecticut Yankee Plant has now been in operation for about four years. No drastic changes have been observed to date in the overall ecology of the Connecticut River as a direct result of the addition of thermal effluents.

However, a statement in the summary of all the environmental studies that were done at Connecticut Yankee, emphasizes that as yet no information is available on the possible sublethal effects of the thermal discharge. Although no fish kills have occurred since the plant operation began, the white and brown bullhead catfishes undergo a marked weight loss (average of 20%) in the warm water of the effluent canal despite a constant availability of food in the canal.

Studies are being conducted at Turkey Point in Biscayne Bay, Fla., where two fossil-fueled units of 432 MW each are in operation, and two nuclear plants of 721 MW each are scheduled to begin operation. Heated effluents from the plant have reduced the diversity and abundance of algae and animals in small areas adjacent to the mouth of the effluent canal. Many plants and animals in a 125-acre area where temperatures have risen 4°C (7.2°F) above ambient have been killed or greatly reduced in number. In a second zone of about 170 acres, corresponding to the +3°C (5.4°F) isotherm, algae have been damaged, and species diversity and abundance have been reduced. In the latter area, mollusks and crustaceans increased somewhat, but the number of fishes decreased.

DISCHARGES. Power plants, such as this one (right), use tremendous amounts of water for process cooling and usually discharge the then heated water into the body from which it came. To assess effects of heated effluents on aquatic biota, . . .





. . . Battelle scientists sampled organisms in the receiving waters (second from top), simulated river ecosystems mathematically (above), and compared oyster growth before and after power plant startup (left) prior to outlining the conclusions discussed

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Studies at the Martins Creek Plant on the Delaware River (Pa.) showed that the heated waters appeared to have attracted fish and enabled them to actively feed throughout the colder months of the year to a greater extent than they normally would, although there was no conclusive evidence that heated waters actually increased fish production or growth rates.

Studies at the Petersburg, Ind. Plant (220 MW) on the White River (Ind.), report that there is no evidence that any adverse effects on fishes, such as death, impaired growth, insufficient reproduction, increased disease, and movement or lack of movement are being observed at Petersburg or in the entire White River with the exception of fish movement away from water above 93°F.

The White River has a sandy bottom and is quite turbid. The principal pollutants are floodwater and suspended material in the water. The major aquatic species at Petersburg are the spotfin shiner, bullhead minnow, spotted bass, longear sunfish, gizzard shad, carp, and white crappie. Since sand and silt are deposited when floodwaters recede, researchers who studied the White River believe that money for thermal pollution abatement could be better "applied to the certain and very real need for flood and bank control."

Recommendations

The result of several ecological studies around actual operating power plants is that, with a few exceptions, there has not been any major damage to the aquatic environment from the heated effluents of existing power plants. However, in the future years, as larger power plants become operational, accompanied by multiple units at a single site, environmental management of heated effluents at these sites will become more difficult.

Standards for limiting the thermal loads imposed on aquatic systems have evolved with the expansion of the electrical generating industry. However, without feasible alternate methods to produce electrical power without waste heat, there are only a limited number of alternatives. At one extreme is employing methods which recycle cooling water and add no waste heat to natural waters. This extreme is not required to ensure well-balanced aquatic communities. The other extreme is to permit unlimited thermal loading on aquatic systems which would, no doubt, be disastrous (based on the projected use of marine and freshwater resources for industrial cooling purposes). The only option remaining is discharging waste heat to waters in amounts approaching the assimilative capacity of the waters in question. Heat generated beyond those amounts will have to be dissipated by methods which recycle cooling water. Based on the knowledge available at the present time, the last option seems to be the only reasonable approach.

Pursuing this course requires total commitment to determine the assimilative capacities of freshwater and marine resources. Management and surveillance programs will be essential as will cooperation between industry and regulatory agencies. Many factors contribute to receiving capacities, and requirements for producers of waste heat will be highly variable depending on their location. Power plant sites should be chosen with the advice of competent ecologists, and base line ecological surveys should begin as soon as a suitable site is selected.

While lethal effects of heated water discharges on fish and other aquatic organisms should present little problem, assuming proper discharge procedures, the sublethal effects of these heated water discharges may produce significant changes in populations. These sublethal effects could produce physiological changes that would decrease growth rate and prevent reproduction. Future studies should be designed to obtain a better understanding of sublethal effects.

The entire food chain is of extreme importance in the balanced aquatic ecosystem. Particular aquatic organisms or plants that fish eat can be affected by waste heat from power plants. Eliminating a single component of this ecosystem would affect the feeding and growth of organisms on all higher trophic levels.

Data are not yet sufficient to permit a proper understanding of the dynamics of this ecosystem. Many laboratory studies have led to understanding many of the physical-chemical functions of aquatic organisms as well as dispersion in water systems. Consequently, regulations based on these studies will be designed to minimize all possible risks of catastrophic kills of desirable organisms. Field studies are necessary to determine the "real-life" mechanisms occurring in the aquatic ecosystems. While laboratory studies are a necessary part of understanding, extrapolating laboratory measurements to field conditions must be done cautiously.

Answers to considerations which could alter regulations will have to be provided from nongovernmental sources such as the electric utilities. As the assimilation capacity of the environment is reached, it is increasingly important to consider long-term effects. Modest investment programs looking at the ecosystem to develop and verify predictive capabilities could themselves pay handsome dividends.

To utilize more fully the assimilative capacities of natural waters to dissipate waste heat, greater ecological management will be required, and operators of steam-electric stations will have to play an important role. In addition to considering effects of heat rejection during normal plant operation, attention must be focused on the effects of temperature changes, even though the actual temperatures may be below the lethal limit.

An effort should be made to establish the assimilative capacity of all natural waters to be utilized for cooling purposes. Based on predictions from the biological, chemical, and physical studies, limiting conditions should be established to accommodate the idiosyncrasies of each site. There is no substitute for on-site experimentation utilizing the resident populations and the local water. After a new unit comes on-line, a less intense program of surveillance should become a matter of routine at all plant sites.

As more of the larger power plants become operative and as more sites are required, the ability to predict the response of the aquatic ecosystem to the heated water discharges must be improved. The systems approach to study ecosystem dynamics offers a valuable tool to individuals who make decisions concerning siting and design criteria for power plants.

Criteria and regulations can only be altered with confidence when accurate predictions can be made. The pre- and post-construction studies by the utilities, if expanded to consider predictive aspects, offer an opportunity to obtain needed data on the system and to verify the predictions.

The satisfactory performance of existing steam-electric plants supports the belief that controlled amounts of heated water can be added to aquatic systems without producing adverse biological consequences. Therefore, in the absence of evidence of damage to the ecosystem involved, it would be difficult to justify requiring steam-electric stations, which have been operating for some time, to install cooling devices because they are not meeting newly

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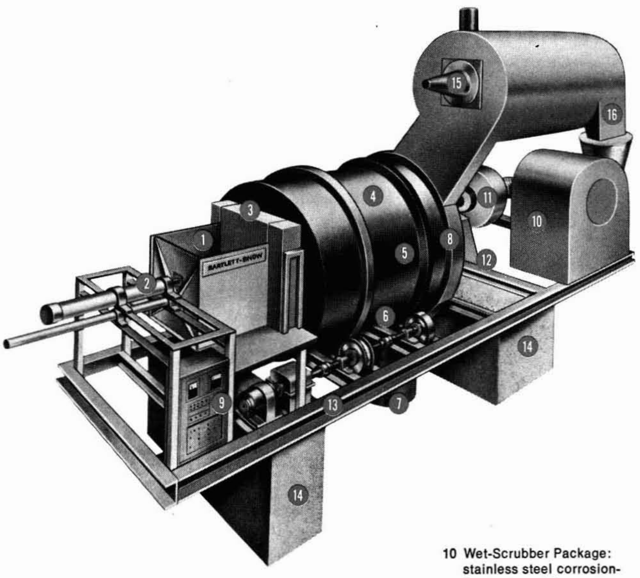

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adopted state or federal regulations. A careful investigation of the issue at each specific plant site should be done prior to any action being taken.

In order to understand the dynamic behavior of the aquatic ecosystem, some long-term studies are required. Of course, there are many and varied types of aquatic ecosystems so that typical rivers, lakes, estuaries, and ocean systems should be studied in a variety of climates. Industry, and, in particular, the steam-electric industry, should participate in these studies since the power plants will be the major waste heat contributor to the aquatic ecosystem. Waste heat from the power plants will become a more significant discharge to the aquatic ecosystem in the future. It may be that the effects of waste heat could be beneficial when other pollutants, such as sewage and industrial waste, are limited or removed (as reported for the Thames River in England).

Although there has been no apparent major damage to the aquatic ecosystems by cooling water discharge, there have been ecological changes. The complex interrelationships of species, populations, and communities in an ecosystem is the result of years of evolutionary trial and error. Therefore, although no major mortalities are noted, shifts in species diversity or abundance might upset delicate balances which exist, and results might not be known for years.

There are some bodies of water presently capable of accommodating more thermal loading without incurring adverse effects on the aquatic biota, while the assimilative capacities of some others have already been exceeded. Thus, it is imperative to evaluate dynamic changes which are presently taking place in aquatic ecosystems, and to be able to predict what is likely to occur as the electrical generating capacity of the nation increases.

Additional reading

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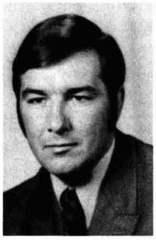
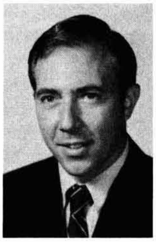
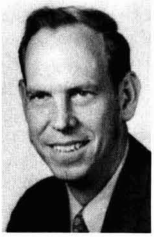


Thomas J. Birch *is a research limnologist with BCL. His work on thermal effects includes laboratory experimentation and field investigations at electric generating stations.*



Robert E. Hillman *is presently chief of Battelle's W. F. Clapp Laboratories in Duxbury, Mass. He is responsible for ecological studies in marine environments adjacent to power plants.*



Gilbert E. Raines, *chief of BCL's Ecology and Environmental Systems Division, is specifically interested in mathematically describing the response of aquatic biota to thermal stimuli.*

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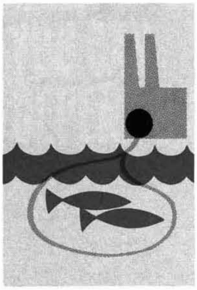
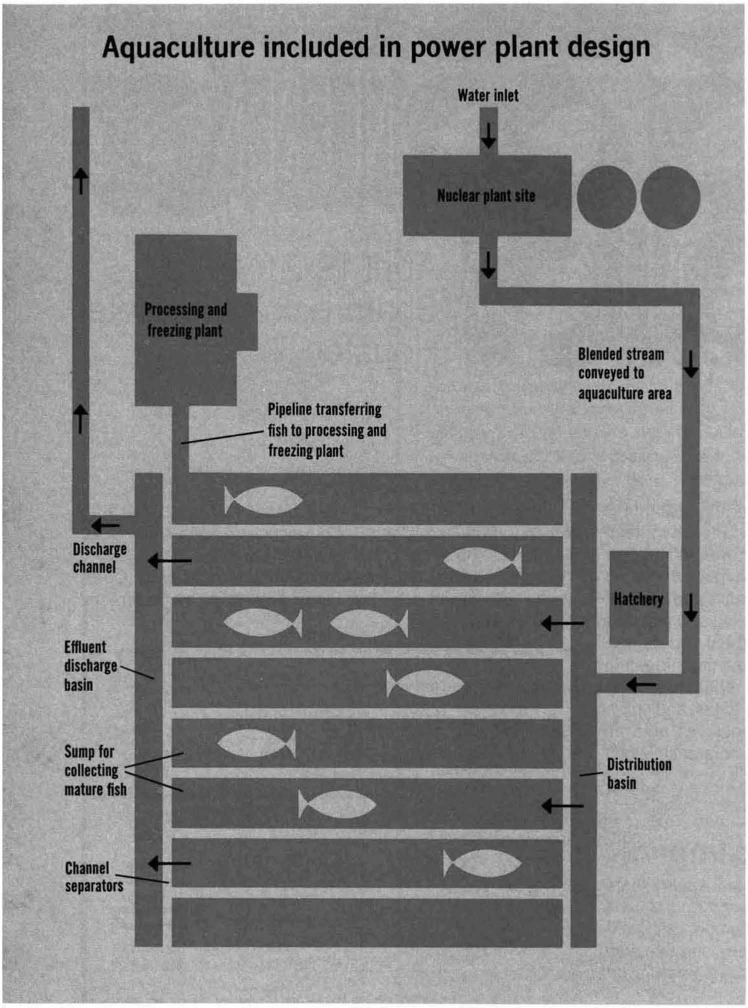


Fish may be raised in warm water discharged from steam electric power plants, but success depends upon costs and profits

Thermal aquaculture: engineering and economics


Aquaculture included in power plant design

Thermal effluents from electric power plants have been a subject of increased environmental concern, and national power demands may double over the next decade. For every kilowatt of electrical energy generated, more than 1 and as high as 2 kW of low-grade thermal energy will be produced and discharged into water or air as a waste.

This waste heat could be considered a resource and examined as to how it may be utilized productively. Very little has been done to demonstrate the value of this waste heat in biological applications, particularly in agriculture and aquaculture.

Much has been published on the potential and possible limitations of utilizing thermal effluents to enhance the culture of aquatic species. Small-scale experiments have been described for shrimp and pompano in the United States, a variety of fin-fish in Great Britain, multispecies culture in Japan, and carp culture in the USSR. However, large-scale application of these effluents for aquaculture will be dependent on its commercial viability. (Figure 1 illustrates increasing demand.)

Status of aquaculture

Aquaculture is a term that in recent times has come to imply a degree of environmental control over the culture medium such that fish yields are enhanced by orders of magnitude. Most impressive are the yields in running water culture with intensive feeding practiced by the Japanese—800,000 to 3 million lb/acre/year. By contrast, hunting wild species on U.S. coastal waters by conventional gathering methods may yield only about 20 lb/acre/year.

feature

William C. Yee
Oak Ridge National Laboratory
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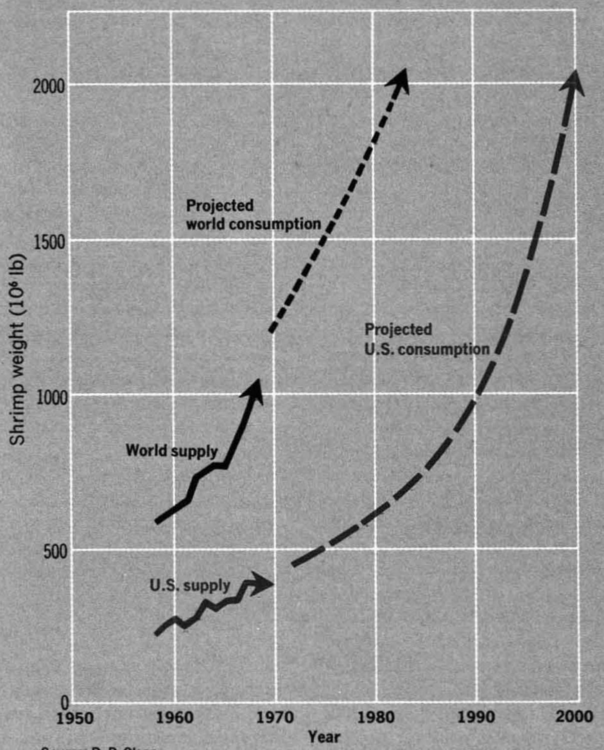
Figure 1

Shrimp consumption is expected to soar



Source: D. P. Cleary

The yield figures demonstrate the potential of aquaculture, but there are also problems. Aquaculture as a technology is still in its infancy. Intensive culture of marine fish species is generally confined to the warm months of the year. The population in culture is dependent on the natural nutrient concentration in drainage from rivers and estuaries. No universally suitable artificial food has been developed yet, and yields may be subject to drastic curtailment by predator attack when the facility is not isolated from the sea.

The thermal discharge from a power plant is a potential source of warm water for maintaining optimum temperature ranges in aquatic environments for year-round fish culture and is a source of flowing water for intensive aquaculture. At large power stations of the 500–1000 MW size, flow volumes of hundreds of thousands of gallons per minute are available.

Precedence for the use of thermal effluents in aquaculture is only of recent vintage. Mollusks such as oysters are currently being cultivated year round on a commercial scale by Long Island Oyster Farms, Inc. (division of Inmont Corp.) using the coolant water of the Long Island Lighting Co. at Northport, L.I.

Intake water, ranging from 40° to 70°F during the year, is warmed by 12° to 18°F and discharged at the rate of 150,000 gpm into a 7-acre lagoon. A continual source of warm water permits year-round culture. Baby oysters from a controlled environmental hatchery are placed on trays, and racks of these trays are immersed into a discharge canal from four to six months. A "finishing" stage follows in which oysters are transplanted to cold water areas to mature. Overall, the growing period is cut in half from about five years under natural conditions to about 2.5 years under culture conditions.

Catfish are being cultured commercially the year round at the fossil-fueled power plant of the Texas Electric Service Co. at Lake Colorado City, Tex. Cages of catfish are put in effluent water in the plant discharge canal that is about 70–75°F in the wintertime. Yields are reported to be the equivalent of 100 tons/acre/year with intensive feeding.

Aquaculture. *Japanese shrimp, raised in warm water, may sell for $11–12/lb*

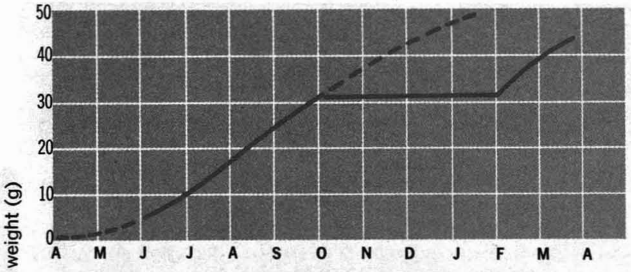
Experimental and/or developmental work in thermal aquaculture includes the following projects: catfish culture at the Gallatin Power Plant of the Tennessee Valley Authority by Trans-Tennessee Industries, oyster culture at Pacific Gas and Electric Plant in Humboldt Bay, and lobster culture at several institutions including a California group (San Diego Gas and Electric Co. and Mariculture Research Corp.) and the Department of Sea and Shore Fisheries, the State of Maine. Florida Power Corp. and Ralston Purina Co. recently announced a joint five-year program to evaluate thermal effluents for the culture of high-value aquatic species including shrimp.

The Japanese have pioneered in the use of thermal effluents for aquaculture. Shrimp, eel, yellowtail, seabream, ayn, and whitefish are among the aquatic species that are being evaluated. Since 1964, at least six generating stations have established demonstration programs. In one reported experiment at a power plant in Matsuyama, shrimp cultured during the summer in controlled temperature ponds had a weight gain of 1.2 times that of shrimp cultured in ponds with no temperature control; in winter, growth as measured by weight gain was seven times that in ambient temperature water.

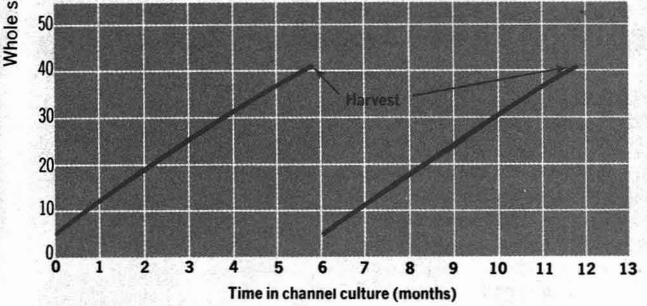
The English commenced tests on the culture of plaice and sole on an experimental basis in 1966 using the thermal discharge from a nuclear plant in Scotland. With some temperature control and supplemental feeding, fish growth from the egg to a 1½-lb size and above was attained in less than two years, which is less than half the time required in nature.

Figure 2

Shrimp normally yield one generation/yr[a], but . . .



. . .warm water could double shrimp production



[a] Shrimp growth in the Gulf of Mexico

Design and cost factors

Fish cultivation in a dynamic system could be a way to utilize a resource that is currently discarded as a waste from steam electric power plants. A flowing stream provides a culture system with a more uniform concentration of dissolved oxygen. Biological oxygen demand is minimized because fish wastes and excess foods are flushed away, and, the system is more responsive to temperature control.

Only the Japanese have developed the technology of culturing shrimp (*Penaeus japonicus*) into a commercially viable operation. Extensive culture is practiced in numerous bays and inlet areas diked off from the sea, while intensive culture with flowing water has only recently been demonstrated.

In the Gulf of Mexico, shrimp growth under natural conditions is limited to the time period between April or May to about October or November when the water temperature ranges from 70° to 85°F. Growth virtually ceases when the water temperature drops below 70°F and does not resume again until the next spring when the water temperature warms up. However, if warm water were available on a year-round basis, two crops instead of one might be produced annually (Figure 2). An increase in the temperature of the water environment from 68° to 78°F increases the growth rate by more than 80%, implying that better control of the water temperature might even produce three crops annually.

A conceptual design is based on the shrimp growth curve but is equally applicable, in principle, to culturable finfish species. As in Japanese culture, a period of up to 60 days is allotted to hatchery growth where mass cultivation from the egg to shrimp fry is done under highly controlled conditions. At this stage, the shrimp population should be developed sufficiently to tolerate the rigor of channel culture with a greater than 90% survival rate.

Continuous culture

For intensive culture of shrimp on a continuous basis, a channel is divided into 26 pens of constant width and increasing length (Figure 3). The surface area of the first pen is proportional to the area under the first segment of the growth curve at the stage where channel culture of shrimp commences. Each succeeding pen area is proportional to the corresponding area formed by a segment of the growth curve.

Shrimp fry are introduced into the first pen of a channel and cultivated for a set period of time until they attain a weight density (g/ft^2) that is common to each succeedingly large pen. They are then advanced to a second pen, and more fry are stocked in the first pen.

Each succeeding week, shrimp are moved forward one pen until the end of the growth period in the 26th pen. They are now ready for harvest, the channel system is in equilibrium, and, ideally, it should be possible to harvest a uniform-sized product, week after week. A dependable source of supply of shrimp fry is assumed, so that, in principle, the number of new young shrimp introduced into the channel system is the same as the number of mature shrimp being harvested.

Flowing water is essential to the practice of intensive fish culture. The linear flow rate has to be high enough to sweep away fish wastes but low enough so that shrimp can maintain their position at the bottom of the channel with minimal expenditure of their food intake energy. The flow rate also has to be high enough to maintain temperature control of the water stream and to minimize atmospheric effects on heat loss.

Weight density is also an important consideration. In the continuous type of operation proposed, there is quite an economic incentive to devise culture procedures such as maintaining constant weight density throughout the culture period which will enhance yield per acre. Aeration is also included in the design so that fish population is not limited by the dissolved oxygen content of the water.

Feed from an external source is assumed so that culture population is not dependent on the nutrient concentration in the water stream. In Japanese culture, specific feeds have been developed for the larval and the post-larval stages of shrimp development. Beyond these stages, low-value fishes constitute the main diet of the shrimp in channel culture. This is suitable for culture economics in Japan where, during the off-season, live species sell on the retail market for $8/lb or more. In the United States, however, premium quality shrimp might be priced at one third of this value. Low-value fish as feed would not be economic in a large-scale continuous culture operation except under unique circumstances, such as a fish processing plant located in the vicinity of the aquaculture facility.

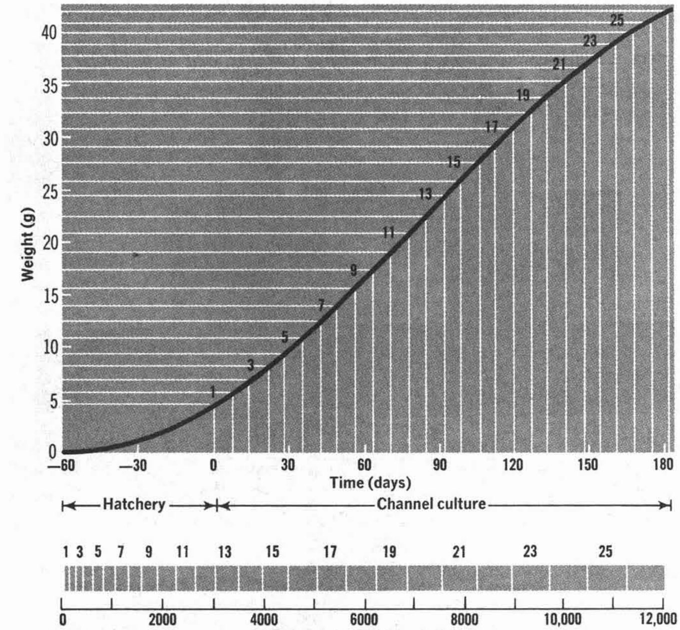
Cost analysis

A hypothetical integrated aquaculture facility that includes a hatchery operation, culture in channels to a marketable size, and a processing plant that converts cultured shrimp to a raw headless frozen product is considered in a cost analysis. A conceptual design is proposed for a plant that is sized to distribute 1000 million gpd of water at 80°F through 17 culture channels in parallel flow. Electricity is furnished from a nearby power plant to drive pumps to blend ambient temperature water with thermal discharge water and to aerate channel water to maintain optimum culture conditions the year round. Power is also furnished for processing and freezing the cultured product. Yields are projected to be 10 million lbs annually when shrimp weight density can be maintained at 110 g/ft^2 over a total water surface of 400 acres.

Capital costs are divided up into land development costs which are variable according to the site chosen, and equipment costs which are fixed. The site-sensitive costs include a water conveyance system to the installation, culture channel construction, and a discharge system. Major capital items for the integrated facility include mechanical equipment to divide each channel into pens, utility and aeration equipment, instrumentation, hatchery, food pelletizing facility, dewatering and harvesting equipment, and shrimp processing and freezing equipment. The total capital cost for such a facility is estimated

Figure 3

Effluent channel design is based on shrimp growth



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to be more than \$47,000/acre (of which \$27,000/acre is for site development).

Annual operating cost is estimated to be \$0.80/lb of headless frozen shrimp. Shrimp feed accounts for 60% of the cost, assuming that the food cost is \$0.10/lb and the food conversion ratio is 3 lbs of dry feed fed/lb of wet meat produced. The remainder of the cost is associated with labor for cultivating and processing shrimp, utilities, processing materials, plant overhead, and contingencies.

With this capital and operating cost schedule as a basis, a sensitivity analysis can be prepared to show the effects of site-sensitive costs, food conversion ratio, wage rate and labor productivity, price of product, and shrimp yield on annual production costs. This is a function of return on investment for an idealized capacity of 10 million lb/year. A standard case for this analysis is: site-sensitive cost of \$27,000/acre, a food cost of \$0.10/lb and a food conversion ratio of 3:1, a labor wage rate of \$2.00/man-hr, and a labor productivity of 100,000 lb of fish handled/man-year. Annual investment costs include only recovery and return on investment and interest on working capital for 90 days. Depreciation is taken over a 15-year period. (Taxes and insurance have been omitted since these items vary from site to site.)

This approach can be used to indicate a range of conditions under which thermal aquaculture might be commercially viable as well as some conditions where such a venture might result in a deficit for the business operation.

One cost factor that was not included in this analysis is the potential expense of effluent waste treatment at the facility. Primary and perhaps secondary treatment may be necessary before discharging the effluent to receiving waters.

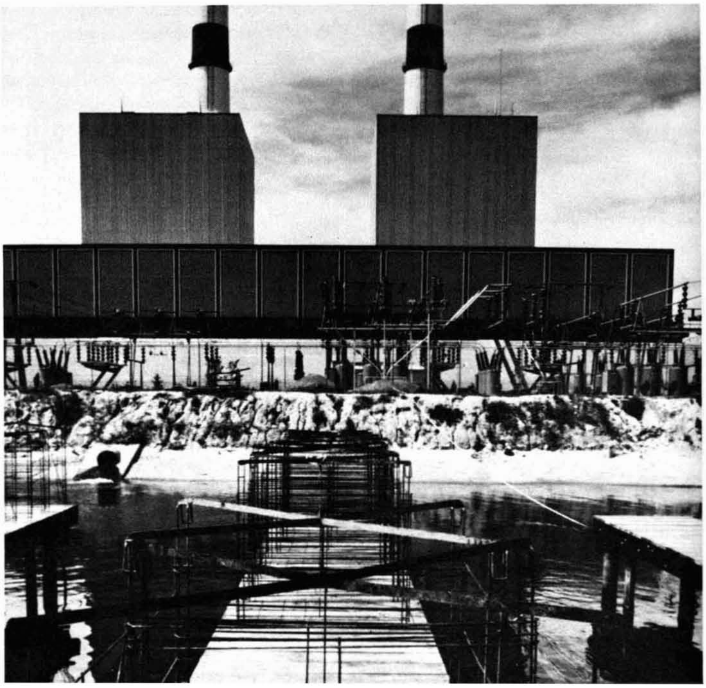
Marketing and economics

The potential for thermal aquaculture can be examined both from an economic and from a marketing point of view. With a source of warm water to culture continuously, the unit cost of production can be reduced significantly below that of a seasonally cultured product. As an example, producing catfish seasonally in open ponds has been estimated to cost about \$0.30/lb while culture in flowing water on a continuous basis has been projected to be \$0.20/lb.

Land availability, large inventory of thermal effluent, and easy access to electric power are attractive synergisms between a power plant site and intensive aquaculture. Nuclear power stations are required by law to have an exclusion area around the plant site. Since the operating utility has complete control over this area, which may be hundreds of acres, there should be ample land to build an integrated facility. Unit size of a new nuclear station would be at least 500 MW, and the coolant water requirement might be 615 million gpd if a water temperature rise of 20°F is specified.

Thermal aquaculture will not be universally possible at all power plant sites. Site specific factors such as water qual-

Oysters. *Long Island Lighting Co.'s discharge canal is used as an oyster nursery*



Fish. *Heated discharge water can easily be diverted into tanks for fish farming*

ity, single-unit or multiple-unit power stations, and plant shutdown and startup patterns would be factors in determining the feasibility of such an operation. For example, coolant water sources should not contain toxic quantities of trace metals. Or economic ways of removing objectional impurities must be available. Biocide residuals in the thermal effluent must be below levels that would be toxic to aquatic species in culture. Provisions may have to be made to cope with unscheduled shutdowns, when sudden changes in coolant water temperature might adversely affect the entire crop of fish in culture. The cost of sewage treatment of fish wastes in the culture facility effluent may be an important factor in the economics of the degree of intensiveness of fish culture. Nuclear plant thermal effluents used for aquaculture must be taken before the stream is used as a diluent for any radioactivity discharged from the installation. These are some of the major factors that would determine the commercial viability of thermal aquaculture for a particular power plant site.

Thermal aquaculture has a potential that remains to be demonstrated. Since thermal effluents are waste products of the utility companies, a regulated-industry, technical feasibility may be only one of several considerations to be reckoned with to prove its commercial viability. Legal and regulatory hurdles on a federal, state, and local level and marketing considerations may also be equally important factors. Ultimately, site-oriented demonstration projects will have to show the revenue-producing potential of thermal aquaculture and the extent to which it can assist in helping to pay for the cost of dissipating waste heat from an electric power plant. The resource value of this waste might then be estimated, and a liability of the present might be turned into an asset of the future.

Additional reading

"Chemurgy—For Better Environment and Profits," Proceedings of 32nd Annual Conference, Chemurgic Council, 350 Fifth Ave., New York, N.Y. 10001, 1971.

Proceedings of the Conference on Beneficial Uses of Thermal Discharges, Albany, N.Y., September 16–18, 1970, p 51. New York State Department of Environmental Conservation, Albany, N.Y., 1971.

"Joint Venture Aims at Thermal Effluent Use," *Amer. Fish Farmer*, **2** (8), 19 (1971).

"The Catfish Industry—1971," *Amer. Fish Farmer*, **2** (4), 12 (March 1971).

William C. Yee *is task force leader in the U.S. Atomic Energy Commission's Environmental Impact Reports Project at Oak Ridge National Laboratory. Dr. Yee has been engaged in waste utilization and waste treatment work since 1959 and has obtained four patents in these fields. Prior to his present position, he spent three years investigating productive uses for waste heat from power generating stations, not only in the technical sense, but also from the legal, regulatory, and product marketing points of view. The research in this article was sponsored by the U.S. Atomic Energy Commission under contract with Union Carbide Corp.*

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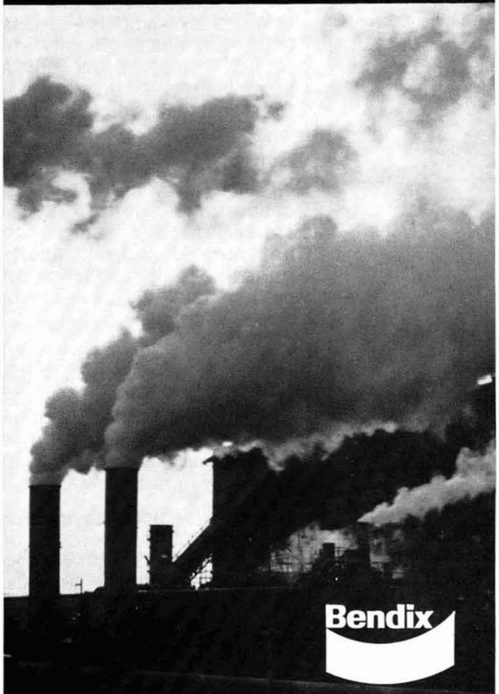

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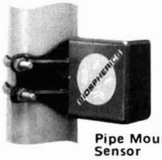

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Effect of Lead on Oxidation Activity of Copper Oxide–Alumina Catalyst

Lee L. C. Sorensen and Ken Nobe[1]

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■ The effect of lead on copper oxide–alumina catalysts in the oxidation of ethylene has been investigated. The catalysts were prepared by impregnation of preformed alumina pellets with an aqueous solution of copper nitrate. Lead contents of approximately 5, 10, and 15% were obtained by further impregnation of the catalysts with an aqueous solution of lead nitrate with subsequent thermal decomposition. The catalytic activity was determined for ethylene concentrations of 300 to 1600 ppm in air, at a gas flow rate of 375 l./hr (25 °C, 1 atm) at temperatures of 240° to 430°C. The catalyst activity was severely reduced by lead.

With tightening of emission standards for automobile exhausts, control by catalytic converters continues to show promise. One serious limitation in their use is the possible deactivation of the catalysts by lead and its compounds due to tetraethyllead (TEL) in the gasoline. It has been recently proposed that lead compounds be severely reduced or eliminated from gasoline. However, until such fuel modification becomes universal, it is important to determine the effects of lead on exhaust control catalysts.

Yolles et al. (1970), in a survey of testing of automotive emission control catalysts, list stationary engine tests ranging generally from 40 to 600 hr with road testing ranging from 1000 to 18,000 miles. A wide range of lead levels on catalysts observed from such testing has been reported. Hofer et al. (1963) reported in their investigation of deposits of lead compounds on catalyst beds that 40 to 50% of the lead in the gasoline is retained by the catalyst. The catalyst weight gains ranged up to 40% in the inlet portion of the catalyst beds when exposed to engine exhausts equivalent to a 20,000-mile trip using gasoline containing 3 ml of TEL per gallon of gasoline. Baker and Doerr (1964) reported lead levels of approximately 2% on a denser catalyst exposed for 350 hr to leaded exhaust, but noted that the dust portion of the catalyst was not included in the lead analysis. Cannon and Welling (1959) reported 10.5% lead on an alumina catalyst after 13,000 miles operation.

Weaver (1969) exposed catalysts to exhausts of engines operating with gasoline containing lead at various levels up to 3 ml/gal during 18,000 miles of service. The data did not include lead analyses on the catalysts, but the lead consumption using 3 ml TEL/gal is given as 0.187 gram Pb/mile. Since the catalyst charge was 2.8 kg, this would correspond to 119% Pb for 18,000 miles. However, as noted above, Hofer et al. (1963) stated that only 40 to 50% of the lead would be deposited on the catalyst. Yarrington and Bambrick (1970), in reporting on the fleet testing of catalytic converters, obtained lead levels up to 28% after 12,000 miles of operation.

This laboratory has been involved in the study of catalysts for the oxidation of hydrocarbons (Sourirajan et al., 1961) and carbon monoxide (Blumenthal and Nobe, 1966) and the removal of nitric oxide (Sourirajan and Blumenthal, 1961). However, except for exposure of catalysts to leaded exhaust for a period of 100 hr (Sourirajan et al., 1961; Sourirajan and Blumenthal, 1961) a quantitative investigation of the effects of lead had not been made. In this paper, lead of varying amounts has been deposited uniformly on the copper oxide catalyst, and its effects on the catalytic oxidation of ethylene has been investigated.

Experimental

Ethylene (CP grade, 99.8%) was obtained from Air Products and Chemicals, Inc. and was used as received. Laboratory air was dried and CO_2 removed by passing through a bed of Linde 13× Molecular Sieve which was periodically regenerated with air at a temperature of 320°C. Alumina, grade 86, nominal $^1/_8$-in. diam cylindrical pellets, was obtained from the Filtrol Corp., Los Angeles, Calif.

Catalyst A was prepared by adding Filtrol grade 86 alumina pellets (300 grams) to a hot solution of copper nitrate trihydrate (180 grams) in distilled water (100 ml), and shaking this mixture to distribute the liquid uniformly on the pellets. These quantities were chosen to permit the solution to be taken up by the pores of the alumina with no excess liquid. The resulting pellets were dried at 200°C. Decomposition of the copper nitrate was achieved by heating a 30-gram portion overnight in a 22-mm o.d. borosilicate glass tube wrapped with heating tape to about 350 °C in an airstream.

Catalyst B was prepared by adding a 30-gram portion of Catalyst A, prior to the thermal decomposition procedure, to a solution of lead nitrate (1.936 grams) in distilled water (10 ml). This mixture was shaken to distribute the solution evenly, and then the water was evaporated by drying the pellets in an oven. The nitrates were decomposed to the corresponding oxides as in the preparation of Catalyst A.

Catalysts C and D were prepared in the same manner as Catalyst B except that the lead nitrate was increased, respectively, to 4.085 grams and 6.488 grams.

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[1] To whom correspondence should be addressed.

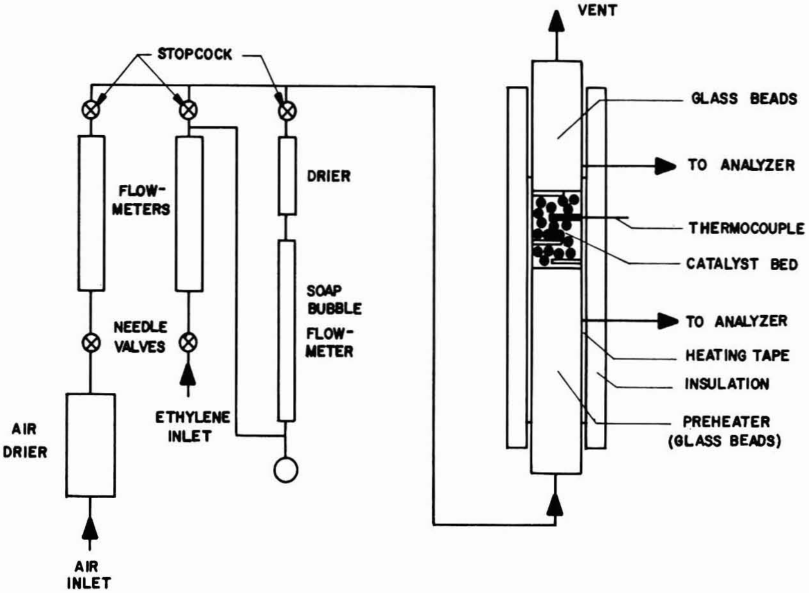

Figure 1. Apparatus

After an experiment, a portion of the catalyst (approx. 1 gram) was dissolved by digesting with nitric acid and then diluting to 500 ml. This solution was further diluted: $^1/_{20}$ for the copper analysis and $^1/_{10}$ for the lead analysis. A Perkin-Elmer Model 303 atomic absorption spectrophotometer was used for the analysis of the solutions. The BET surface areas were determined by nitrogen adsorption at liquid nitrogen temperatures. The pore volume of the catalysts was determined from skeletal and particle densities determined by displacement of isopropyl alcohol and mercury, respectively. From the surface area and pore volume of each sample, an average pore diameter was calculated. These values are given in Table I.

Table I. Catalyst Characteristics and Kinetic Parameters

	Catalyst			
	A	B	C	D
% CuO (lead-free basis)	19.1	19.0	19.3	19.2
% Pb added	0	5.1	9.8	15.2
Surface area, m^2/g	244	197	196	190
Particle density, g/cm^3	1.485	1.721	1.809	1.915
Skeletal density, g/cm^3	3.807	3.804	3.885	4.064
Pore volume, cm^3/g	0.41	0.32	0.30	0.28
Av pore diam, Å	67	65	61	59
Reaction order	0.7	0.7	0.7	0.7
Frequency factor, mol/g cat.-sec-atm$^{0.7}$	325	281	496	61
Activation energy, kcal/mol	10.1	10.5	11.3	9.5

A schematic diagram of the apparatus and instrumentation is shown in Figure 1. The flow of the dried laboratory air was controlled with a Nupro needle valve and measured with a Fischer and Porter flowmeter which had been calibrated with a wet testmeter. The ethylene was also controlled with a Nupro needle valve and passed into a Matheson Model 610 flowmeter for indicating purposes. The ethylene was then passed through a soap bubble flowmeter for accurate determination of the ethylene flow rate, on to a short drying tube charged with indicating Drierite, and then into the gas-mixing manifold. The air and ethylene passed through a series of perforated glass discs in the gas-mixing manifold and then to the reactor preheater.

The reactor was a fixed-bed bench scale unit constructed from a borosilicate glass tube (19-mm i.d.). The preheating section, approximately 32 cm in height, was packed with 5-mm glass beads, followed by a short section filled with glass Raschig rings. The catalyst bed, 6 cm in height (14 grams of catalyst), was followed by another short section filled with glass Raschig rings. The rest of the reactor was then filled with 5-mm glass beads. The gas stream passed through this bed to a vent. The reactor was equipped with sample lines so that gas analysis could be obtained before or after the gases had passed through the catalyst bed. The reactor was equipped with seven glass radial thermowells containing Chromel-Alumel thermocouples connected to a Honeywell multipoint stripchart temperature recorder. Two of these thermocouples were in the preheater zone, four in the catalyst bed, and one in the section following the catalyst bed. The reactor was heated with three heating tapes, two in the preheater zone and one covering the catalyst bed. The temperature of the catalyst bed was maintained at isothermal conditions by controlling the power to the heating tapes. This was achieved with a Honeywell temperature controller with the control thermocouple positioned between the heating tape and the glass reactor. The power to the two preheater heating tapes was manually controlled with variacs to obtain the most

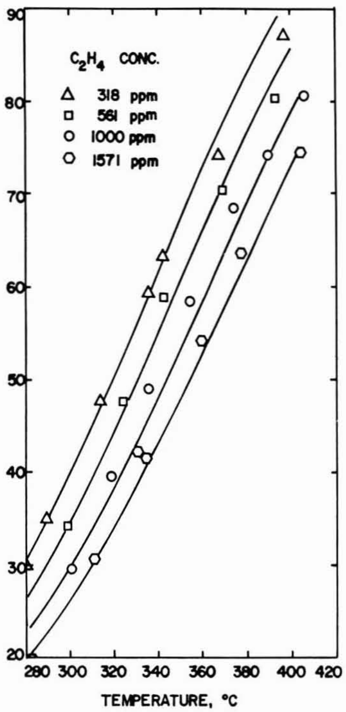

Figure 2. Catalytic oxidation of ethylene on Catalyst A (0% Pb)

Solid lines represent calculated data

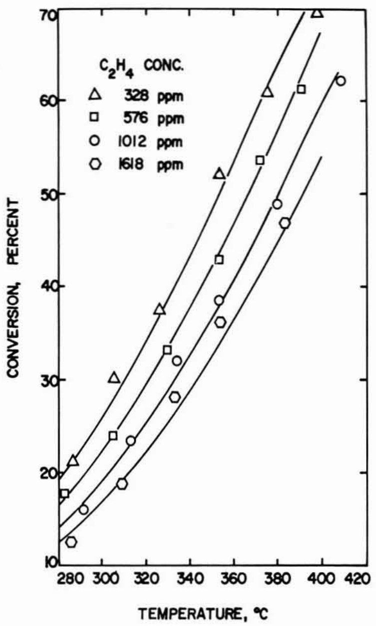

Figure 3. Catalytic oxidation of ethylene on Catalyst B (5% Pb)

Solid lines represent calculated data

uniform temperature profile through the catalyst bed. The reactor and heating tapes were insulated with J-M Thermobestos pipe insulation.

The catalysts were oxidized in place by passing air through the catalyst bed at the same rate, 375 l./hr, as in the experimental runs, for 48 hr at a temperature of 500°C. This was followed by a break-in period of 24 hr during which time ethylene at an initial concentration of 1000 ppm, airflow rate of 375 l./hr, and catalyst temperature of 400°C, was oxidized. For an experimental run, the flow rate of the air was set at 375 l./hr, and the ethylene concentration was determined accurately by adjusting the ethylene flow rate with a precision needle valve and the soap bubble buret flowmeter. After the temperature was adjusted to the desired value and steady state was achieved, the flame ionization detector (FID), Beckman Model 108, was zeroed with nitrogen. Then, the exit and inlet hydrocarbon concentrations were determined with the FID.

Results and Discussion

Table I gives the characteristics of the catalysts prepared with no lead and with nominal lead levels of 5, 10, and 15% Pb. The surface area and pore volume decreased with increase in the lead content of the catalyst with the greatest change occurring from the unleaded to the 5% Pb catalyst. Subsequent increases in lead content did not greatly decrease the values of these two properties.

The oxidation of ethylene on the four catalysts was studied at four concentrations of ethylene nominally 300, 600, 1000, and 1600 ppm at temperatures ranging from 240° to 430°C.

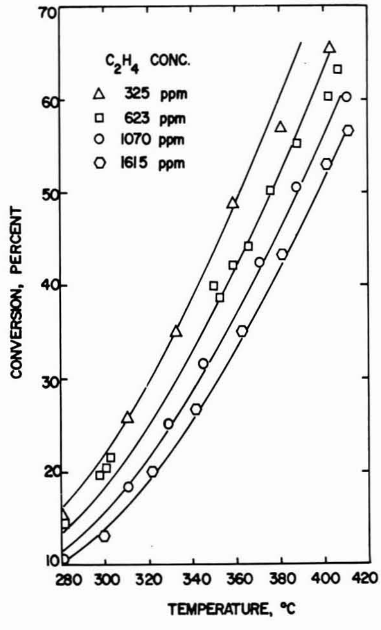

Figure 4. Catalytic oxidation of ethylene on Catalyst C (10% Pb)

Solid lines represent calculated data

The experimental data for catalysts A (0% Pb), B (5% Pb), C (10% Pb), and D (15% Pb), presented as the points, are shown in Figures 2–5, respectively. Considerable care was taken to ensure that reproducible activity was attained for all the catalysts. As an indication of the effect of lead content on the catalytic activity, Figures 2–5 show that at 300°C and approximately 1000-ppm ethylene, the oxidation of ethylene decreased from 30% for the unleaded catalyst to 19, 16, and 9% for catalysts with lead levels of 5, 10, and 15%, respectively. Previous work indicated that complete combustion of ethylene on copper oxide–alumina catalysts is achieved (Caretto and Nobe, 1969).

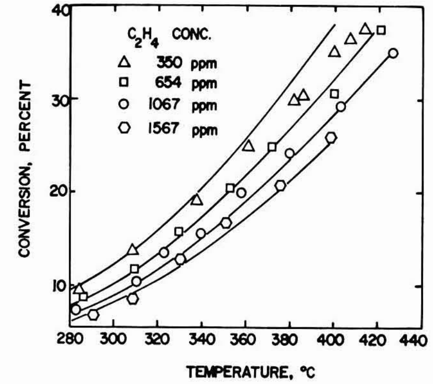

Figure 5. Catalytic oxidation of ethylene on Catalyst D (15% Pb)

Solid lines represent calculated data

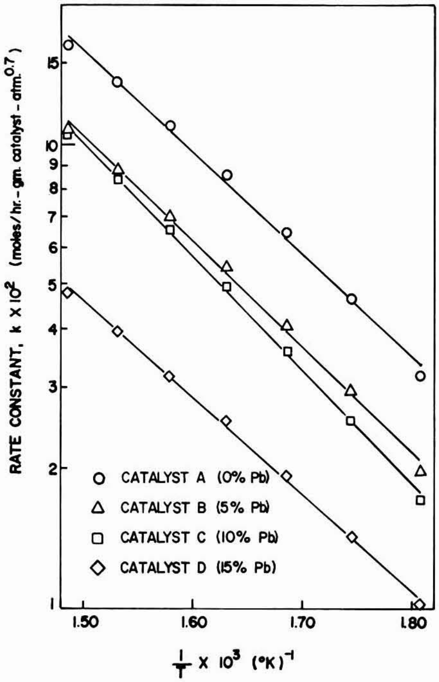

Figure 6. Arrhenius plots

Solid lines represent calculated data

The ethylene oxidation was correlated with an empirical power law rate equation

$$r = kP_E^n \qquad (1)$$

where

$$k = Ae^{-E/RT} \qquad (2)$$

r is the rate of oxidation (mole/g cat.-sec), k is the rate constant (mol/g cat.-sec-atm^n), P_E is the partial pressure of ethylene (atm), n is the apparent reaction order with respect to ethylene, A is the frequency factor (mol/g cat.-sec-atm^n), E is the apparent activation energy (cal/mol), R is the gas constant (cal/mol-°K), and T is the absolute temperature (°K).

The kinetic parameters n, A, and E were determined with a computer program developed by Accomazzo and Nobe (1965). The apparent reaction order of 0.7 was found to give the best fit of the data for all the catalysts. The values of E and A determined for each catalyst are given in Table I. Plots of the logarithm of the rate constant k vs. the reciprocal of the absolute temperature are given in Figure 6. The experimental data are presented as the points, and the continuous line is the least mean square fit of the data from the computer calculations. As shown in Figure 6, the experimental data for all the catalysts followed linear Arrhenius relationships.

With the empirical rate equation for each catalyst, calculated ethylene conversion vs. temperature data are obtained and are shown in Figures 2–5 as the continuous lines. Comparison of the experimental data (points) and the calculated data (continuous lines) shows that a good correlation was obtained.

A direct comparison of the activity of each catalyst in the oxidation of ethylene can be obtained in Figure 6. The magnitude of the rate constant k is a direct measure of the catalytic activity. The Arrhenius plots in Figure 6 show that an increase in lead content decreases the catalytic activity for ethylene oxidation.

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pH-Controlled Differential Voltammetry of Certain Trace Transition Elements in Natural Waters

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■ The technique of anodic stripping voltammetry has been made applicable to the direct analysis of Zn, Cd, Pb, and Cu in natural waters. The state and concentration of these ions were studied in the parts-per-billion range in fresh, saline, and artificial media. The sensitivity of conventional stripping analysis has been enhanced by opposing two hanging mercury drop electrodes; this differential approach eliminates the large background current and allows maximum signal amplification.

Advantage to the direct analysis of trace metals in natural waters include the elimination of reagents and preconcentration steps. Anodic stripping voltammetry (ASV) is well suited for analysis of metal ions such as Zn, Cd, Pb, and Cu, which form amalgams on mercury electrodes. The method is highly sensitive, requires few or no reagents, and major ions such as the alkaline earths do not interfere. The process has been described by Shain (1963) and Nickelly and Cooke (1957).

Several workers have applied ASV to the analysis of natural waters. Ariel and Eisner (1963) and Ariel et al. (1964) used ASV to analyze Dead Sea brine. They determined Zn, Cd, and Cu by using the hanging mercury drop electrode (HMDE) described by Ross et al. (1956). Macchi (1965) used a synchronized dropping mercury electrode with long dropping times to measure the ionic zinc content of a Mediterranean Sea water sample. Matson et al. (1965) developed a composite mercury graphite electrode (CMGE), and Matson determined the Pb content of various natural waters other than open ocean water (Matson, 1968). Recently, Whitnack and Sasselli (1969) determined Zn, Pb, Cd, and Cu in seawater samples by single electrode anodic stripping voltammetry and discussed some of the problems encountered in the determinations.

This paper describes a method which was developed primarily for open ocean water but has general applicability. Even with conventional strip chart recorders it is highly sensitive, incorporates a simple, noncontaminating technique for controlling the pH, and has been used successfully at sea for several months. Increased sensitivity has been achieved by opposing two hanging mercury drop electrodes in the same cell, thus eliminating the large residual current. The cancellation of both the residual currents and to some extent the hydrogen reduction current allows high amplification of the signal from the plated trace metals, making possible slow voltage scans and improved resolution. This approach is differential and varies from that of Martin and Shain (1958) because both electrodes are immersed in the same solution.

The determination of metals in natural waters can be highly dependent on pH (Fukai and Huynh-Ngoc, 1968; Duursma and Sevenhuysen, 1966). Treating samples for pH studies generally involves the purification of an acid and subsequent titration of the water sample, a procedure that risks contamination and is cumbersome in the field. In our work, the pH of the sample is controlled by replacing the usual inert purging gas with a mixture of CO_2 and N_2. By varying the ratios of the gases, the pH can be controlled over a range of three or four units.

The scope of this paper is to present a routine method for the determination of ionic and labile Zn, Cd, Pb, and Cu in natural waters under a given set of experimental conditions. In open ocean water, with a 5-min plating cycle, the sensitivity is $0.005 \mu M$ for Zn and $0.001 \mu M$ for Pb, Cd, and Cu. However, the Cu determination is qualitative in seawater. All four metals were determined quantitatively in distilled water with approximately the same detection limit as in seawater. For freshwater samples, the dissolved carbonic acid acts as the supporting electrolyte, thus the addition of foreign salts is eliminated. Nonroutine experiments become necessary to obtain information about chelation, ion pairing, and total metal content in organic rich or polluted waters. These experiments are described by Matson (1968) and are beyond the scope of this work.

Experimental

The basic console, designed by Enke and Baxter (1964), is constructed with chopper-stabilized operational amplifiers and is marketed by the Heath Co. as the Controlled Potential Polarography System. The differential display is achieved by connecting the second working electrode to the input of an additional variable gain inverting operational amplifier with a gain of −1. The output of the added amplifier is coupled in parallel with the conventional cell circuitry to the summing point of the cell-current amplifier in the analyzer (Figure 1).

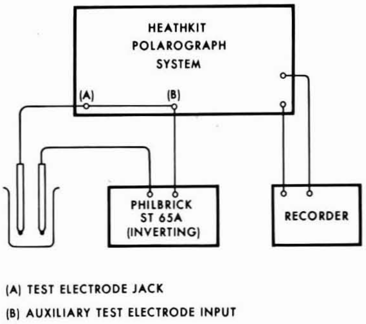

Figure 1. Schematic diagram of the assembly for differential anodic stripping voltammetry

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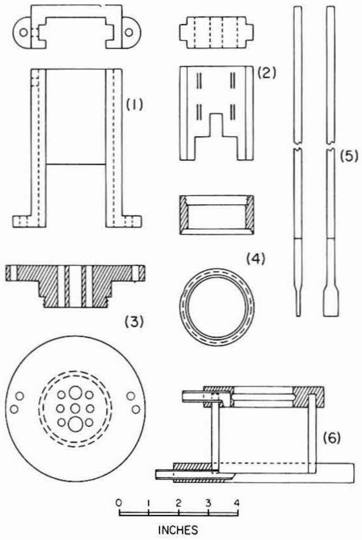

Figure 2. Diagram of the cell assembly parts

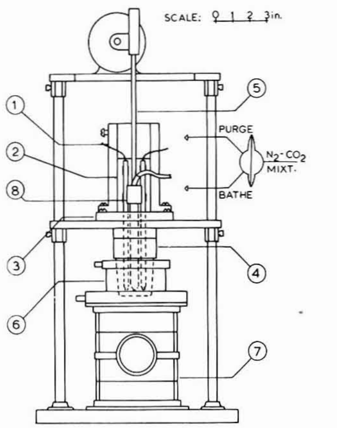

Figure 3. Installed cell assembly

The inverting amplifier is a Philbrick SP 65A chopper-stabilized solid-state unit. Circuit design and details have been given by Healy and Chapo (1969).

The first working electrode is active during the plating stage. The second working electrode is active only during the stripping cycle and its signal is opposite in polarity from the first. With matched electrodes, the summation of these two signals results in cancellation of nearly all residual currents, and only the current resulting from metal oxidation passes.

Apparatus

The electrolysis cell is installed in framework of four Flexaframe (*R*) rods. Its seven principal parts, described below, are shown in Figures 2 and 3.

Electrode Slide and Support Assembly (1, 2). The two pieces are machined from polyvinyl chloride (PVC). The electrodes are attached to the slide by means of electrical fuse clips and the entire assembly is fastened to the cell cover by 0.6-cm ($^1/_4$-in.) nylon bolts.

Cell Cover (3). Since the electrodes must be placed symmetrically, the machined PVC cell cover has nine openings placed to give two planes of symmetry across the center. The central opening is for the stirrer shaft. The two holes lateral of center permit the electrodes to be raised or lowered and also act as vents. The large hole forward of the shaft opening seats the reference electrode (SCE) without binding to permit its removal during standard additions. The anode chamber, a hollow PVC cylinder, fits into the opening behind the shaft. A thin plug of porous polyethylene (Bel-Art Products) is fitted in the lower end of the chamber to decrease the exchange of solution between the chamber and the rest of the cell.

The two openings on the sides of the reference seat accommodate short glass tubes. Since no stirring is required during the stripping cycle, gas flows through these tubes above the solution. The two holes on each side of the anode chamber seat two longer glass tubes that permit passage of gas during the purging stage. Construction of the ends limits the size of the bubbles.

Plexiglass (*R*) Cylinder (4). This piece is threaded at one end to screw into the cell cover while the other end is recessed to fit the 50-ml Teflon beaker (Cole-Palmer Instruments Co.)

Paddle Stirrer (5). The paddle section of machined PVC screws into a threaded stainless steel shaft. The paddle-shaft connection is well above the level of the solution. The paddle shaft is attached with Tygon tubing to the slow shaft of a variable-speed laboratory mixer (Gerald K. Heller Co.) and turned at about 200 rpm.

Water Jacket (6). The water jacket is machined from Plexiglas (*R*) and incorporates the Teflon beaker for maximum heat conduction. An "O" ring provides a water-tight seal between the beaker and the jacket. The water jacket rests on a laboratory jack (7).

Hanging Mercury Drop Electrode. The HMDE's are constructed by sealing 0.4-mm platinum wire in 4-mm flint glass tubing. The platinum-glass surface is sanded flat with 120 emery paper and polished with 240 emery paper. The platinum cross section is plated for about 15 min with mercury from a saturated $Hg(NO_3)_2$ solution using a 1.50-V dry cell as current source. The freshly plated surface readily takes up one or two mercury drops from a DME. Although the DME of a Polarotron Polarographic Analyzer (Leeds and Northrup Co.) was used, a conventional DME would be suitable. The electrodes need to be plated about once a day and are sanded with 240 emery paper just before electrolysis. The preparation of these electrodes is simpler than the procedure recommended by Ross et al. (1956) and can be done conveniently in the field. Although the HMDE's are not as sensitive as the CMGE, they can be consistently duplicated as matched pairs for the differential application.

To transfer the Hg drops, a small glass ladle was constructed from the conical end of a centrifuge tube. The ladle is filled with water, and the mercury drops are exposed to air as little as possible during the transfer from Polarotron to electrolysis cell.

Platinum Anode. Platinum wire (3.8 cm long) is imbedded in 4-mm flint glass tubing, leaving about 2.5 cm exposed. The wire is wound into a small coil, and the assembly is submerged in the anode chamber. Liquid from each sample automatically flows through the porous plug into the anode chamber to provide electrolyte.

Reagents and Solution. MERCURIC NITRATE. A concentrated solution of mercuric nitrate is prepared by placing an excess of triple-distilled mercury in concentrated nitric acid. Distilled deionized water is then added. This solution has a pH of approximately 1.

NITRIC ACID (8*N*). Concentrated reagent grade HNO_3 (Baker and Adamson, 70.0–71.0%) is diluted with an equal amount of deionized water.

DEIONIZED WATER. Distilled water is passed through a mixed-bed ion exchanger (Illinois Water Treatment Co.).

ARTIFICIAL SEAWATER. This is prepared according to the recipe of Sverdrup et al. (1942), with the omission of SrCl.

Nitrogen and Carbon Dioxide. The flow of gas from the respective cylinders was controlled by needle valves and rotometers. To prevent contamination of the sample, mixing was effected in a coil. Although the gases were not water-saturated, evaporation of the sample during an analysis was found to be negligible. Nitrogen purging for extended periods can strip CO_2 from seawater samples and cause pH changes. To reduce such changes a large seawater trap can be installed between the tank and flowmeter. However, care should be taken not to contaminate the sample with condensed water vapor from the trap.

Standard Stock Solutions. Standard solutions of $5 \times 10^{-3}M$ Zn, Cd, and Cu are prepared by dissolving the appropriate amount of the pure metal in 3 ml of concd HNO_3 and diluting to 1 liter with deionized water. A Pb stock solution of the same concentration was made from reagent grade $Pb(NO_3)_2$. Portions of these solutions were diluted as required to $5 \times 10^{-6}M$ for standard addition.

Cell Design

The cell (Figure 3) was designed with three objectives: geometrical stability, facility of sample handling, and reduction of contamination.

It has been shown by Macchi (1965) that fixed cell geometry is essential for reproducible measurements. Although all elements of the electrolysis cell are in fixed positions relative to one another, the electrodes can be moved in and out of solution (sometimes necessary to remove gas bubbles from the Hg drops) without changing the geometry of the cell. Electrodes can also be removed from the solution and drops can be changed without exposing the cell contents to the atmosphere.

Stirring is from above to eliminate the variations in magnetic stirring caused by irregularities in the bottom of the cell. This makes possible the use of commercial 50-ml Teflon beakers. In addition, the sample can be replaced in the beaker without handling a stirring bar. Warming of the sample by a magnetic stirring motor is avoided.

Plastics are used whenever possible to reduce metal contamination. Because purging causes samples of seawater to froth, the sample occupies only the lower half of the Teflon beaker, preventing the liquid from climbing above the beaker-Plexiglas ring joint and eliminating the scavenging of dust from the cell cover, a major source of contamination. When samples are changed or after replacement of the Hg drops, the surfaces in the cell are rinsed first with deionized distilled water and then with the sample. Contamination is minimized by limiting sample and equipment handling between runs.

Sampling

Seawater samples were collected in PVC oceanographic sampling bottles and, when possible, were transferred immediately to the 50-ml Teflon beaker for analysis. Samples that could not be run within a few hours were stored and frozen in 500-ml polyethylene screw-cap bottles. These bottles were previously rinsed once with 8*N* nitric acid and four times with the water sample.

Procedure

The following controls are set before an analysis is carried out: (1) Preelectrolysis potential and voltage scan rate are selected on the instrument. (As the parts-per-billion level, a scan of 0.5 V/min combined sufficient sensitivity with maximum peak resolution.) (2) Instrument selector switch is placed on "standby." (3) Both HMDE's are turned off. (4) The recorder pen is nulled in the middle of the chart paper.

A complete run is carried out as follows: New Hg drops are placed on the electrodes and the beaker is filled to the 25-ml calibration mark with the sample. The gas valve is turned to purge and the stirring motor is activated. The sample is purged for 5 min or longer, then both electrodes are turned on and the selector switch is placed on "cell." The voltage scan is initiated and allowed to progress to 0 V vs. SCE, at which point the selector switch is returned to "standby" and the scan is turned off. This procedure cleans the Hg drops of any sur-

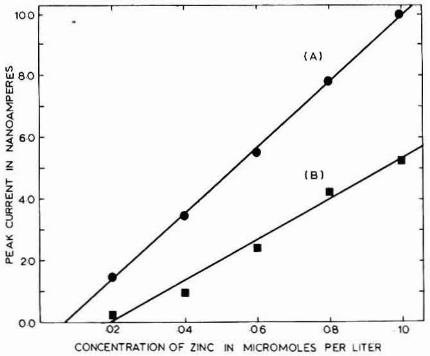

Figure 4. Calibration curve for zinc in seawater

Curve (*A*), pH = 5.8; curve (*B*), pH = 8.3; voltage scan rate, 0.5 V/min

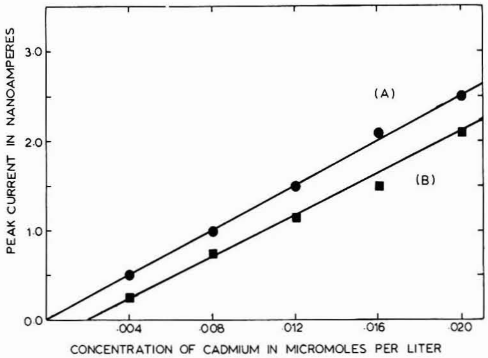

Figure 5. Calibration curve for cadmium in seawater

Curve (*A*), pH = 5.8; curve (*B*), pH = 8.3; voltage scan rate, 0.5 V/min

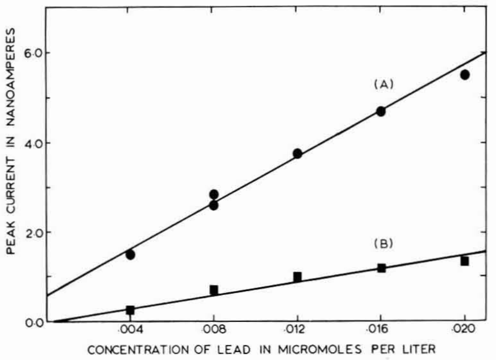

Figure 6. Calibration curve for lead in seawater

Curve (*A*), pH = 5.8; curve (*B*), pH = 8.3; voltage scan rate, 0.5 V/min

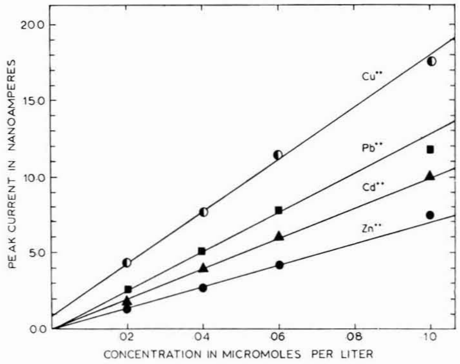

Figure 7. Standard curves in dilute carbonic acid–distilled water solution, pH = 4.4; voltage scan rate 0.5 V/min

face coatings that may have developed during purging. The differential electrode is now switched off. Purging and stirring are continued for an additional 2 min to homogenize the ion distribution in the sample.

Electrolysis is initiated by placing the selector on "cell," and a preset potential is applied to the first working electrode. Plating is continued for an accurately timed, desired period, usually 300 sec. On completion of the electrolysis, the gas valve is turned to bathe, the stirrer is turned off, the differential electrode is turned on, and the recorder selector switch is placed on "pen." While the solution comes to rest, the sensitivity control of the instrument is turned to the desired value, and the cell current is nulled by manipulating the feedback control on the differential amplifier. The procedure requires at least 60 sec, after which time the voltage scan and the recorder are turned on simultaneously and the cell current is recorded. The instrument is allowed to scan through 0 V vs. SCE and is then returned to "standby." The recorder and differential electrode are turned off, purging gas and stirrer are turned on, and the entire process can be repeated if desired. For standard addition, the calomel electrode is removed, standard solution is introduced into the sample with a microburet, and the calomel electrode is replaced. The standard is allowed to mix in the solution, and the procedure is repeated.

Peak currents are obtained by drawing an appropriate base line under the current-voltage curves and measuring the distance from the base line to the inflection point of the peak ($di/dv = 0$). From the peak height of the sample and sample plus standard, the concentration is calculated by direct proportion. For greater precision, or as a check on linearity and the presence of strong complexing agents, standard addition may be repeated.

Results

Standards. To establish linearity between peak current and concentration, standard curves for Zn, Cd, and Pb in seawater were run at pH 5.8 and 8.3 (Figures 4–6), the lower pH being produced by purging with the CO_2–N_2 gas mixture. Standard additions were made by adding to the 25-ml sample 0.100-ml volumes of a solution $5.00 \times 10^{-6}M$ in Zn and Cu and $1.00 \times 10^{-6}M$ in Cd and Pb. A standard curve was also developed for a dilute carbonic acid–distilled water solution of pH 4.4 (Figure 7). Each standard addition increased the concentration of the solution by 0.02 μM/l. in Zn, Cd, Pb, and Cu.

Precision. Unfiltered seawater samples were analyzed for Zn aboard the University of Washington research vessel *Thomas G. Thompson*. Replicate analyses (4 each) at Zn concentrations of 5.9, 4.7, and 2.7 μg/l. produced an almost constant standard deviation of 0.7 μg/l. At the 1 μg/l. level, the coefficient of variation (σ/μ) was estimated to be 50% (Zirino and Healy, 1971).

A bucket sample was collected off the Washington coast and analyzed for Pb and Cd. The Pb content was 0.9 μg/l. (σ = 0.3 μg/l.) and the Cd content was 0.4 μg/l. (σ = 0.1 μg/l.). These values should be taken as a measure of precision only.

Repeated plating and stripping analysis in a closed cell produced highly reproducible Zn peak currents. Standard additions also performed with a closed cell produced calibration curves of much greater precision than would be expected from the analytical error observed from the replicate analyses (Figures 4–6). Thus, the large analytical error may be introduced during the transfer of samples into the cell. It may be caused by incomplete flushing of the cell (Whitnack and Sasselli, 1969) between analyses.

Peak Height vs. Plating Time. Peak height was proportional to plating time for an indefinite period. Zn, Cd, and Pb were plated out of a 0.5*N* NaCl solution (0.044μM in Zn and 0.0088μM in Cd and Pb) for periods of up to 2 hr (Figures 8 and 9). The Pb curve in Figure 9 shows a small positive deviation from linearity owing to contamination from the SCE. The insert illustrates the increase in Pb peak current of a seawater sample with storage time in the cell. The amount of contamination, 2.9×10^{-9} g Pb/15 min, is consistent with impurity and leakage rate specifications supplied by the manufacturer of the SCE. By use of a mercury pool electrode, this source of contamination can be reduced by electroplating the Pb in the saturated KCl reference electrolyte.

Analyses of some natural water samples by standard addition are shown in Tables II and III. The freshwater samples were collected in clean 500-ml polyethylene containers held several inches below the water surface. Eastern Pacific seawater samples were collected and analyzed on Cruise 34 of RV *Thomas G. Thompson* during January 1968.

Discussion

Sorption. At the 0.01 and 0.001μM levels, sorption must be reckoned with during analysis. Robertson (1968) has shown that it is nearly impossible to find materials totally free of trace metals. However, the rates at which trace metals are transferred from material surfaces to the sample can be con-

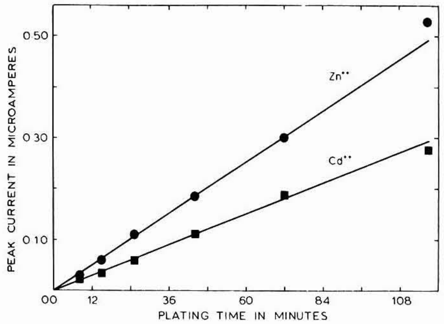

Figure 8. Increases in peak height vs. plating time for Zn^{2+} and Cd^{2+} in 0.5*N* NaCl solutions

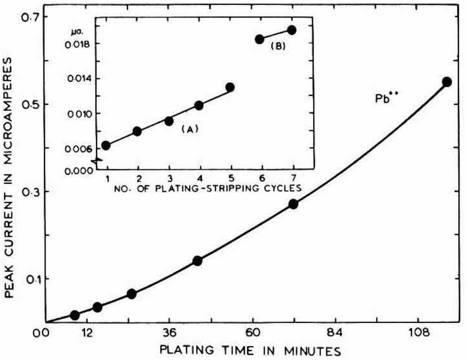

Figure 9. Increases in peak height vs. plating time for Pb^{2+} in 0.5*N* NaCl solutions

Insert: Increase in peak height with successive cycles of plating and stripping the same sample

trolled. We have tried to limit the amount of trace metals gained or lost by sorption by equilibrating the sample with all surfaces with which it comes in contact.

Before analysis, all containers (polyethylene storage bottles, Teflon beakers, cell parts, etc.) are rinsed with dilute nitric acid, followed by deionized water, to remove contaminants and to reduce the problem to one of adsorption. Therefore, all surfaces are equilibrated with subsamples of the sample for extended periods (hr); these subsamples are then discarded. Since exchange of the trace metal from the surface to the sample is pH-controlled, the container walls should be rinsed at approximately the pH used in the final analysis. Drastic changes of pH between samples will lead to a desorption error. Although these steps are time-consuming, it is generally necessary to perform them only once for a particular sample locality. If the concentration range of the samples to be analyzed covers less than a factor of 10, repeated acid cleaning is not necessary. Open ocean samples have a narrow concentration range, and it is not necessary to equilibrate each sample with the cell environment.

Generally, newly machined cell parts should be acid-cleaned and equilibrated with the medium for periods of days. After several days, contamination from the cell components becomes negligible, as can be verified by storing deionized water in the cell for an extended period. If the cell parts are well equilibrated with the medium, adsorption becomes negligible. In a 5-hr experiment, Alexander and Corcoran (1967) found that aged PVC bottles removed no copper from seawater.

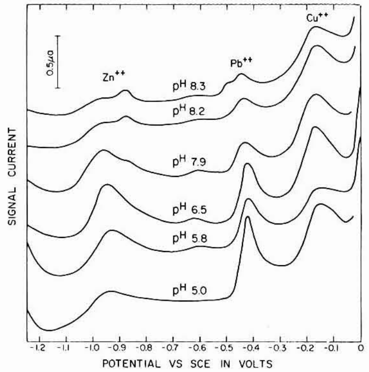

Figure 10. Current-voltage traces at various pH values of metal contaminants remaining in purified artificial seawater

Zinc adsorption peak at −0.87 V vs. SCE

Influence of pH. In seawater, Zn and Pb calibration curves produced at pH 5.8 have greater slopes than those produced at pH 8.3 (Figures 4 and 6), presumably because these metals combine with weak acid anions to form inert complexes. The increase in peak current at the lower pH is accompanied by an anodic shift in peak potential of approximately 30 mV. Cu also appears to be complexed by these agents, but the latter effect is more difficult to determine because, in seawater at the 1 μg/l. level, it is usually difficult to resolve the Cu peak from the Hg dissolution peak. Open ocean samples that were analyzed produced higher Zn peaks at the lower pH, providing additional evidence that pH-dependent complexes occur in seawater. Pb and Cu were generally undetectable unless the acidity of the sample was increased.

The pH dependence of metals in artificial seawater was studied in the laboratory (Figure 10). The artificial seawater showed no absorbance at 260 mμ on the Beckman DK spectrophotometer, indicating that little organic matter was present. Peaks are due to metals that have remained in solution after purification by precipitation (Joyner et al., 1967). The acidity was changed by using various ratios of CO_2 and N_2. The Cu and Zn stripping current reached a maximum value at a pH of about 6 and became small at pH 8. The Pb peak current appeared to be directly proportional to the acidity of the solution. The decrease of Zn and Cu peak currents at low pH values may indicate some interference from carbonic acid. In the more basic solutions, a small, symmetrical peak appeared at a potential approximately 100 mV less negative than the main Zn peak (Figure 10). This is attributed to the adsorption of $ZnCO_3^0$ or $Zn(OH)_2^0$ or a mixed Zn hydroxycarbonate on the electrode as the Zn(Hg) amalgam is oxidized. Adsorption on stationary electrodes has been studied by Wopshall and Shain (1967). The pH dependence of the stripping currents of Zn, Pb, and Cd in seawater has been studied by Zirino and Healy (1970) and Zirino and Yamamoto (1971). In seawater, the increased concentration of carbonic acid does not appear to affect the determination if the pH is not lowered below 5.6. The major effect of adding CO_2 is to decrease the concentration of CO_3^{2-}, thus any complexation with that species would be reduced. Complexing of the metals by the

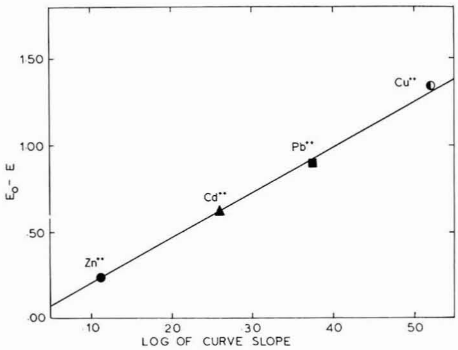

Figure 11. Difference in applied potential and standard potential vs. log of the slope of calibration curves in Figure 7

various species of carbonic acid in distilled water has not been studied but does not appear to interfere with the analysis.

Identification of Peaks. Peaks in the current-voltage trace can be identified tentatively by the potentials at which they appear. Both the peak potential E_p, and the potential at half-peak height, $E_{p/2}$, have been used (Macchi, 1965; Ariel and Eisner, 1963). In a seawater–carbonic acid medium with a pH of 5.8, the peak potentials agree closely with polarographic half-wave potentials ($E_{1/2}$) measured in dilute KCl, which can be used as a guide. Although two metals may have the same stripping potentials in natural media (Ariel and Eisner, 1963) this does not present a great problem for most seawater samples. Despite the great variety of trace metals present, few of those present in measurable amounts have peak potentials between 0 and 1.25 V vs. SCE (Table I).

Interferences. The electrodeposition of Zn from seawater appears to be free of interferences. Macchi (1965) has verified that at an initial plating potential of −1.3 V, small quantities (less than 20 times the concn of Zn) of Co, Ni, Mn, Cr, Fe, and Al do not interfere with its determination. At pH 5.6, $10^{-5}M$ Ni(II) and Fe(III) do not affect the peak current from 10^{-7} Zn. However, at pH 8.1, both metals suppress this current, presumably by adsorption of Zn on Ni and Fe hydroxides.

The reaction $Sn(0) \rightarrow Sn(II)$ may interfere with the determination of Pb in seawater. Spikes of $SnCl_2$ are not resolvable from Pb over the interval of pH 5.6 to pH 6. Above pH 6, the Sn peak is greatly suppressed, but the Pb determination is not very sensitive. The addition of a suspension of Sn(IV) to seawater at pH 5.6 produced no peaks but slightly broadened the peak current from $10^{-7}M$ Zn.

Addition of $SnCl_2$ to distilled water at pH 4.4 does not produce a peak. Unlike seawater, complexation with chloride does not occur to retard hydrolysis and colloid formation.

The formation of intermetallic compounds of Zn and other metals present in seawater may reduce the Zn peak current (Shain, 1963). However, because Zn is considerably more concentrated in seawater than other metals which may interact, such interference is probably small and should not affect analysis by standard addition. Freshwater samples are less similar than seawater samples, and each body of water must be examined individually.

Interaction between Zn, Cd, Pb, and Cu at the $0.01\mu M$ concentration level is negligible as indicated by the results in Figure 11. A linear relationship exists between the mantissa of the logarithm of the slopes of the calibration curves in Figure 7 and the difference between the applied potential (E = −1.25 V) and the standard potential (E^0) of each metal as predicted by the Nernst equation. Therefore, barring kinetic effects, the system is most sensitive for Cu and least sensitive for Zn.

Measurements of Natural Waters. If thermodynamic equilibrium between the added standard and the sample is assumed, the method described herein should measure all of the metal present in solution as the hydrated ion or as a labile complex. For natural samples analyzed at low pH values, the measured concentration includes those metallic ions which might be desorbed from particulate surfaces by the increase in the hydrogen ion concentration. The assumption of equilibrium was tested for seawater by spiking a freshly collected surface sample from San Francisco Bay with enough Zn, Cd, and Pb to increase the concentration of the sample to $0.03\mu M$ in Zn and $0.006\mu M$ in Cd and Pb. The peak currents

Table I. Characteristic Stripping Peak Potential

(E_p in volts vs. SCE)

Metal	$E_{1/2}$[a]	SW, pH 5.8	DW, pH 4.4
Zn	−0.995	−0.98	−0.93
Cd	−0.599	−0.63	−0.53
Pb	−0.396	−0.43	−0.35
Sn(II)	−0.47[b]	−0.43	not obsd
Cu	+0.02[b]	−0.15	+0.07

[a] Kolthoff and Lingane (1941).
[b] 0.1N HCl.
[c] $0.1N$ KNO_3.

Table II. Comparison of Zinc Data from Eastern North Pacific

Slowey (1966)			Zirino and Healy (1970a)		
Position	Zinc, meter	Zinc, µg/l.	Position	Depth, meter	Zinc, µg/l.
30° 27′N			08° 41.0′N		
122° 02′W	10	4.5	83° 24.1′W	0	4.3
	300	4.3		20	0.5
	600	5.6		50	2.4
	1000	3.3		80	2.6
	2000	3.3		200	1.0
	3500	1.6			
			08° 58.0′N		
30° 19′W			85° 57.4′W	0	1.1
124° 03′W	10	4.0		20	ND[a]
	400	1.7		50	3.2
	750	1.4		300	0.4
	1500	1.4		1000	ND[a]
	2800	4.4		3000	1.2
30° 36′W			10° 18.0′N		
123° 55′W	10	3.3	86° 48.0′W	500	2.6
	400	1.7		1000	0.7
	750	1.2		3000	1.4
	1000	1.0		3400	0.8
	1500	1.2		4000	1.3
	2800	0.5		4800	0.8

[a] Not detectable at 0.2-µg/l. level.

Table III. Trace Metal Data from Natural Waters—High Altitude Lakes and Rivers

	Zn		Cd		Pb		Cu	
	Concn, μg/l.	E_p, V	Concn, μg/l.	E_p, V	Concn, μg/l.	E_p, V	Concn, μg/l.	E_p, V
Trinity River, Shasta-Trinity Natl. Forest, Calif.[a]	0.3	−0.955	0.2	−0.555	2.5	−0.370	2.2	+0.07
Sulphur Springs, Kittitas County, Wash.	3.2	−0.933	added	−0.525	1.8	−0.340	[b]	[b]
Park Lake, Kittitas County, Wash.[c]	4.3	−0.945	1.0	−0.525	1.0	−0.325	0.2	+0.070
Rachel Lake, Kittitas County, Wash.	0.4	−0.950	0.2	−0.550	<0.2	−0.350	0.6	+0.070
Roosevelt Lake, Okanogan County, Wash.	1.6	−0.935	0.3	−0.530	1.6	−0.350	1.3	+0.090

[a] Unidentified peak at −0.170.
[b] Not possible to determine because of a −0.25-V shift in the mercury dissolution.
[c] Unidentified peak at −0.165.

of the three metals showed no decrease with time when measured at intervals over a 1-hr period.

The presence of ligands which form inert complexes with a substantial fraction of the metals to be measured leads to peak currents which cannot be directly interpreted as concentrations by single spike methods. Matson (1968) has made a detailed study of the effects of natural ligand systems on trace metal peak currents obtained with the CGME. The principles discussed in that work are also applicable to differential voltammetry with the HMDE.

Although a direct comparison between the results obtained by voltammetry and other methods has not been made, in Table II, Zn data obtained by the differential voltammetric analysis of unfiltered water samples from the eastern tropical Pacific Ocean (Zirino and Healy, 1971) may be compared to the Zn values obtained for the northeast Pacific by neutron activation after oxidation of the seawater samples with a peroxidisulfuric–sulfuric acid mixture (Slowey, 1966).

The data in Table III present values obtained from samples collected from relatively uncontaminated fresh water from high-altitude lakes and rivers. The values were obtained by the single spike technique, with CO_2–H_2CO_3 as the supporting electrolyte. They agree well with the values of Durum et al. (1960) for waters from similar sources. Although there are only a few distinct variations in concentration levels, the potential shifts indicate there exist characteristic complexing agents at each locality. The influence of these agents would be an interesting subject for future study.

Conclusions

Differential anodic stripping voltammetry is a useful tool for the study of certain trace metals in natural waters. The increased sensitivity gained by the differential electrode method permits the use of slow-voltage scan rates and produces clear current peaks above a low, level background. The electrodes are almost insensitive to ship's motion and the technique is useful in the field. The addition of CO_2 to the purging gas provides both pH control and electrolyte so that determinations can be made on both saline and fresh samples without other reagent addition. Increasing the acidity of the sample decreases adsorption of metals on surfaces and for Zn, Cu, and Pb, enhances the peak current by reducing complexation of these metals with weak acid anions.

The use of pH-controlled DASV with short plating times is a sensitive, nondestructive technique. Because the activity of the metal ions in the sample is controlled by the nature of the medium, there are many possibilities for examining the trace metal environment in the hydrosphere.

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Quantitative Separation of Nitric Oxide from Nitrogen Dioxide at Atmospheric Concentration Ranges

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■ Extensive experimental trials have shown that an absorber containing triethanolamine on firebrick is capable of quantitatively absorbing NO_2 from NO + NO_2 mixtures in dilute gas streams. Various molecular sieves used for the same purpose showed either high NO generation from NO_2 or retention of NO. Soda lime and ascarite showed large losses of NO from mixtures of NO and NO_2. While these latter materials may be used to obtain an NO_2-free stream of NO, they do not quantitatively allow passage of NO, and are useless for precise analytical work. The triethanolamine-firebrick absorber can be used for the direct quantitative analysis of NO at ambient air concentrations in any ratio of NO/NO_2 from zero to infinity.

Dilute concentrations of NO and NO_2 in air are of importance to analysts involved in air pollution studies and ambient air monitoring. To obtain pure gas streams of NO in air for evaluating and developing analytical techniques it has been commonplace to use solid alkaline surfaces such as ascarite and soda lime, or reactive surfaces such as manganese dioxide or activated carbon which remove residual amounts of NO_2 usually present in cylinders of NO.

During a project to improve the existing technique of NO and NO_2 determination, it was found that while a host of materials removed NO_2 from a mixed gas stream, these materials also affected the resultant NO concentration either positively or negatively after NO_2 removal. After checking numerous substances, an absorber using triethanolamine (TEA) on firebrick was found which completely removed NO_2, while quantitatively passing NO in any NO/NO_2 ratio normally occurring in ambient air. The passage or removal of organic nitroxy compounds was not evaluated. Organic nitrates are the only class of compounds which could possibly interfere (Ripperton and Kornreich (1970), and their ambient concentrations are probably extremely low. The peroxyacyl nitrates (PAN) which can hydrolyze to yield nitrite ion have been found in the atmosphere (Darley et al., 1963). PAN, however, is an extremely reactive compound and its transport through an impregnated firebrick surface is highly improbable.

To be analytically useful, an absorbing system which removes NO_2 and quantitatively passes NO must meet three conditions:

• It must remove *all* NO_2 in the gas stream • it *must not* generate any NO from NO_2 which may be in the gas stream • it must allow the NO to pass quantitatively whether *alone* or in the *presence* of NO_2.

Experimental

Reagents. Saltzman NO_2 absorbing solution (Saltzman, 1954).

Solid Oxidizer. 100% converter of NO to NO_2 at approximately 50% r.h. (relative humidity) (Siu and Levaggi, 1967). Soak 50–100 grams 4–8-mesh porous quartz chips (Hengar granules) in a mixture of equal weights of CrO_3, H_2O, and 85% H_3PO_4. Drain off excess liquid, blot granules rapidly with tissue paper, and store in an airtight container. Place a layer of approximately 1 to 1.5 in. of the granules in a midget impinger. Replace the upper portion of the impinger and pass ambient air (30–70% r.h.) through for approximately 1 hr at 0.5 l./min to condition the chips. Oxidizer is now ready to use for oxidation of NO to NO_2 in gas streams of 40–70% r.h.

Liquid Oxidizer. 2.5% potassium permanganate in 2.5% sulfuric acid (w/v). Use 50 ml in a 125-ml round-bottomed flask. This oxidizing solution has an efficiency of about 80% in the conversion of NO to NO_2.

TEA on Firebrick. Prepare a 20% w/v solution of TEA in water. Add the solution to about 50 ml of 14–16-mesh celite-22 firebrick in sufficient quantity to completely cover the firebrick. Stir the mixture and allow to stand for approximately 15 min. Decant off as much surplus solution as possible and transfer to a porcelain dish. Allow to dry for 2 days in an operating hood. Transfer to an oven at 105°C for approximately 15 min. Cool and place in a stoppered bottle for storage. To prepare the absorber tube, fill a 100 mm × 15 mm polyethylene drying tube with the prepared TEA-firebrick using small glass wool plugs on both ends to hold the material in place.

Other absorbers which were evaluated consisted of approximately 10–15 ml of material contained in a glass U tube.

Stock NO gas mixtures were prepared by volumetric dilution in 34-liter stainless steel tanks at a concentration of approximately 50-ppm NO in nitrogen.

Stock NO_2 gas mixtures were prepared by volumetric dilution in 34-liter stainless steel tanks at a concentration of approximately 100-ppm NO_2 in nitrogen.

Sampling Systems. The sampling train used in evaluating the ability of an absorbing system to remove NO_2 is shown in Figure 1. NO_2 gas streams were used at concentrations from 0 to 1.0 ppm, and 50% r.h. Complete removal or leakage of NO_2 was determined by the Saltzman Method (Saltzman, 1954). Table I shows the results of the various materials tested.

The sampling system described in Figure 2 was used to determine NO generation from NO_2 concentrations ranging from 0.20 to 1.0 ppm at 50% r.h. The use of a solid oxidant in the parallel sampling trains ensured the complete oxidation of residual traces of NO which may have been in the diluent air. A completely NO-free dynamic stream is mandatory when evaluating NO generation from NO_2, for an NO background

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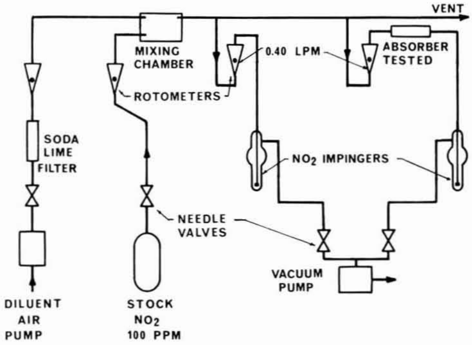


Figure 1. System for evaluation of NO_2 absorption

concentration in the dilution air of 0.02 ppm would give an apparent 4% NO generation at an NO_2 concentration of 0.50 ppm. Additionally, air and/or light oxidation of the reagent by long sampling times was compensated for by control runs (Scaringelli et al., 1970). Table I contains results using this experimental procedure.

Figures 3 and 4 illustrate the sampling trains used on promising materials for assessing the ability of passing quantitatively NO whether alone (Figure 3) or in the presence of NO_2 (Figure 4). The use of soda lime prior to the parallel sampling trains was for ensuring removal of all traces of NO_2. Gas concentrations were varied from 0–0.8 ppm, with r.h. at 50%.

In all cases where acidified permanganate was used as the oxidizer, the same batch and amounts of chemicals were used in each leg of the sampling train. This added attention to sameness of reagent was to assure a comparable oxidation of NO to NO_2 in each leg of the sampling train.

Figure 4 used for mixed streams of NO and NO_2 requires some explanation as to how the NO concentration was determined. The generation of NO from NO_2 in Saltzman reagent was first reported by Ellis (1964). He found an average of 14% generation of NO from NO_2 using fritted bubblers. Mueller and Tokiwa (1968) found a 10% generation using coiled columns used in continuous analysis instruments. Using the sampling train as described in Figure 2, replacing the absorber with a NO_2 impinger, we obtained an average of 12% generation (based on NO_2 concentration), which is the mean of some 20 trials.

A series system for NO_2 and NO then requires a correction

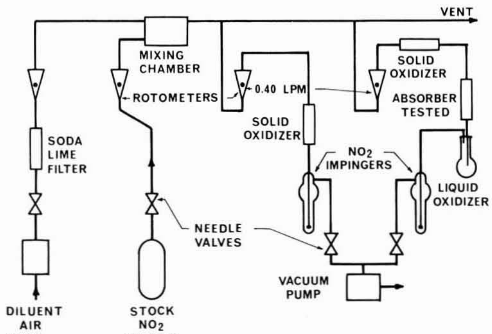


Figure 2. System for determining NO generation from NO_2

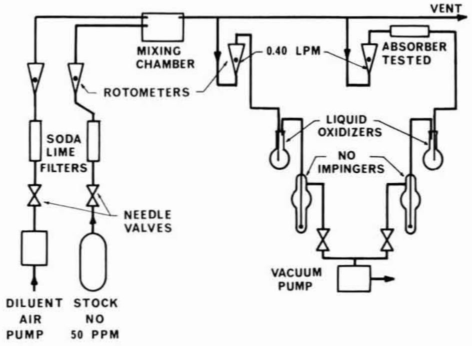


Figure 3. System to determine quantitative passage of NO

Table I. Absorption of NO_2 and Generation of NO by Various Absorbing Systems

Absorber material	NO_2 absorbed, %	NO generated, %[a]
TEA-firebrick	99–100	0–2
Silica gel, 20 mesh	40	10
Alumina, activated, 40 mesh	35	18
Soda lime, 8 mesh	100	<2
Ascarite, 14 mesh	100	<2
Nylon wool	50–70	11
Molecular Sieve 3A (bone dry)	98	<2
Molecular Sieve 3A (humidified)[b]	40–80	20
Molecular Sieve 5A (bone dry)	90	13
Firebrick + 10% hexamine	12	9
Molecular Sieve 13X (bone dry)	99	<2
Molecular sieve 13X (humidified)[b]	70–90	10–20
Silica gel–10% sulfamic acid	3	0
Alumina + 10% Na_2CO_3	84	7
Saltzman reagent (fritted bubbler)	99–100	12[c]
Molecular Sieve 4A (bone dry)	40–50	7

[a] Expressed as % of NO_2 concentration.
[b] Conditioned to room air (40–70 r.h.)
[c] Average of 20 runs.

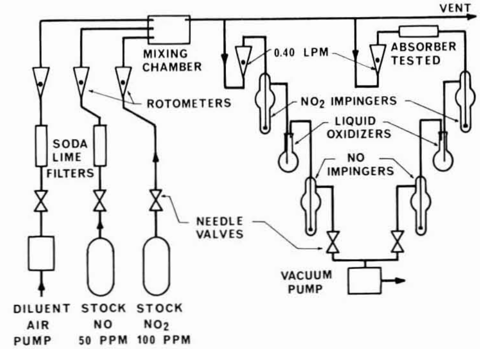


Figure 4. System to determine quantitative passage of NO in NO_x mixtures

to be made for the NO generated from NO_2 by the Saltzman reagent. This 12% NO generated from NO_2 is proportional to the NO_2 concentration up to 1 ppm, and is subtracted from the total NO found in the "NO" impinger by using the following calculation:

$$\text{True NO (ppm)} = [\text{NO (ppm) (found in NO Imp.)}] - [0.12 \times NO_2\,\text{(ppm)}]$$

Table II shows the NO absorption or loss by reaction with the absorber systems which were evaluated. It can be seen that the TEA-firebrick absorber meets the three conditions set forth in the introduction.

Additionally, the TEA-firebrick was evaluated under prolonged exposure to oxides of nitrogen under both low (20% r.h.) and high (90% r.h.) humidities. The long-term sampling was accomplished with a continuous dual-channel nitrogen oxide air-monitoring instrument Beckman Model K-75. The channels were modified to meet sampling needs as described earlier in the text. The instrument was dynamically calibrated using the procedure recommended by the Air and Industrial Hygiene Laboratory, California State Department of Public Health (1968). Periodically, manual samples were taken to verify stream concentrations. Following are results of these runs:

- NO_2 at 0.5 ppm for 18 hr at 20% r.h.: complete absorption and trace NO generation (0–2%)
- NO_2 at 0.5 ppm for 18 hr at 90% r.h.: complete absorption and trace NO generation (0–2%)
- NO at 0.5 ppm for 18 hr at both 20% and 90% r.h.; with and without added NO_2, complete passage of NO.

Discussion

NO_2 absorption from an airstream is readily accomplished with the use of strongly alkaline surfaces such as soda lime and absorptive surfaces such as molecular sieves. It has been shown, however, that these materials also either absorb NO or generate NO from NO_2 by surface reaction. The generation of NO from NO_2, shown in Table I, is quite interesting. The effect of moisture on NO generation is readily seen in the case of Molecular Sieves 13X and 3A. The mechanism for NO formation proceeds as follows and is well-known (Greene and Pust, 1958).

$$2\,NO_2 + HOH \rightarrow HNO_3 + HNO_2 \qquad (1)$$

$$3\,HNO_2 \rightarrow HNO_3 + 2\,NO + H_2O \qquad (2)$$

The loss of NO on soda lime and ascarite is shown in Table II. The fact that NO passed quantitatively when present in airstreams without NO_2 but not when present with NO_2, or after exposure of the alkaline absorber to NO_2 would indicate strongly that nitrite ion is involved in the reaction, but the mechanism is not known. Two recent papers have proposed the use of ascarite for specific NO analysis in the presence of NO_2. Miller et al. (1971) and Ripperton and Kornreich (1970). This suggests there may be a general misconception about NO not being affected on passage through ascarite when in presence of NO_2. The loss of NO in mixtures with NO_2 is related to the NO/NO_2 ratio as seen in Table II.

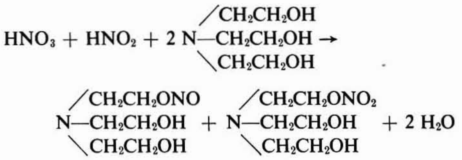
Table II. Percentage Loss of NO With Various NO_2 Absorber Systems at Varying NO/NO_2 Ratios

Absorber system	Composition of gas stream, ppm				
NO	0.5	0.8	0.5	0.2	0.1
NO_2	0	0.3	0.5	0.5	0.5
TEA firebrick	0	0	0	0	0
Soda lime 8 mesh	0^a	~12	30–35	50–65	65–75
Ascarite 14 mesh	0^a	~12	30–35	50–65	65–75
Molecular Sieve 3A (dry)	75	...	...	...	...
Molecular Sieve 13X (dry)	63	...	...	...	...

[a] Only if fresh; if material had been previously exposed to NO_2, losses of NO occur.

The chemistry of absorption of NO_2 by the TEA absorber is as yet undetermined. The experimental runs indicate that absorption is not due to the alkaline surface of TEA but is possibly due to nitrite and nitrate ester formation which could proceed as follows:

$$2\,NO_2 + HOH \rightarrow HNO_3 + HNO_2 \qquad (1)$$



$$HNO_3 + HNO_2 + 2\,N\!\begin{array}{l}\diagup CH_2CH_2OH\\ -CH_2CH_2OH\\ \diagdown CH_2CH_2OH\end{array} \rightarrow N\!\begin{array}{l}\diagup CH_2CH_2ONO\\ -CH_2CH_2OH\\ \diagdown CH_2CH_2OH\end{array} + N\!\begin{array}{l}\diagup CH_2CH_2ONO_2\\ -CH_2CH_2OH\\ \diagdown CH_2CH_2OH\end{array} + 2\,H_2O \qquad (3)$$

Another indication that alkaline surface absorption is not occurring is the extremely low NO generation from NO_2 on TEA as compared to other basic amines without alcohol groups. If salt formation such as $HNO_2 \cdot N\!\begin{array}{l}\diagup CH_2CH_2OH\\ -CH_2CH_2OH\\ \diagdown CH_2CH_2OH\end{array}$ was occurring, the breakdown of HNO_2 to HNO_3 + NO would most likely occur as we have noted on various other surfaces (Equation 2).

Summary

An absorber suitable for the direct determination of NO has been developed which will quantitatively pass NO and absorb completely NO_2 in a mixed NO–NO_2 gas stream, in the low and sub-ppm range. A large number of materials tested has shown that TEA on firebrick is the only substance capable of performing this separation in NO/NO_2 ratios normally found in ambient air.

The absorber has a relatively long lifetime. Tests have showed that the absorber was still removing NO_2 after 150 hr of sampling at 0.15 ppm. NO generation was insignificant under humidity conditions ranging from 20–90% r.h.

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Effects of Hydrocarbon and Nitrogen Oxides on Photochemical Smog Formation

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■ The role of hydrocarbon (HC) and nitrogen oxides (NO_x) in photochemical smog formation was investigated. Samples of automobile exhaust with varying HC and NO_x levels were irradiated in a smog chamber under conditions that resulted in levels of smog manifestations similar to those observed in the atmosphere. HC levels ranged from 0.3 to 5.0 ppmC, and NO_x levels ranged from 0.08 to 1.4 ppm. Photooxidation of nitric oxide (NO) and formations of oxidant, peroxyacyl nitrate (PAN), formaldehyde (HCHO), and nitrogen dioxide (NO_2) were used as smog manifestations. Results showed that except for the NO_2 yield, all smog manifestations were intensified by increasing HC; NO_x inhibited the oxidant, PAN, and HCHO yields but promoted the rate of NO oxidation and the NO_2 yield. By use of these data, it was estimated that to achieve an air quality equivalent to the current California standards for oxidant and NO_2, NO_x should be less than 0.33 ppm and HC less than $2.5 \times (NO_x)$.

Since its inception, photochemical smog abatement has been oriented toward reduction of hydrocarbon emissions in the atmosphere. This approach to control has been taken because laboratory studies have demonstrated that reduction of one of the major photochemical smog reactants, the hydrocarbon (HC), would be beneficial and because the technological problems in implementing such control were relatively simple. Conversely, control of the other major reactant, the nitrogen oxides (NO_x)—i.e., nitric oxide (NO) plus nitrogen dioxide (NO_2), has not been applied as yet, primarily because of the uncertainty about its merits and, secondarily because the related technological problems are more difficult.

This report covers experimental work performed to determine the relative contribution of HC and NO_x in the atmospheric smog formation and to associate air quality with the HC:NO_x ratio using currently existent atmospheric quality criteria. This work comprised an experimental study of the photochemical smog potential of automotive emissions as a function of HC and NO_x levels. Automobile exhaust was used because it constitutes a readily available source of sample mixtures nearly identical in composition to that of the mixture in smog-infested atmospheres.

The role of HC and NO_x in smog phenomena had been studied (Altshuller et al., 1969; Buchberg et al., 1963; Glasson and Tuesday, 1966; Romanovsky et al., 1967; Hamming and Dickinson, 1966; Korth et al., 1964; Nicksic et al., 1966); however, interpretation of those earlier data was subject to uncertainty because test conditions and/or samples differed from those representing a typical urban atmosphere. In this study, composition and levels of the HC and NO_x reactants in the test mixtures were controlled to approximate pollutant makeup in present-day problem atmospheres and in atmospheres anticipated as a result of current controls. Further, a smog chamber was used in which irradiation of reactant mixtures similar to those in early morning atmospheres was found to result in levels of smog constituents comparable to levels observed in the atmosphere.

Experimental

The experimental program consisted of a series of chamber irradiation tests in which reactivity or smog potential of exhaust was measured for HC and NO_x levels ranging within 0.3 to 5.0 ppmC and 0.08 to 1.4 ppm, respectively. These initial reactant levels are shown in Figure 1 as points in the (HC, NO_x) plane. As arranged in the two-dimensional space (Figure 1), these points represent conditions appropriate for determining the effect of NO_x for constant HC, the effect of HC for constant NO_x, and the effect of HC and NO_x at a constant HC:NO_x ratio. Reactivity was measured and expressed in terms of five smog manifestations: Rate of NO_2 formation (Dimitriades, 1967) and oxidant, peroxyacetyl nitrate (PAN), formaldehyde (HCHO), and nitrogen dioxide dosages (Dimitriades, 1967). Additionally, reactivity was expressed in terms of the same units used to express the California air quality standards for oxidant and NO_2 (California State Air Resources Board, 1969), namely, time during which oxidant exceeded 0.1 ppm and time during which NO_2 exceeded 0.25 ppm.

Generation and Preparation of Exhaust Sample. Exhaust gas was generated using a 1963 automobile equipped with a 283-in.^{3} engine and operated to follow the seven-mode California cycle. The engine was fitted with a modified carburetor for wide-range adjustment of the air-to-fuel ratio (*A/F*). With normal carburetor settings, the HC:NO_x ratio in exhaust was 6:1, approximately. To study ratio effect at ratios to 12:1, the *A/F* ratio was adjusted for a richer fuel mixture.

The exhaust stream was sampled with a heated, variable-rate proportional sampler (Fleming et al., 1965), the output of which was received in a Tedlar bag that had been covered with dark cloth and precharged with dry nitrogen. Resultant exhaust-to-N_2 ratio in the bag was approximately 1:5. Immediately after sample collection, the bag content was used to charge the chamber (a 10- to 15-min operation) and to provide samples for chromatographic analysis. These chroma-

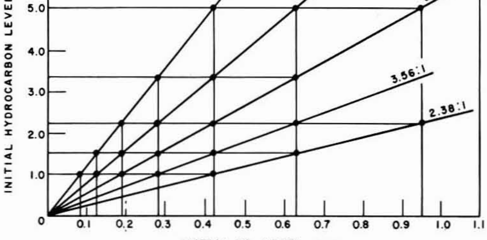

Figure 1. Hydrocarbon and NO_x levels in tested exhaust samples

Table I. Data from Light-Intensity Measurements Using Irradiation of Propylene + NO Mixtures in Bags

	Bag on rooftop		Bag inside chamber	
Date	9/12/69	9/18/69	9/17/69	9/19/69
Irradiation source	Sun	Sun	Chamber lights	Chamber lights
Irradiation time, hr	6	6	6	6
Start time	10:00 A.M.	10:37 A.M.		
Average bag temp, °F	91	78	92	92
Ambient humidity				
Relative, %	64 → 33	77 → 53	≈40	≈40
Absolute, %	≈2.0	≈2.0	≈2.0	≈2.0
Initial HC, ppmC	3.0	3.0	3.0	3.0
Initial NO_x, ppm	1.0	1.0	1.0	1.0
Initial NO_2, ppm	0.06	0.05	0.13	0.08
R_{NO_2}, ppb/min	6.2	8.3	8.4	8.6
Oxidant dosage, ppm × min	58	87	57	74
PAN dosage, ppm × min	28	43	30	36

tographic data were used to establish the extent to which composition of exhaust hydrocarbons varied (unavoidably) from test to test.

Smog Chamber and Associated Instrumentation. Detailed description of the smog chamber has been reported (Dimitriades, 1967, 1970). Analytical instrumentation includes two Beckman 109 analyzers for measurement of total hydrocarbon, two Mast meters for oxidant, and two Beckman K-1008 analyzers for NO_2 and NO_x. Instrument duplication safeguards instrument malfunction and provides more reliable analytical data. The HC analyzers were calibrated at the beginning of the study with synthetic hydrocarbon mixtures of exhaustlike composition and daily with a standard propylene blend. Details on measurement of NO_2, NO_x, PAN, oxidant, and formaldehyde have been reported (Dimitriades, 1967).

Light-Intensity Measurement. It has been shown that measurement of light intensity in the chamber by the commonly used method of NO_2 photolysis (Tuesday, 1961) gives uncertain results (Dimitriades, 1970). For this reason, light intensity in this study was evaluated through direct comparison with natural sunlight. For this evaluation, a 300-liter Tedlar (2-mil thick) bag was charged with purified air containing propylene and NO at 1 ppm each and was irradiated inside the chamber and on a rooftop against a background of light grey concrete. During each 6-hr irradiation test, NO_2, NO_x, oxidant, and PAN were monitored and results were expressed in terms of rate-of-NO_2 formation, oxidant dosage, and PAN dosage. Table I summarizes detailed experimental conditions and test results. The difference between the two rooftop measurements was attributed to difference in experimental conditions that included partial overcast (clear to slightly cloudy) during the 6-hr tests. From these results, light intensity in the chamber was judged comparable to that of natural sunlight in a typical "irradiation" day in the United States during the smog season.

Variability of light intensity was investigated using data from biweekly measurements of the reactivity of a standard ethylene–NO_x mixture (at 3 ppmC/ppm) and parallel measurements of light intensity with a light monitor. Details from this investigation and results have been reported (Dimitriades, 1970). These results indicated that output of fluorescent lamps varied significantly as a result of lamp-temperature variation, and reactivity measurement results correlate well with the light monitor response data. From such light monitor response data it was deduced that during this study, light intensity in the chamber varied from test to test by about ±10%. No correction of the reactivity data for light intensity variation was attempted, other than screening off tests in which the monitor response was clearly much higher or much lower than the average level.

Test Procedure. In test preparation, the chamber is flushed for 3 hr with prepurified air (Dimitriades, 1967) under infrared lamps that heat the walls to about 125°F. Next, the chamber is sealed, the chamber air is recirculated overnight through a catalytic combustor, a charcoal column, and a particulate filter. Chamber air, so purified, contains less than 0.1 ppmC of total organic material and less than 0.02 ppm NO_x.

For an irradiation test, the chamber air is first humidified by a stream of pure air that bubbles through heated distilled water; resultant relative humidity is 25% of 92°F. The chamber is then charged with the bag sample of exhaust + N_2 to the desired HC_t levels, and additional NO and NO_2 are injected to attain the specified levels. Initial NO_2 level, $(NO_2)_i$, is adjusted to about 10% of initial NO_x (from about 5%, as present in the bag mixture) but not less than 0.03 ppm or more than 0.15 ppm. Tests showed that at extremely low levels, $(NO_2)_i$ affected the rate of NO photooxidation (R_{NO_2}). At levels above 0.03 ppm, $(NO_2)_i$ did not affect R_{NO_2} but affected the appearance time for oxidant and PAN; however, such an effect was quantifiable, and corrections for variation in $(NO_2)_i$ were easily made. Chamber wall temperature during run was maintained at 92(±1)°F by circulating room air in the space between the chamber windows and the lights.

Results

Treatment of Raw Experimental Data. Results from the exhaust reactivity measurements are given in Table II along with detailed data on initial chamber charge. The data of Table II represent results that were corrected for unavoidable variation in exhaust hydrocarbon composition and in $(NO_2)_i$ (Dimitriades, 1970). In each case the correction ranged from 0 to 10%.

For interpretation, the data of Table II have been plotted (Figures 2 and 3) to depict reactivity as a function of HC for constant NO_x and as a function of NO_x for constant HC [more complete plots can be found (Dimitriades, 1970)]. Graphical depiction of the HC and NO_x effects was preferred to statistical

Table II. Initial Reactant Levels and Exhaust Reactivity Measurements

Initial reactant levels			Reactivity measurements						
HC/NO_x	HC, ppmC	NO_x, ppm	Rate of NO_2 formation, R_{NO_2}, ppb/min	NO_2 dosage, ppm × min	Oxidant dosage, ppm × min	PAN dosage, ppm × min	HCHO dosage, ppm × min	Time,[a] min	Time,[b] min
0	<0.1	0.081	...	13.4	4.9	0.16	11.8	0	0
2.7	0.20	0.075	...	16.5	23.3	0.64	19.6	111	0
2.6	0.70	0.265	1.95	50.5	16.3	0.51	31.0	53	0
2.5	1.53	0.618	...	104.5	12.5	0.55	43.2	0	266
3.2	0.30	0.093	1.02	15.5	26.5	1.20	20.4	137	0
3.5	0.44	0.124	1.27	22.7	23.3	1.05	22.7	105	0
3.8	0.67	0.175	...	33.5	25.9	1.43	27.4	128	0
3.5	0.97	0.276	2.62	53.6	22.6	1.16	36.0	109	0
3.7	1.50	0.409	2.91	82.8	16.0	1.66	55.3	79	173
3.7	2.25	0.606	5.01	123.9	21.2	1.70	66.5	110	300
3.7	3.66	0.923	6.41	174.4	13.9	2.50	79.1	63	310
3.6	3.37	0.936	6.17	160.7	16.3	1.76	72.4	0	307
3.7	5.96	1.384	9.24	217.9	13.5	2.41	97.3	0	322
5.4	0.44	0.081	1.02	15.2	41.4	1.65	28.0	225	0
5.6	0.70	0.125	1.87	22.4	44.4	3.19	33.2	218	0
5.6	0.98	0.175	2.69	33.7	40.7	3.42	39.5	204	0
5.5	1.49	0.272	3.27	50.3	44.5	3.77	51.5	202	0
5.6	2.24	0.398	4.49	79.1	50.8	4.71	63.7	207	155
5.5	3.29	0.599	6.00	114.1	76.0	5.01	87.7	228	253
5.3	5.06	0.946	9.48	167.8	59.5	8.96	114.5	196	310
6.9	0.63	0.091	1.52	11.2	43.8	3.80	34.1	224	0
8.4	1.02	0.121	2.06	18.8	49.7	5.07	53.3	248	0
7.7	1.02	0.133	2.38	22.2	49.3	4.76	49.5	234	0
7.7	1.45	0.188	3.40	30.4	70.3	5.92	56.7	256	0
7.5	1.45	0.192	3.81	25.5	70.2	7.63	55.4	262	0
8.8	2.25	0.256	...	40.6	...	5.44	76.3	...	0
8.1	2.25	0.276	...	42.3	...	6.94	69.7	...	0
8.4	2.34	0.278	5.04	45.8	...	...	79.1	...	0
8.1	3.30	0.409	...	59.2	101.7	8.23	82.5	256	101
8.0	3.30	0.414	6.52	57.3	97.6	11.85	96.1	268	91
7.8	5.00	0.641	8.15	86.2	113.1	14.41	134.6	256	168
12.0	1.00	0.083	1.56	13.8	62.6	...	38.6	276	0
10.9	1.00	0.092	...	10.7	60.9	5.48	45.6	286	0
12.1	1.49	0.123	2.93	20.0	99.1	...	56.2	290	0
12.7	1.50	0.118	2.90	19.3	83.0	6.26	56.6	294	0
11.8	1.50	0.127	...	18.9	...	...	43.7	...	0
11.5	2.25	0.195	4.56	22.4	105.9	7.71	68.8	296	0
12.3	2.25	0.183	4.47	19.0	93.4	12.29	70.7	297	0
12.3	3.38	0.274	5.92	30.6	109.0	11.35	104.5	288	0
12.0	3.38	0.281	6.40	28.4	...	16.63	111.2	...	0
11.0	4.76	0.434	8.88	42.6	143.3	20.36	146.5	309	68
12.2	5.06	0.416	9.92	42.7	164.5	16.51	115.0	310	72

[a] Time during which oxidant exceed 0.1 ppm.

[b] Time during which NO_2 exceeded 0.25 ppm.

analysis because it allowed some freedom in assessing reliability of the data individually. For example, the reliability of each oxidant yield value was judged by the consistency of the patterns that described dependence of oxidant on HC, dependence of oxidant on NO_x, correlation of oxidant and PAN yields, and the agreement of results from the two oxidant-measuring instruments.

Oxidant Yield. Of the reactivity data obtained in this study, those of oxidant and PAN yields seem to be the least precise. For oxidant, part of the observed imprecision was caused by day-to-day variation of the Mast meter response to oxidant and to NO_2. Furthermore, variation in light intensity and in composition of HC in tested samples could also have introduced variability.

Figures 2 and 3 show the dependence of oxidant yield on HC and NO_x; oxidant yield in these figures is expressed as time during which oxidant exceeded 0.1 ppm. Similar dependence patterns were shown by the oxidant dosage data.

Diagrams in Figure 3 show that change in NO_x was never accompanied by a codirectional change in oxidant reactivity.

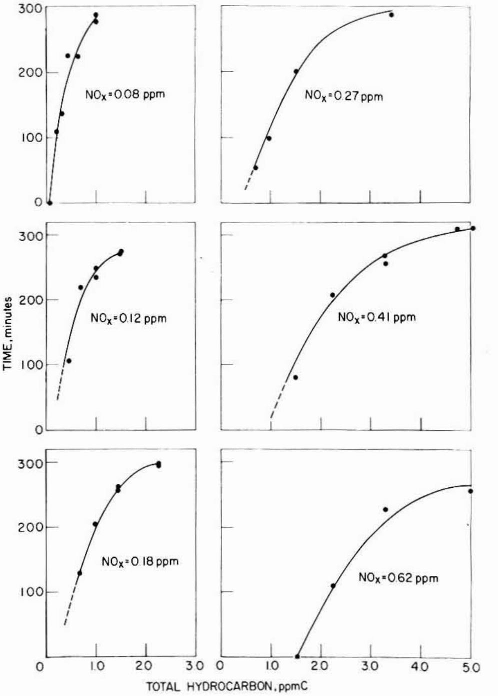

Figure 2. Time during which oxidant exceeded 0.1 ppm as a function of total hydrocarbon at various NO_x levels

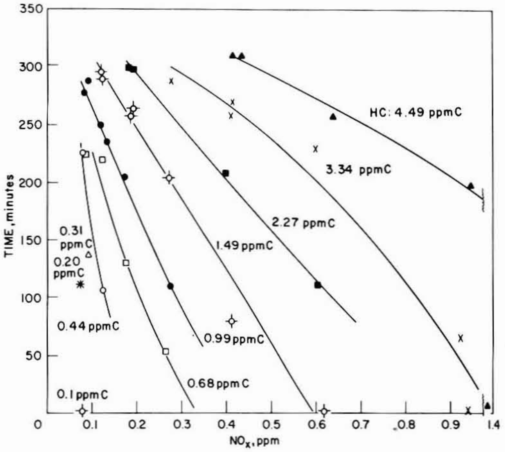

Figure 3. Time during which oxidant exceeded 0.1 ppm as a function of NO_x at various HC levels

This is contrary to what has been observed in irradiation of synthetic HC:NO_x mixtures. Altshuller et al. (1970) reported such data for hydrocarbons, including the fairly reactive propylene and xylene and the relatively unreactive toluene and butane. Similar data were also reported by Glasson and Tuesday (1970). These reported data show that the dependence of oxidant on NO_x does show a maximum; however, the same data also seem to support the generalization that this oxidant maximum occurs at lower NO_x levels for less reactive HC:NO_x systems. Such oxidant maxima may, therefore, also exist in the exhaust system, but they occur at NO_x levels lower than those used in this study. This, in turn, suggests that effect of NO_x reduction on oxidant cannot be predicted by extrapolating the diagrams of Figure 3 to lower NO_x levels.

PAN Yield. Of the known PAN compound family, only the first member, peroxyacetyl nitrate was measured routinely. The presence of peroxypropionyl nitrate (PPN) and peroxybenzoyl nitrate (PBZN) in the irradiated exhaust samples was also occasionally checked. Results showed undetectable levels of PBZN and PPN levels equivalent to 10 to 20% of those of PAN. The PAN yields, in general, follow the same patterns of dependence on HC and NO_x as oxidant yields. Also, the ratio of PAN to oxidant dosages was 1:10, approximately; this compares well with the level of ratios found in the atmosphere—1:5 to 1:10.

Table III. Slope and Intercept Values of the HCHO Dosage Vs. HC Lines for Varying $(NO_x)_i$

	$(NO_x)_i$, ppm					
	0.08	0.12	0.18	0.27	0.41	0.62
Intercept[a]	11	11	11	11	10	10
Slope[a]	33	31	28	27	25	23

[a] Units are the same as those used in diagram of Figure 4—i.e., ppm × min for HCHO dosage (ordinate) and ppmC for HC (abscissa).

HCHO Yield. Formaldehyde yields showed extremely well-defined dependencies on HC and NO_x. A typical example is given in Figure 4. Formaldehyde dosage appears to be a linear function of HC, with slope depending slightly on NO_x. The effect of NO_x is inhibitive, as shown in Table III. The intercept point on the HCHO-dosage axis is constant and equal to 11 ppm × min; this latter level was attributed to contaminants in background air. The formaldehyde level naturally present in exhaust is too low to affect appreciably the results obtained on HCHO dosage; therefore, the effect from such formaldehyde on observed patterns should be unimportant.

NO_2 Yield. The NO_2 yield, in terms of time during which NO_2 exceeded 0.25 ppm, appeared to be the only manifestation that, within the confines of this study, was inhibited, although only slightly, by HC. The inhibitive effect of HC was shown more clearly at the higher HC levels (Figure 5) and pre-

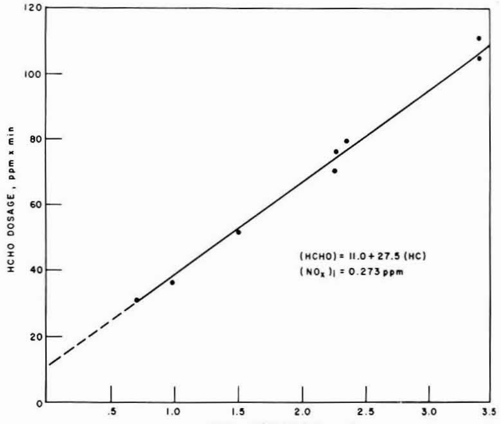

Figure 4. Formaldehyde-dosage reactivity of exhaust as a function of total hydrocarbon at NO_x = 0.273 ppm

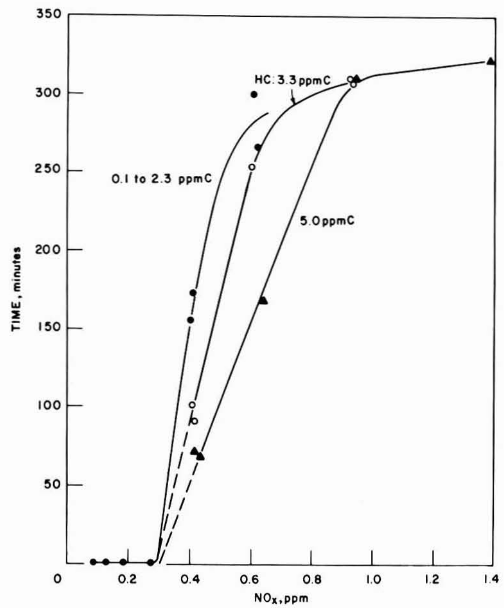

Figure 5. Time during which NO_2 exceeded 0.25 ppm as a function of NO_x at various HC levels

sumably was caused by accelerated consumption of NO_2 in reactions with oxidant and to a lesser extent with hydrocarbons. Similar patterns were shown by the NO_2 dosage data.

Nitrogen dioxide accounted for less than one half of the NO_x present in the initial chamber charge. Of the nitrogen compounds known to form in such reaction systems (namely, peroxyacyl, alkyl, and inorganic nitrates), only PAN, PPN, and inorganic nitrates were expected to affect nitrogen balance significantly (Altshuller et al., 1970; Gay and Bufalini, 1969). The ratio of NO_2 dosage to PAN dosage ranged from 200:1 in the low HC:NO_x ratio samples to 2:1 with the highest HC:NO_x ratio samples. The sum of NO_2, PAN, and PPN levels at the end of irradiation ranged from 20 to 60% of the sum of initial NO and NO_2; therefore, much of the NO_x initially present must have been converted to nitric acid and nitrate.

Evidence that nitric acid or its anhydride, N_2O_5, forms at significant levels was also provided by experimental data on oxidant measured by the Mast method and by an NO-titration technique. The latter method involved NO injection in the chamber at the end of each run and invariably gave higher oxidant results by 0 to 0.15 ppm. The difference called nonozone oxidant, was attributed to N_2O_5 that reacts with NO to NO_2 but fails to cause response to the Mast instrument because of nearly total loss in the sampling line. Final levels of such nonozone oxidant or N_2O_5 were related to initial HC and NO_x levels in fairly well-defined and unique patterns (Figures 6–7). Specifically, diagrams of Figures 6 and 7 show that the dependence of N_2O_5 on either HC or NO_x shows a maximum, suggesting that, within the concentration ranges used in this study, both HC and NO_x can either promote or inhibit N_2O_5 yield. Considering the inadequacies of the analytical method used to measure N_2O_5, these results are submitted merely as evidence to suggest that significant levels of inorganic nitrates should be expected to form in ordinary polluted atmospheres and that the dependence of such nitrate yields on reactant HC and NO_x does not parallel those established for other smog manifestations.

Rate of NO_2 Formation. Rate of NO_2 formation (R_{NO_2}) was strongly dependent on HC and, at NO_x levels lower than 0.2 ppm, on NO_x also. At higher NO_x levels, R_{NO_2} was insensitive to NO_x variations. At constant HC:NO_x ratio, R_{NO_2} increased with increasing NO_x because of the HC effect. Such dependence of R_{NO_2} on HC and NO_x was similar to reported patterns (Glasson and Tuesday, 1966) for single HC:NO_x systems.

Discussion

Comparison of Smog Levels in Real and Simulated Atmospheres. Considering the differences between the experimental system of this study and the natural atmosphere, it would be of interest to compare smog levels observed in this study with smog levels in the atmosphere for similar mixtures of pollutants. For such comparison, atmospheric data not readily attainable must be used; for example, HC and NO_x levels in an air parcel during early morning hours and levels of smog in the same air parcel after several hours of sun irradiation. Alternatively, the necessary data can be obtained by measuring smog levels in an atmospheric sample directly and obtaining data on the sample's initial levels of HC and NO_x indirectly. This latter approach is applicable only to samples of atmospheres for which the sources and detailed compositions of atmospheric pollutants have been established. Such information is currently being pursued, and in at least one instance, data have been reported that led to establishment of corresponding values for initial atmospheric levels of reactants—HC and NO_x—and resultant levels of smog (Stephens and Burleson, 1969). Specifically, the reported information included data on oxidant and PAN levels in an atmospheric sample taken in Riverside, Calif., at 4:10 P.M. on a smoggy day. Total HC and NO_x levels in the unreacted sample were also estimated by

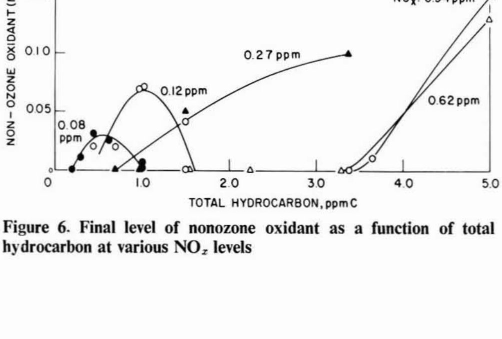

Figure 6. Final level of nonozone oxidant as a function of total hydrocarbon at various NO_x levels

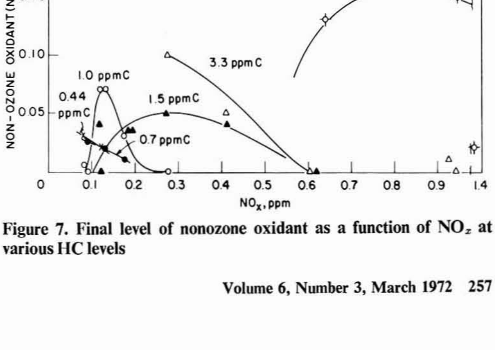

Figure 7. Final level of nonozone oxidant as a function of NO_x at various HC levels

Table IV. Comparison of Smog Levels from an Atmospheric Sample and a Chamber Sample that Contain the Same Initial Reactant Levels

	Initial reactant levels		Smog levels	
	Total nonmethane hydrocarbon, ppmC	NO_x, ppm	Oxidant, ppm	PAN, ppm
Atmosphere (Riverside, Calif., 10/24/68)	3.05	0.30		
At 16:10 PST			0.40	0.034
Smog chamber	3.13	0.27		
After 2-hr irradiation			0.26	0.034
After 4-hr irradiation			0.49	0.047
After 6-hr irradiation			0.49	0.044

Table V. Values of $(NO_x)_i$[a] Levels and $(HC)_i$[a] Levels Corresponding to Oxidant Yield Equivalent to the California Air Quality Standard for Oxidant

Time during which oxidant exceeded 0.1 ppm, min	$(NO_x)_i$, ppm	HC_i, ppmC
60	0.08	0.13
60	0.12	0.25
60	0.18	0.40
60	0.27	0.70
60	0.41	1.23
60	0.62	1.90

[a] Subscript designates level in initial chamber charge.

the use of established compositional patterns in the sampled atmosphere and knowledge of relative hydrocarbon disappearance rates. Table IV summarizes resultant and corresponding data from this research. The data of Table IV show generally good agreement in observed smog levels. Note that atmospheric hydrocarbons mostly originate from automotive exhaust but include also emissions from natural gas, oilfields, and gasoline evaporation (Stephens and Burleson, 1969). The predominant hydrocarbon from these secondary sources, however, is methane with zero reactivity; the average reactivity of the others is comparable to that of exhaust. Therefore, with methane excluded, the comparison of the atmospheric and chamber data shown in Table IV is valid because distribution of reactive hydrocarbons in the compared systems can be reasonably assumed to be the same. The good agreement between data from the chamber and the data associated with one atmospheric sample (Table IV) certainly does not resolve the issue of comparability (of atmospheric and smog chamber systems), but it does add an element of realism to the experimental data of this study in that both the reactants and the products are present at levels close to those in smoggy atmospheres.

Comparison of patterns that describe oxidant and PAN dependence on HC and NO_x shows a striking disagreement in results between this exhaust study and reported studies of simple HC:NO_x mixtures. Specifically, in the exhaust study the oxidant dependence on NO_x did not show a maximum within the range of HC:NO_x ratios used (Figure 3). In contrast, the propylene–NO_x and xylene–NO_x systems at comparable HC:NO_x ratios do show such maxima, a pattern that is probably real because it has been verified by several independent studies (Romanovsky et al., 1967; Altshuller et al., 1970; Glasson and Tuesday, 1970). Therefore, we must conclude that use of simple HC:NO_x systems, for example, propylene + NO_x, as substitutes for exhaust or atmospheric samples is unrealistic. Exhaust behavior can probably be simulated in synthetic mixtures; however, such mixtures should be carefully designed and should be tested by direct comparison to exhaust at various HC:NO_x ratios before they are accepted as exhaust substitutes.

Patterns that describe dependence of other reactivity manifestations on HC and NO_x were generally in good agreement with those reported (Altshuller et al., 1969; Buchberg et al., 1963; Glasson and Tuesday, 1966; Korth et al., 1964; Altshuller et al., 1970; Stephens and Burleson, 1969). Within the range of initial concentration levels used in this research, these dependencies are as follows: At low NO_x levels, the NO_2 dosage is nearly proportional to NO_x and is slightly inhibited by HC at higher HC levels, the HCHO dosage is nearly proportional to HC level and slightly inhibited by NO_x, and rate of NO_2 formation is nearly proportional to HC and varies similarly with NO_x in the lower NO_x level range; at higher NO_x levels, R_{NO_2} is nearly independent of NO_x.

Air Quality Benefits From HC and NO_x Reduction. Results from this study can be used to define the dependence of certain types of air quality on HC and NO_x. This is illustrated by using these results to estimate the HC and NO_x levels necessary to meet the California air quality standards for oxidant and NO_2. Such estimates were obtained as follows: First, from the diagrams in Figure 2, combinations of HC and NO_x were defined that result in an oxidant yield equal to the California standard, namely, 0.1 ppm for 1 hr. For example, for $(NO_x)_i = 0.08$ ppm, $(HC)_i$ should be 0.13 ppmC or less in order that resultant oxidant exceed 0.1 ppm for 1 hr or less. Such optimum $(HC)_i$ and $(NO_x)_i$ values (listed in Table V) were used to draw the equal-response line *aeb* in Figure 8. Points above this equal-response line represent values of $(HC)_i$ and $(NO_x)_i$ that meet the California standard for oxidant; points below correspond to high oxidant yields in general except for those that represent extremely low NO_x levels. For those NO_x levels, experimental data on oxidant yields are not available, however, gross approximations can be made. These approximations are based on the assumption that the oxidant dependence on NO_x (Figure 3) has a maximum and that at sufficiently low NO_x levels—lower than those used in this study—oxidant increases with NO_x. Thus, assuming that oxidant dependence on NO_x for HC at 5 ppmC, has a maximum at NO_x = 0.4 ppm (see Figure 3) and that oxidant yield is proportional to NO_x within the range 0–0.4 ppm, then the NO_x level corresponding to the California oxidant standard is estimated (from Figure 3) to be

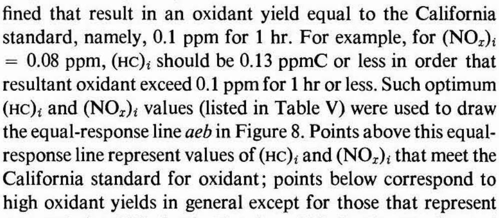

Figure 8. Equal response lines representing combinations of total hydrocarbon and NO_x corresponding to oxidant and NO_2 yields equal to the California standards

Shaded area represents all points in the (HC, NO_x) plane that meet the California oxidant and NO_2 standards of air quality

0.08 ppm, yielding an HC:NO_x ratio of 4.99:0.08 or 62. In actuality, the oxidant maximum would probably occur at NO_x less than 0.4 ppm and yield a ratio higher than 62. When similar treatment was applied on the oxidant-NO_x curves (Figure 3) for 3.34 ppmC, 2.27 ppmC, 1.49 ppmC, and 4.99 ppmC, resultant ratio values were 61, 64, 60, and 67, respectively. These results suggest that within the concentration ranges of this study, the California standard for oxidant can be met when the HC:NO_x ratio is about 63 or higher; HC and NO_x levels at this ratio are represented by points that comprise line *bc* in Figure 8. Unlike line *ab*, line *bc* is shown as a dashed line to designate that the associated data were, in part at least, deduced through use of assumptions rather than obtained experimentally. To summarize, line *aebc* in Figure 8 is an equal-response line consisting of (HC, NO_x) points that correspond to an oxidant yield equal to the California standard. Points above *aeb* and below *bc* represent HC and NO_x levels corresponding to oxidant yields lower than the California standard.

To meet the California standard for NO_2, additional restrictions must be placed on the HC and NO_x levels. From Figure 5, it can be estimated that for any HC level, the California NO_2 standard is met simply when NO_x is 0.33 ppm or less. HC and NO_x levels satisfying this condition are represented by points that comprise line *def* in Figure 8. All points below line *def*—obviously including those below line *bc*—correspond to NO_2 yields lower than the California standard. The resultant line *debc* in Figure 8 outlines an area (shaded) in the (HC, NO_x) plane, within which lie all HC:NO_x combinations that correspond to air quality meeting the California standards. Point *g* was also included in Figure 8 to show the currently typical levels of HC and NO_x in atmosphere, relative to the desired levels.

From diagrams such as Figure 8, it is possible to estimate the direction and extent to which current atmospheric levels must be modified to achieve a specified air quality level. To illustrate this, such estimates of optimum HC and NO_x levels were obtained for different sets of air quality standards, existent and hypothetical, and are listed in Table VI.

Table VI. Optimum NO_x and HC Levels to Meet Prescribed California Air Quality Standards

Standards (existent)			
Oxidant not to exceed 0.1 ppm for more than 1 hr NO_2 not to exceed 0.25 ppm for more than 1 hr	NO_x: ≤ 0.08 ppm HC: $\geq 62 \times (NO_x)$ (Requires at least 80% NO_x reduction and no HC reduction from current levels)	or	NO_x: ≤ 0.33 ppm HC: $\leq 2.5 \times (NO_x)$ (Requires at least 15% NO_x reduction and drastic HC reduction from current levels)
Standards (hypothetical)			
Oxidant not to exceed the dosage level of 0.1 ppm × hr NO_2 not to exceed the dosage level of 0.25 ppm × hr	NO_x: ≤ 0.017 ppm HC: $\geq 300 \times (NO_x)$ (Requires drastic NO_x reduction and no HC reduction)	or	NO_x: ≤ 0.10 ppm HC: $\leq (NO_x)$ (Requires at least 75% NO_x reduction and drastic HC reduction)
Oxidant not to exceed the dosage level of 0.25 ppm × hr NO_2 not to exceed the dosage level of 0.25 ppm × hr	NO_x: ≤ 0.04 ppm HC: $\geq 125 \times (NO_x)$ (Requires drastic NO_x reduction and no HC reduction)	or	NO_x: ≤ 0.10 ppm HC: $\leq 2.0 \times (NO_x)$ (Requires at least 65% NO_x reduction and drastic HC reduction)
Oxidant not to exceed the dosage level of 0.25 ppm × hr Daily maximum NO_2 or NO_x not to exceed 0.25 ppm	NO_x: ≤ 0.04 ppm HC: $\geq 125 \times (NO_x)$ (Requires drastic NO_x reduction and no HC reduction)	or	NO_x: ≤ 0.25 ppm HC: $\leq 2.5 \times (NO_x)$ (Requires at least 30% NO_x reduction and drastic HC reduction)

The estimates given in Table VI are based directly or indirectly on exhaust reactivity data obtained in this study. Application of these estimates to the actual atmospheric system is valid depending on the extent to which the following conditions are satisfied:

- Interdependence of initial reactants and resultant smog levels are the same in the smog chamber as in the atmosphere
- Hydrocarbon composition is the same in exhaust as in the atmosphere
- Change in HC:NO_x ratio in the atmosphere is not accompanied by unavoidable change in hydrocarbon composition.

Comparison of the reactants-smog interdependencies in the chamber and in the atmosphere cannot be made easily, and it is unlikely that agreement will be achieved for all smog manifestations. An approach, however, for such comparison is available, and the data of Table IV suggest that at least for some smog manifestations, the atmospheric reactant-smog interdependency can be reproduced in smog chambers.

Hydrocarbon composition in the atmosphere is closely similar to that in exhaust, except for the relatively higher atmospheric levels of methane, ethane, propane, and some heavier hydrocarbons that result from gasoline evaporation. Stephens and Burleson (1969) have, however, demonstrated that these composition differences can be defined quantitatively and that the portion of the total atmospheric HC level which originates from exhaust can be calculated. Furthermore, the reactivities of the methane, ethane, and propane, under ordinary HC:NO_x ratios, are zero, whereas the reactivity of gasoline evaporative emissions, under summer temperature conditions, is comparable to that of exhaust (Eccleston et al., 1970). All in all, exhaust HC and atmospheric HC values can be used almost indistinguishably if methane, ethane, and propane are not included in the expression for total HC. Optimum levels of atmospheric HC can then be obtained from the optimum levels of exhaust HC by addition of the levels of methane, ethane, and propane typically present in the atmosphere.

A change of HC:NO_x ratio in the atmosphere as a result of emission controls may or may not be accompanied by a change in hydrocarbon composition, depending on the control method used. Use of devices currently produced by automobile manufacturers for exhaust hydrocarbon control does not seem to affect composition of exhaust hydrocarbons (Altshuller, 1968). Composition of hydrocarbons in exhaust from NO_x-controlled autos may, however, depend decidedly on whether NO_x control is effected by catalytic treatment of the exhaust stream or by other methods, such as exhaust recirculation and modification of spark schedule or carburetion. For example, catalytic NO_x control was found to alter hydrocarbon composition drastically by preferentially removing reactive hydrocarbons (Weaver, 1969). The other control methods are not expected to have a drastic effect. Because no NO_x-control method has been specified for application, no compositional effects that would unavoidably accompany the effect of NO_x reduction can be predicted or even studied at this time.

Summary and Conclusions

The roles of HC and NO_x in smog formation were investigated by photoirradiating samples of automobile exhaust at levels equal to or lower than those in a typically polluted atmosphere.

Smog levels observed in the smog chamber were comparable to similar atmospheric levels of reactants.

Data were developed which showed that use of simple HC:NO_x systems—e.g., propylene/NO_x, as substitutes for natural atmosphere or exhaust is unrealistic.

The relative effects of HC and NO_x reduction were discussed in terms of modifications of atmospheric HC:NO_x ratios required to meet the currently existent as well as some hypothetical atmospheric air quality standards.

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Nitrogen Removal from Municipal Waste Water by Columnar Denitrification

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■ Among the available methods to remove nitrogen from waste water, the biological method of denitrification appears most promising. The work reported herein describes the results of a pilot plant investigation of columnar denitrification on three sizes of inert media, utilizing methanol as a substrate for the biochemical reduction of the nitrate ion. These studies were conducted on the nitrified effluent of a municipal waste treatment plant receiving sewage of domestic origin. The work was directed toward extending the state of the art of columnar denitrification and to specifically define the optimum conditions for this process. The effects of media size, gradation, column porosity, and contact time, and the effect of influent dissolved oxygen on nitrate reduction efficiency were determined. Hydraulic characteristics and solids removal efficiencies were examined for each column. Results indicated that greater than 90% denitrification was achieved at methanol/nitrate ratios of 2.50/1.0 and 2.75/1.0 at contact times of 5 min for coarse sand and 15 min for $^3/_4$-in. stone.

Nitrogen, in its many forms, has long played a fundamental role in the aquatic environment. It is now apparent that ecological imbalances in the natural environment have been caused, in part, by the excessive discharges of nitrogenous materials into natural waterways. Although phosphorus has been identified more frequently than nitrogen as the limiting algal nutrient, field studies have shown that, under certain circumstances, nitrogen occupies a critical role in the eutrophication of lakes (Dean, 1970). For instance, it has been demonstrated that nitrogen is the critical element causing eutrophication of the upper San Francisco Bay. In addition to the nutrient value of nitrogen, the oxygen demand of reduced nitrogen forms in treated municipal effluents can represent as much as 70% of the total oxygen demand of these effluents.

The State of Maryland now sets a limit of 1 mg/l. ammonia in effluents discharged into the Patuxent River. The Potomac Enforcement Conference requires 85% removal of the total

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nitrogen from waste water discharged in the Washington metropolitan area (Potomac Enforcement Conference, 1969). The State of Illinois, recognizing the deleterious effects of ammonia discharges, has now set an effluent standard of 2.5 mg/l. ammonia. These actions of responsible regulatory agencies have been quite specific in establishing effluent standards for nitrogenous discharges. The increasing importance of controlling these discharges from municipal waste water has stimulated the development of several nitrogen removal processes. These include selective ion exchange for both ammonia and nitrate-nitrogen removal, ammonia stripping by air at elevated pH, stimulated algal growth and harvesting, chemical oxidation using a variety of oxidants such as chlorine, ozone, and free radicals, and the biological process of nitrification-denitrification.

Theoretical Considerations

The oxidation of ammonia proceeds in two distinct stages. In the first stage, ammonia is oxidized to the nitrate form by autotrophic bacteria of the genus *Nitrosomonas* according to the following reaction:

$$NH_4^+ + 1.5\ O_2 \xrightarrow{\text{organisms}} NO_2^- + H_2O + 2H^+\ \Delta F = -84\ \text{kcal} \quad (1)$$

The nitrite thus produced is further oxidized to nitrate by *Nitrobacter* bacteria according to Reaction 2 below:

$$NO_2^- + 0.5\ O_2 \xrightarrow{\text{organisms}} NO_3^-\ \Delta F = -17.8\ \text{kcal} \quad (2)$$

The bacterial reduction of nitrate, the remaining step in the biological nitrogen removal process, has been observed by many during the normal operation of the activated sludge process. Recently, a number of investigators, both American and European, have studied various modifications of conventional treatment processes to optimize nitrogen removal via biological nitrification. Wuhrman (1960, 1968), has published widely on his studies of both processes. Finson and Sampson (1959), were two of the earlier investigators to use a columnar contacting system to achieve nitrate reduction. Several American investigators have studied various adaptations of both the columnar and suspended growth contacting systems for denitrification. Most agree that a supplemental organic carbon substrate is necessary to provide energy required for the fermentative reactions that ultimately result in the reduction of the nitrate ion. While there is some argument as to the exact enzymatic pathways involved and as to the inhibiting effect of dissolved oxygen, it is well-established that a number of facultative bacteria, including the genera *Pseudomonas* and *Bacillus*, are able to bring about the biochemical reduction of the nitrate ion. Schroeder and Busch (1967) make a distinction between assimilatory and dissimilatory nitrate reduction, defining the latter in a broad sense as the reduction of nitrate, where nitrate serves as the terminal exogenous hydrogen acceptor for the oxidation of a substrate. If methanol is used as the supplemental organic carbon source, the total two-stage denitrification reaction can be represented as:

$$5\ CH_3OH + 6\ NO_3^- \xrightarrow{\text{organisms}} 5\ CO_2 + 3\ N_2 + 7\ H_2O + 6\ OH^- \quad (3)$$

In this reaction, 5 moles of methanol are required to reduce 6 moles of nitrate-nitrogen to elemental nitrogen. This is equivalent to 1.9 mg of methanol for each mg of nitrate-nitrogen reduced to nitrogen gas.

McCarty et al. (1969), studying upflow denitrification of agricultural waste water, showed that, in addition to this theoretical amount, an additional 30% was needed to satisfy the growth requirements of a viable denitrifying population. If dissolved oxygen is present in the feed to a denitrification process, this will create an additional methanol requirement. The total methanol requirements, including those needed for growth, are combined by McCarty as:

$$C_m = 2.47\ N_0 + 1.53\ N_1 + 0.87\ D_0 \quad (4)$$

where C_m is the methanol required, mg/l.; N_0 and N_1 are the initial nitrate and nitrite-nitrogen concentrations, mg/l., respectively; and D_0 is the initial dissolved oxygen concentration in mg/l.

English (1969), in a pilot plant investigation using carbon and sand in a downflow columnar contactor, formulated the following equation to predict total methanol requirements:

$$Q_T = 2.0\,(NO_3\text{-}N) + 1.5\,(\text{D.O.}) \quad (5)$$

where Q_T is the methanol required, mg/l., (NO_3-N) is the nitrate-nitrogen concentration removed, mg/l.; and D.O. is the influent dissolved oxygen concentration, mg/l. Q_T, here, included that component which McCarty indicated was necessary for growth.

Recognizing the work of the above-mentioned investigators, most notably that of Finson and Sampson (1959), English (1969), and McCarty (1969), who dealt with columnar contacting systems, a short pilot plant program was conducted to substantiate and extend their findings.

Objectives

The work reported herein describes the results of a controlled pilot plant investigation of columnar denitrification on three different sizes of inert media, utilizing methanol as the essential electron donor for the biochemical reduction of the nitrate ion.

Principal objectives of the study were to determine if denitrification was practical using media intermediate between the fine material, 1.0 mm in diam, used by English (1969), and the large material, about 25 mm in diam, studied by McCarty (1969) and Tamblyn and Sword (1969); to determine the functional relationship between media size and process efficiency; to verify the relationship of methanol required to influent nitrate and dissolved oxygen concentration; and to determine if methanol can be proportioned automatically as a function of influent nitrate concentration.

Experimental Approach

A 2500-gal/day (gpd) pilot plant, shown in Figure 1, was used throughout this experiment. The pilot plant consists of a nitrification stage having a 2-hr aeration period followed by a clarifier operated at an overflow rate of 400 gal/ft²/day. The nitrification stage received a good quality secondary effluent of municipal origin at a constant flow rate of 1.8 gal/min (gpm). The effluent from the clarifier entered a holding tank containing a thermostatically controlled immersion heater. This holding tank was also equipped with a recirculating pump and a nitrogen gas-fed countercurrent stripping column to remove dissolved oxygen from the clarifier effluent. After passage through the holding tank, the nitrified effluent was pressurized to 20 psi and, after methanol addition, was passed downflow through the three denitrification columns.

The nitrification stage was operated as a functional unit to provide a biologically nitrified feed to the denitrification

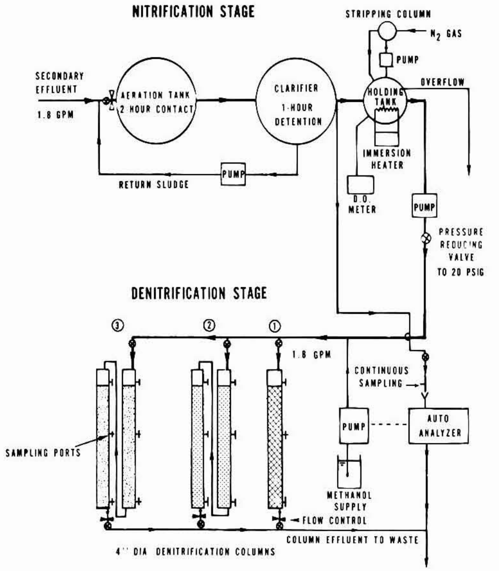

Figure 1. Flow diagram of 2500-gpd pilot plant

columns. It was felt that a biologically nitrified effluent would produce a more realistic feed with respect to solids carryover than a secondary effluent to which a nitrate salt had been added. Abnormally low total nitrogen entering the plant did, at one time, require the temporary addition of supplementary nitrogen for a short period of time to maintain realistic feed concentrations. This was accomplished by the addition of ammonium chloride to the nitrification stage which caused a corresponding increase in the effluent nitrate-nitrogen concentrations. Sludge produced during nitrification was continuously recirculated and no deliberate wasting was required during this investigation. The nitrification stage was operated continuously during this investigation while the denitrification stage was operated intermittently as dictated by the program plan and by operational requirements.

The experimental program was divided into two runs. The first run was made to determine denitrification efficiency at low to moderate dissolved oxygen levels, and the second run was made to determine the effect of increasing the dissolved oxygen concentration on methanol dosage and nitrate reduction efficiency. Both runs were conducted downflow at a constant column flow rate of 0.60 gpm corresponding to a surface loading rate of 7.0 gpm/ft^2. Three columns were employed for each run and received identical feeds. The physical data for each column are presented in Table I. Column 1 contained 10 ft of media and was equipped with three sampling ports. Columns 2 and 3 contained 20 ft of media and were each equipped with six sampling ports. During each run, the denitrification efficiency was examined as a function of methanol/nitrate ratios at various column depths for each of the three columns containing the three sizes of media. The temperature of the column feed stream was maintained near 27 °C throughout the experimental program. The denitrification columns were backwashed for a period of several minutes as required when the pressure drop for the entire column exceeded 12 psig.

The nitrate concentrations of the feed to the denitrification columns were monitored continuously for 16 hr each day, and the column effluent and intermediate samples were analyzed during the remaining 8 hr. A Technicon AutoAnalyzer of quarter-speed was used. This equipment and method employed was capable of continuous operation for a week without attendance. The analytical procedure was a modification of the hydrazine reduction method (Kamphake et al., 1967), where the nitrate is stoichiometrically reduced to nitrite without the loss of the initial nitrite in the sample, and then the total nitrite is colorimetrically determined.

Table I. Physical Column Data

Parameter	Column 1	Column 2	Column 3
Diam of Column, in.	4.0	4.0	4.0
Media	No. 3 gravel	No. 8 stone	$^3/_4$-in. stone
Median particle diam, mm	3.40	5.87	14.50
Depth of media	10.0′	20.0′	20.0′
In-place bed porosity	28%	33.8%	36.8%
Surface loading rate, gal/ft^2/min	7.0	7.0	7.0
Empty-bed contact time, min	10.7	21.4	21.4
Actual contact time, min	3.0	7.2	7.9

Results of all nitrate analyses were displayed on a recorder. Response time of the system from the time of sampling to recorder tracing was 37 min. Because of this rapid method of nitrate analysis, it was possible to manually maintain excellent control of the methanol/nitrate-nitrogen ratio by adjusting the stroke of the methanol feed pump every 2 hr. Periodic analyses of grab samples from the nitrified and denitrified effluents contained less than 0.5 mg/l. of nitrite-nitrogen or ammonia-nitrogen. All nitrate data herein are expressed as concentrations of nitrogen.

The residual methanol concentration was monitored at various depths of each column during the course of this investigation. This was accomplished by withdrawing samples daily and determining the methanol concentration by a semi-automated method. Samples were first manually steam-distilled to remove interferences. The distillates were then analyzed on an AutoAnalyzer by controlled oxidation of the methanol to formaldehyde with acid-permanganate and subsequent colorimetric determination of the formaldehyde using chromotropic acid. The pumping manifold used in the AutoAnalyzer procedure was sensitive over a range of 0.5 to 100 mg/l. methanol (Bricker and Vail, 1950).

Column effluent turbidities were measured by passing the entire column flow through a Hach Model 1032 surface scatter turbidimeter. Influent turbidities were measured using a Hach Model 1800 during run 1 and a Hach Model 2100 during run 2. Dissolved oxygen concentrations of the column influent and effluent were measured using a Yellow Springs Model 51 dissolved oxygen analyzer. These results were compared periodically to those determined using the azide modification of the Winkler Method and found to agree within 5% at D.O. levels above 3.0 mg/l. and 10% at D.O. levels below 3.0 mg./l. Total organic carbon concentrations of the column influent and effluent samples were measured using the Beckman Carbonaceous Analyzer equipped with a Beckman Model IR315 Infrared Analyzer. Surface area measurements were made by sieve analysis of the media, followed by utilization of the appropriate sphericity factor (Fair et al., 1966).

Results and Discussion

Run 1 was conducted at a planned dissolved oxygen concentration of 2.5 mg/l., at an influent nitrate-nitrogen concentration between 8 and 12 mg/l., and an average temperature of 27 °C. Actual performance data for this run averaged 7.8 mg/l. of nitrate-nitrogen at a dissolved oxygen level of 2.5 mg/l. and a temperature of 26.9 °C. Run 2 was conducted at a planned dissolved oxygen level of 6.0 mg/l., with the other parameters the same as above. Actual performance data for this run averaged 9.9 mg/l. nitrate-nitrogen at a dissolved oxygen level of 6.2 mg/l. and an average temperature of 26.5 °C. Residual nitrate and methanol concentrations as a function of column depth are shown in Figures 2–4 for run 1. Similar curves were obtained during run 2, and therefore are not presented here. Summary curves of nitrate removal efficiencies as a function of methanol/nitrate (M/N) ratios for both runs are shown in Figures 5 and 6. The relationship between required column depth and specific surface area of the media appears in Figure 7.

The nitrification stage operated routinely throughout the experimental program, producing a well-nitrified effluent. The total organic carbon entering the nitrification stage averaged 18.2 mg/l. and was considered normal. Ammonia-nitrogen concentrations ranged from a low of 1.1 mg/l. to a high of 19.2 mg/l. The lower value was caused by a period of nitrification in the secondary treatment plant preceding the nitrification stage.

The mixed liquor solids concentration ranged from 1315 mg/l. to 2160 mg/l. during normal operation, corresponding to a sludge residence time of 8.3 to 12.8 days. The effluent suspended solids averaged 12.9 mg/l. and provided the only means of wasting solids from the system. There was a noticeable variation in the suspended solids carryover, which is reflected in the average pressure drop increase per day by each of the columns as shown in Table II. A similar variation was observed in the feed turbidities during both runs.

Table II shows that the three columns reduced the feed turbidity to 1 JTU during run 1. Similar results were achieved for Columns 2 and 3 during run 2. Effluent turbidities for Column 1 were somewhat higher (3 JTU) during run 2. A possible explanation is that the feed pressure was increased

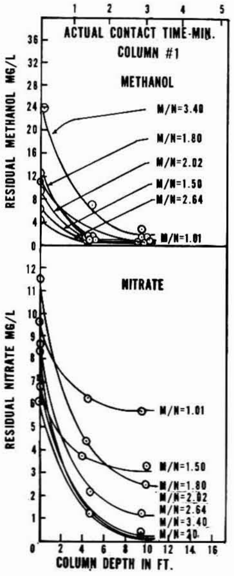

Figure 2. Residual nitrate and methanol concentration vs. time, run no. 1

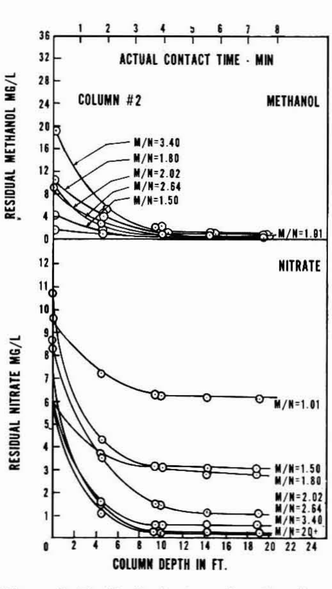

Figure 3. Residual nitrate and methanol vs. time, run no. 1

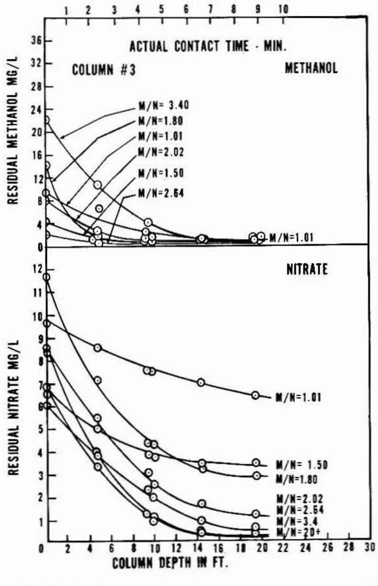

Figure 4. Residual nitrate and methanol concentration vs. time, run no. 1

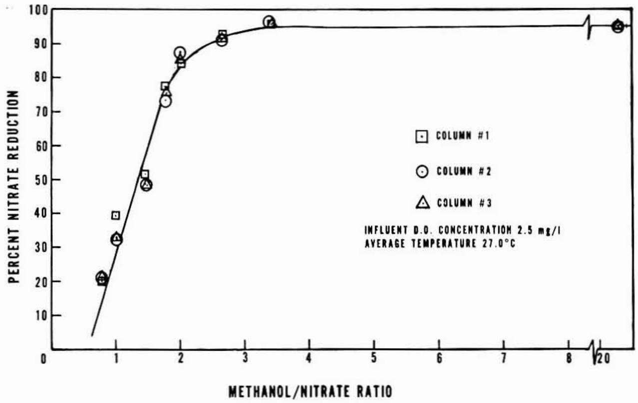

Figure 5. Percent nitrate reduction vs. methanol/nitrate ratio, run no. 1

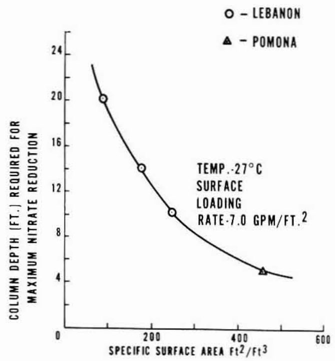

Figure 7. Column depth vs. specific surface area

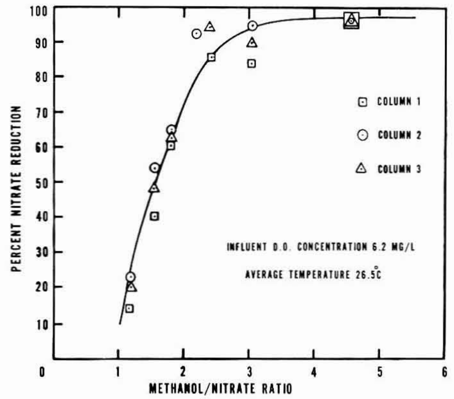

Figure 6. Percent nitrate reduction vs. methanol/nitrate ratio, run no. 2

from 20 to 30 psig on the 14th day of this run and was maintained at the higher pressure for the remainder of the run. This increased effluent turbidity would not have been expected in the remaining two columns due to their added depth.

The residual nitrate concentrations for run 1, as shown in Figures 2–4, clearly indicate that nitrate reduction varies exponentially with column depth for a given M/N ratio. Each point represents the average of 5–10 days data at a particular M/N ratio, preceded by a two-day acclimation period. The residual nitrate concentration progressively decreased with increasing column depth, eventually reaching a substrate-limited value, the magnitude of which depended on the M/N ratio. As the M/N ratio was increased and approached the theoretical value given by Equation 4, the residual nitrate concentration was proportionately reduced. It is evident that the column depth at which residual nitrate reduction becomes substrate-limited is independent of M/N ratio, but directly related to media size and packing characteristics. For Columns 1 and 2, minimum residual nitrate concentrations were reached for all M/N ratios at a column depth of 10 ft. Column 3, containing the largest media, required 14 feet to achieve a steady-state residual nitrate concentration.

Figures 5 and 6 indicate that nitrate removal efficiencies at a specified M/N ratio were similar for each column, but that run 2 required a somewhat higher M/N ratio to bring about comparable removals. For 90% nitrate reduction to occur, an M/N ratio of 2.5/1.0 was necessary for a feed containing 2.5 mg/l. dissolved oxygen. This includes the methanol required to satisfy growth requirements and that oxidized by the net change in dissolved oxygen within the column. This ratio increased to 2.75/1.0 for the higher influent dissolved oxygen level of 6.2 mg/l. The additional methanol requirements can be attributed to the difference in feed dissolved oxygen concentrations. One mg/l. oxygen was removed within the column during run 1 compared to 4.5 mg/l. during run 2.

During both runs, it was necessary to backwash the columns, to relieve the pressure drop due to the accumulation of suspended solids on or near the surface of the columns. The frequency of backwash, solids removal efficiency, and volume of water required for each column appears in Table III. These results show that the volume of backwash water used for each

Table II. Column Performance Data

	Infl.	Run no. 1[a] column effl. 1	2	3	Infl.	Run no. 2[b] column effl. 1	2	3
Dissolved oxygen, mg/l.	2.5	1.6	1.5	1.5	6.2	1.8	1.5	1.5
Turbidity, JTU	10	1	1	1	8	3	1	1
Average pressure drop increase/day, psig		10	8	5		10	8	6
Average water temp, °C	26.9				26.5			

[a] Length of time, 46 days.
[b] Length of time, 48 days.

Table III. Column Backwash Requirements and Suspended Solids Removals

Parameter		Column 1	Column 2	Column 3
Av frequency of backwash, days[a]		2.05	1.55	3.01
Gal required/backwash cycle[a]		27.0	34.5	53
Total requirements, % of throughput vol[a]		2.1	2.5	2.0
Influent suspended solids, mg/l.				
Range	4–40			
Av[b]	13			
Effluent suspended solids, mg/l.				
Range		1–12	1–6	1–6
Av[b]		4	2	3

[a] Shown for run 1.
[b] Based on analysis of 24 samples withdrawn at regular intervals throughout run 2.

Table IV. Specific Surface Area and Equivalent Slime Removed

Characteristic	Column 1	Column 2	Column 3
Median particle diam, mm	3.40	5.87	14.50
Sp. surface area,[a] ft²/ft³	245	178	85
Relative ratio	2.88	2.07	1
Slime removed from media (vss), equiv. concn, mg/l.	21,400	15,400	7,275
Relative ratio	2.94	2.14	1

[a] The specific surface area was determined by sieve analysis of the media using a sphericity of 0.98 for Column 1 and 0.70 for Columns 2 and 3 (Fair et al., 1966). Porosities were determined in place for each column after initial backwashing and prior to slime formation.

of the three columns was less than 3% and was independent of media size within the range investigated. The effluent suspended solids concentrations were similar for each column, being less than 5.0 mg/l. It is important to note in comparing columns that Column 1 contained a well-rounded coarse sand, in contrast to the angular material contained in Columns 2 and 3. In general, the angular material tended to pack much tighter in the column and was more troublesome during backwash operations.

Estimates of specific surface area for the three columns and the equivalent amount of surface-bound slime removed from the media after extensive backwash are shown in Table IV. The estimated specific surface area of the media is seen to correlate remarkably well with the amount of attached slime as measured by the equivalent volatile solids concentration. The high equivalent concentration of slime (21,000) and high surface area available for contact (245 ft²/ft³) readily accounts for the short contact times (5–10 min actual contact time) required to achieve 90% denitrification using a columnar contacting system. This can be compared to a MLVSS concentration of 2000–3000 mg/l. used in suspended growth reactors which require contact times of 2–3 hr. Figure 7 shows the column depths necessary for essentially complete nitrate reduction as a function of specific surface area for the three media sizes investigated. By using this relationship and selecting a known specific surface area, one can predict the column depth needed for complete or substrate-limited denitrification at the flow rate shown. Since contact time is proportional to column depth at constant flow, the dependence of efficiency on depth may also be considered a dependence on contact time. It should be recognized that the work was conducted at near steady-state conditions at a higher than average feed temperature (27 °C). Operation at ambient temperature will undoubtedly cause an increase in the column depths required for 90% removal efficiency.

Both the areal surface loading and the areal surface removal rates were quite low throughout this investigation because of the characteristic high equivalent concentration of solids that was maintained within the system. For run 1, M/N = 3.4/l., the average areal surface loading rate was 2.7×10^{-4} lb of NO_3-N/ft² slime/day with a high value of 6.8×10^{-3} lb of NO_3-N/ft² slime/day occurring within the uppermost part of the column. This is equivalent to an average of 5.0×10^{-2} lb of NO_3-N/lb of MLVSS per day, with a high of 1.3×10^{-1} lb of NO_3-N/lb of MLVSS per day. The areal removal rate varied as a function of loading, but averaged 2.3×10^{-4} lb of NO_3-N removed/ft² of slime/day, which is equivalent to 4.2×10^{-2} lb of NO_3-N/lb of MLVSS per day.

Typical removal rates for a suspended growth denitrification reactor are $40–50 \times 10^{-2}$ lb of NO_3-N removed/lb of MLVSS per day (Mulbarger, 1970). While not conclusive, this

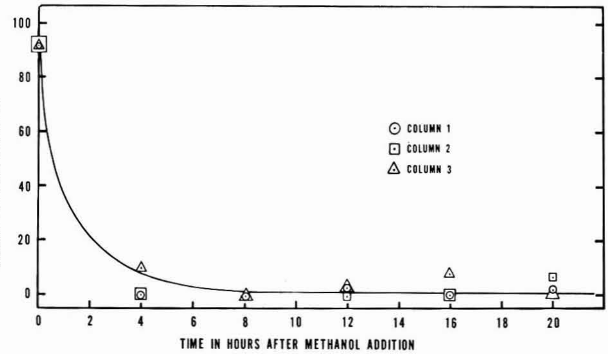

Figure 8. Nitrate reduction following methanol termination for M/N ratio for 3/1

suggests that significantly higher NO_3-N concentrations and higher column surface loading rates could have been employed without loss of denitrification efficiency.

Following both runs, a short experiment was conducted to determine the background denitrification that would occur using the same feed, but without the addition of a supplemental organic substrate. Also investigated was the change in denitrification rate that would occur after terminating the methanol addition to an "aged" column supporting a flourishing population of denitrifying organisms. Results of this experiment are shown in Figure 8 for an M/N ratio of 3/1 and a 20-hr time period. Here it is seen that the nitrate reduction in all three columns decreased rapidly after the addition of methanol was stopped, and reached a background level of less than 3% after 5 hr. The average influent total TOC during this time was 9.2 mg/l. compared to an average effluent total TOC of 7.1 mg/l.

Of particular interest during both runs was the consistent presence of 1.0 to 1.5 mg/l. dissolved oxygen in the column effluent, which was shown to be independent of M/N ratio, influent dissolved oxygen concentration, and media characteristics. In no case did the dissolved oxygen present in the effluent appear to inhibit denitrification, although it did slightly increase the methanol requirements during run 2, as shown earlier. A dissolved oxygen profile for Column 2 during run 2 is shown in Figure 9, and indicates that most of the dissolved oxygen present was removed in the first 4 ft of the column with a much smaller change occurring over the remaining length of the column. The presence of 1.0 to 1.5 mg/l. of effluent oxygen can be explained by noting the extremely short contact times of 3–10 min that are available within the columns for the transfer of dissolved oxygen from the bulk stream into the available aerobic surface slimes. The smaller proportion of aerobic bacteria in the lower section of the column combined with the reduced concentration of dissolved oxygen which acts as the driving force for oxygen diffusion both contribute to a lower mass transfer rate that would allow dissolved oxygen to remain in the bulk stream. A similar argument can be advanced for the

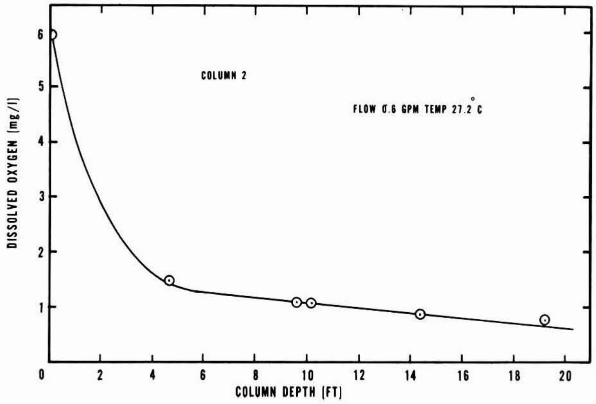

Figure 9. Variation of dissolved oxygen as a function of column depth

Table V. Identification of Denitrifying Bacteria

Sample no.	*Pseudomonas* sp.[a]	*Achromobacter* sp.[a]	*Bacillus* sp.[a]	Misc. species[b]	Total no. strains
NDNP-1[c]	...	...	...	...	...
NDNP-2	42.5%	8.5%	0.0%	49%	47
NDNP-3	30.8%	7.5%	1.9%	59.8%	107
NDNP-4	7.5%	4.5%	3.0%	85%	67
NDNP-5	30.0%	2.5%	3.8%	63.7%	80
NDNP-6	17.6%	4.6%	1.6%	76.2%	130
NDNP-7	...	...	...	...	...
NDNP-8	37.0%	4.0%	6.0%	53.0%	49
NDNP-9	15.0%	6.8%	8.5%	69.7%	59
NDNP-10	9.5%	9.0%	2.8%	78.7%	178
NDNP-11	11.5%	10.2%	6.4%	71.9%	78
NDNP-12	26.0%	9.2%	4.2%	60.6%	120
NDNP-13	26.9%	9.1%	5.0%	59.0%	121
NDNP-14	...	...	...	...	...
NDNP-15	13.2%	12.0%	4.4%	70.4%	136

[a] Denitrifying bacteria.

[b] The remaining percent of bacteria are mainly *Flavobacterium* sp. and soil *Pseudomonas* sp. which may or may not reduce nitrates to nitrites or nitrogen gas. Special tests for *Acetobacter* sp. were set up and, after 5 days, were negative.

[c] The sample number refers to the relative position of the sample port on each column. Sample port 1 is located at the top of Column no. 1. Sample port 4 is located at the top of Column no. 2. Sample port 9 is located at the top of Column no. 3. The port numbers of each column increase with increasing column depth.

diffusion of nitrate into the available slimes except that the diffusivity of nitric acid is about 20% greater than that of oxygen and accounts for the presence of the 0.5 to 1.0 mg/l. nitrate seen in the column effluent.

Following completion of the experimental program, the denitrification columns were dismantled. Samples of media from each sampling port were examined by biological assay procedures to determine the proportion of denitrifiers present as attached slimes. Results of this analysis are presented in Table V. It is noteworthy that a significantly lower percentage of denitrifiers—*Pseudomonas* species, *Achromobacter* species, and *Bacillus* species—and a much higher proportion of miscellaneous species was found at the top of each of the three columns receiving nitrified effluent. Since the bulk of the denitrification was also found to occur in the uppermost 4 ft of each column, it is clear that less than 50% of the total bacterial slime population as denitrifiers was necessary to achieve efficient nitrate reduction.

The chemical costs (based on 2.75 lb of methanol per lb of nitrate-nitrogen removed) to remove 20 mg/l. of nitrate-nitrogen in the presence of 6.0 mg/l. dissolved oxygen will be 1.9 cents/1000 gal. Cost of methanol is taken as 4.1cents/lb.

Conclusions

Results of this study have firmly established the technical feasibility of removing nitrogen from waste water by biological nitrification, followed by columnar denitrification. The latter was found to be practical on inert media ranging from 3.40 mm to 14.50 mm in diam. The actual contact time required for 90% nitrate reduction at a constant surface loading rate of 7.0 gal/min/ft^2 at an average temperature of 27°C varied from 5 min for coarse sand to 15 min for $^3/_4$-in. stone.

The factors that affect process efficiency have been sufficiently well described to allow rational design of a full-scale or demonstration size treatment plant. The advantage of using a columnar contacting system stems from the high equivalent concentration of slime and the intimate contact afforded by the large available surface area. Construction costs for the type of system will be significantly less than for a suspended growth reactor that requires 1 to 2 hr contact time and must be followed by a clarification step and the attendant sludge return equipment. The added advantage of using a denitrification column as a tertiary filter to remove suspended solids further improves the economic position of this process. The ability to select media characteristics to control the available solids, the rapid response of the system to methanol dosage, and the ability to control the M/N ratio automatically, fulfills the fundamental requirement of being able to control the process. The fact that this process places the nitrogen removed from waste water back into the ecosystem as elemental nitrogen, the most stable and natural state, is testimony that it is truly a pollution control process and not a separation process that moves the problem to another geophysical location.

Acknowledgment

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Reactions of Gaseous Pollutants with Solids. II. Infrared Study of Sorption of SO_2 on MgO

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■ Sorption of SO_2 on MgO at 25°C, and thermal decomposition at the sorbed layer in vacuum at temperatures up to 775°C, were studied using infrared spectra recorded with a Fourier transform spectrometer. SO_2 was sorbed in at least four forms. The main interaction of SO_2 with degassed MgO resulted in the formation of monodentate- and bidentate-like surface sulfites which could only be removed by degassing at high temperatures. A reversible chemisorption occurred at high degrees of surface coverage. SO_2 was then physically adsorbed on top of the more tightly bound species. Heating in vacuum at temperatures below about 300°C resulted in the removal of a large portion of the bidentate-like species, while at temperatures above 300°C the monodentate species was desorbed. Temperatures of up to 775°C were used to remove completely all of the sorbed material. Heating in oxygen converted the adsorbed material to species resembling bulk $MgSO_4$. In general, the SO_2 sorption on MgO differed considerably from that on CaO.

This report deals with a part of a continuing investigation of the nature and structure of surface species produced by gas-solid interactions during the removal of SO_2 from stack streams by powder injection processes. The fundamental aspects of the gas-solid interactions occurring in such processes have so far not been extensively studied. An earlier report (Low et al., 1971b) described infrared spectroscopic studies of SO_2 sorbed by CaO. It was proposed that SO_2 was sorbed in at least three forms, the main interaction of SO_2 with degassed CaO being irreversible and leading to the formation of a surface sulfite species. A reversible SO_2 chemisorption was found at high degrees of surface coverage, as well as SO_2 physically adsorbed on top of more tightly bound species. The latter could be converted to surface sulfates at temperatures of 550°C and higher.

A similar study of the sorption of SO_2 by MgO was carried out and is the subject of the present report. MgO was of interest because of its use for SO_2 removal (Bienstock and Field, 1964; Field et al., 1967; Uno et al., 1967).

Experimental

Most experimental procedures have been described elsewhere (Low et al., 1971b). MgO powder (J. T. Baker Co.) was formed into a self-supporting sample disk of 3/4-in. diam by compressing about 65 mg of powder in a steel die at a pressure of 70–80 tons/in.^{2}. A sample was placed in an infrared cell and degassed at 825°C for 2 hr, heated in 15 torr of O_2 at 800°C for 1 hr, and then degassed at 800°C for 1 hr. The BET nitrogen surface area of the MgO after the final degassing was 16.5 m^2/g. The SO_2-MgO reactions were carried out at room temperature, nominally 25°C, the extent of the reactions being kept low because it was desirable to study only surface effects.

Ir spectra of the degassed adsorbent were recorded after the adsorbent had been exposed to SO_2, after the SO_2-treated adsorbent had been subjected to degassing at various temperatures up to 775°C, and after the SO_2-treated adsorbent had been heated in 10 torr of O_2 at 500°C. Spectra were also recorded after a degassed sample had been exposed to rather large amounts of SO_2 for several hours, and of samples which had been heated in a closed cell.

Spectra were recorded with a Digilab, Inc. Model FTS-14 Fourier transform spectrometer system (Low, 1970a,b). As only the region of S—O absorptions below 1700 cm^{-1} was of interest, the instrument was modified so that only a triglycine sulfate pyroelectric detector was used (Low et al., 1971a). The various spectra shown are ratioed spectra digitally computed from single-beam spectra of the sample and background, ordinate- and abscissa-expanded over a preset spectral region, and automatically plotted under control of the instrument's digital computer. Usually, 200 consecutive 1.5-sec scans were summed to obtain a spectrum having a constant resolution of 2 cm^{-1} over the entire spectral range. The ordinates of the spectra of the various figures are displaced to prevent overlapping of traces.

Results and Discussion

Trace A of Figure 1 is a typical background spectrum of degassed MgO. The spectral features below 1200 cm^{-1} are characteristic of the adsorbent and are not pertinent. When such a freshly degassed sample was exposed to SO_2—e.g., Figures 1 and 2, 11 new absorptions attributable to surface species were formed; the bands are listed in Table I. The

Table I. Band Summary

Group	Cm^{-1}	Assignment	Structure
I	1088 1041	ν_3, asymmetric stretch	monodentate surface sulfito complex Structure I
	956	ν_1, symmetric stretch	
II	1134 1122 1062 954		bidentate surface sulfito complex Structure II
III	1323	ν_3	chemisorbed SO_2 Structure III
	1140	ν_1	
IV	1336	ν_3	SO_2 physically adsorbed on surface layer Structure IV
	1149	ν_1	
	1300–1050 1250 1092		sulfate

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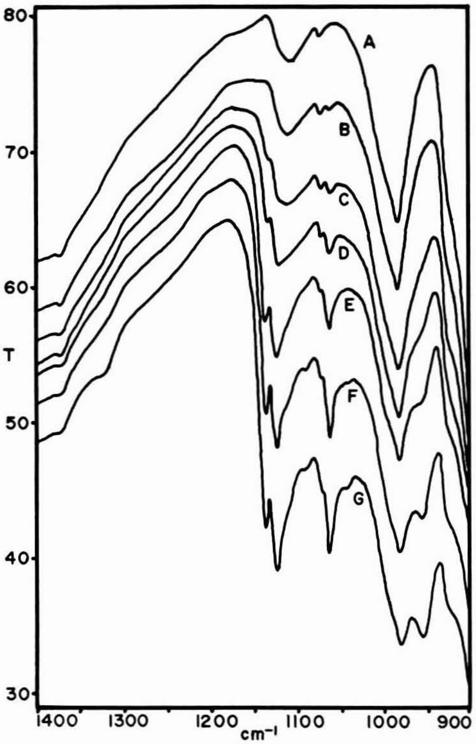


Figure 1. SO_2 sorption

Background spectrum A was recorded after a fresh MgO sample had been degassed for 2 hr at 825°C, heated in 10 torr of O_2 for 1 hr at 800°C, and then degassed for 1 hr at 800°C. Successive increments of SO_2 were then added at 25°C, all the SO_2 being taken up by the sample. The estimated surface coverages in monolayers were: A, 0; B, 0.09; C, 0.15; D, 0.21; E, 0.33; F, 0.45; G, 0.57

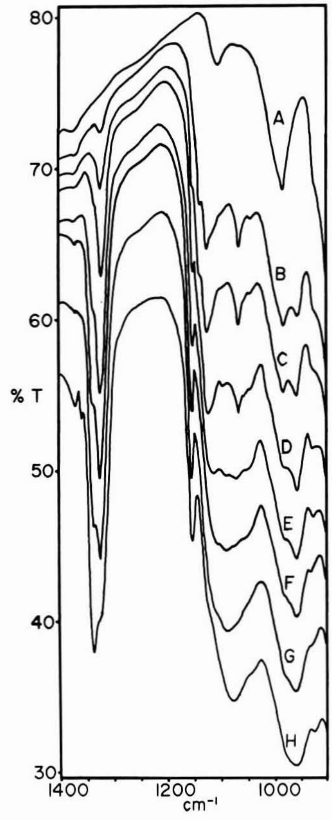


Figure 2. SO_2 sorption

Continuation of the sequence of Figure 1; see legend of that figure. Estimated surface coverages in monolayers were: A, 0; B, 0.65; C, 0.85; D, 1; E, 1.5; F, 3; G, ~3.5; H, ~4

band pattern is complex but can be resolved into four groups of bands by considering the relative band intensities at various stages of coverage. In general, the first bands to appear when MgO was exposed to SO_2 occurred below 1140 cm^{-1} (Figure 1). Additional bands then appeared at higher stages of coverage above 1140 cm^{-1} (Figure 2).

The SO_2 was added to the cell incrementally by means of a calibrated dosing system and, after the addition of an increment, the pressure within the cell rapidly fell to below 1 μ except where noted. Also, gaseous SO_2 was not detected, so that it is reasonable to assume that the known amounts of SO_2 introduced into the cell were taken up by the MgO sample. It is then possible to estimate the surface coverage using the known surface area of the adsorbent and a cross-sectional area of 19.2Å² for the SO_2 molecule (Anderson et al., 1965). It is readily estimated that monolayer coverage would occur after ~3.2 ml NTP/g had been adsorbed. Similarly, taking the Mg^{2+}—O^{2-} separation of the (100) plane of MgO as 2.1Å (Anderson et al., 1965), it can be estimated that ~3.5 ml NTP/g would be taken up if one SO_2 molecule were adsorbed on each surface oxide ion. Such estimates cannot be strictly valid because, as will be shown, tightly bound as well as weakly bound surface species were formed. However, it seems not unreasonable to assume that the various types of surface species have similar if not identical cross-sectional areas.

Sorbing very small amounts of SO_2 caused the appearance of three very weak absorptions. These appeared near 1134 and 1122 cm^{-1} as shoulders on the 1106-cm^{-1} background band and as a distinct band at 1062 cm^{-1}, as shown in traces B and C of Figure 1. These absorptions became more distinct, and a shoulder appeared at 954 cm^{-1} on the 983-cm^{-1} background band when more SO_2 was taken up. The 954-cm^{-1} absorption probably was not observed at lesser stages of coverage because of its position near the intense and broad 983-cm^{-1} background band (traces D and E, Figure 1). Further addition of SO_2 caused the 1134-, 1122-, and 1062-cm^{-1} bands to increase. Also, the 954-cm^{-1} absorption increased and developed into a band at 956 cm^{-1}; and two new bands, both weak, were observed at 1088 and 1041 cm^{-1} (trace F, Figure 1). All bands increased when additional SO_2 was sorbed. The behavior described (and anticipating band patterns observed on desorption) suggests that the bands be grouped as follows:

Group I: 1134, 1122, 1106, and 954 cm^{-1}

Group II: 1088, 1041, and 956 cm^{-1}

All bands increased in intensity, as shown in the sequence of traces of Figure 2, but those of Group II grew more rapidly than others. As the coverage increased, the bands coalesced and became less distinct.

A small, broad band at 1322 cm^{-1} and a weak shoulder

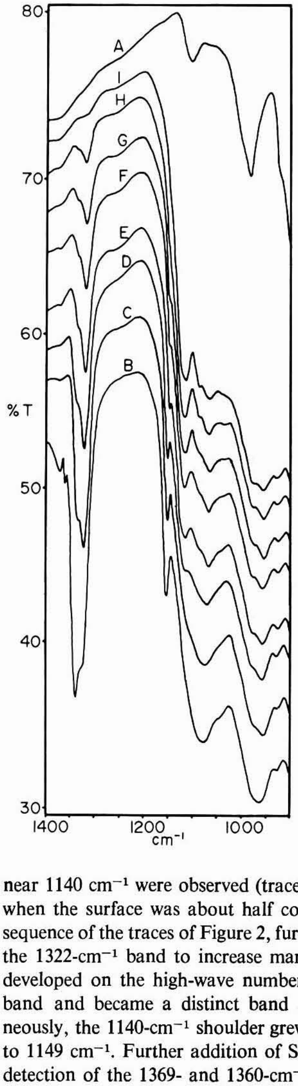


Figure 3. Degassing at 25 °C

A fresh MgO sample was degassed (A) (see spectrum A of Figure 2) and then treated with excess SO_2 (B). The sample was then degassed at 25 °C for the following periods: C, 1 min; D, 5 min; E, 20 min; F, 45 min; G, 2 hr; H, 3 hr; I, 18 hr

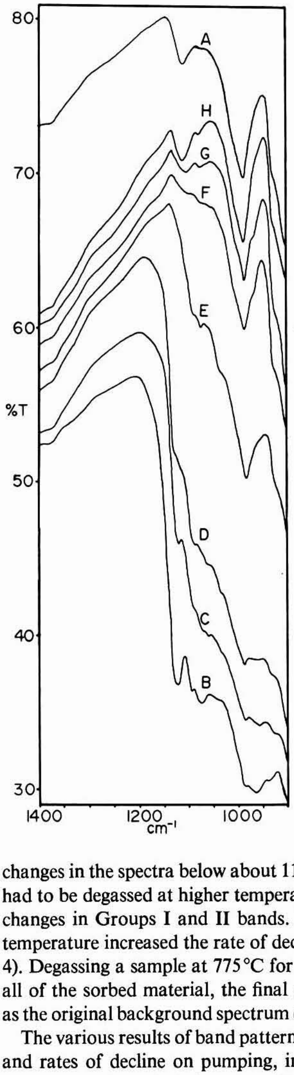


Figure 4. Degassing at elevated temperatures

A fresh MgO sample was subjected to the standard degassing treatment (A) (see spectrum A of Figure 2), treated with an excess of SO_2, and degassed at 25 °C for 24 hr (B). The sample was then degassed for approximately 3 hr at each of the following temperatures: C, 100 °C; D, 150 °C; E, 300 °C; F, 550 °C; G, 600 °C; H, 775 °C

near 1140 cm^{-1} were observed (trace G, Figure 1) at a stage when the surface was about half covered. As shown in the sequence of the traces of Figure 2, further SO_2 sorption caused the 1322-cm^{-1} band to increase markedly. Also, a shoulder developed on the high-wave number side of the 1322-cm^{-1} band and became a distinct band at 1336 cm^{-1}. Simultaneously, the 1140-cm^{-1} shoulder grew in intensity and shifted to 1149 cm^{-1}. Further addition of SO_2 to the cell led to the detection of the 1369- and 1360-cm^{-1} bands of gaseous SO_2 (traces G and H of Figure 2). The MgO surface had taken up all SO_2 introduced in the cell until the bands of gaseous SO_2 were detected. In view of this behavior, and again anticipating results from desorption experiments, the new bands detected after the Groups I and II bands had appeared are grouped as follows:

Group III: 1322 and 1140 cm^{-1}

Group IV: 1336 and 1149 cm^{-1}

A series of degassing experiments showed that the bands were removed in inverse order of their appearance, and that the rates of decline of certain bands were related—e.g., the 1336- and 1149-cm^{-1} bands declined in concert. Such behavior was used in making up the four-band groups. Some results are shown in Figures 3 and 4.

Pumping at 25 °C caused Group IV bands to decline more rapidly than those of Group III until, after prolonged pumping, both Groups III and IV bands were almost entirely removed (Figure 3). The 25 °C pumping caused some minor changes in the spectra below about 1100 cm^{-1}, but the samples had to be degassed at higher temperatures to cause significant changes in Groups I and II bands. Increasing the degassing temperature increased the rate of decline of the bands (Figure 4). Degassing a sample at 775 °C for 3 hr removed practically all of the sorbed material, the final spectrum being the same as the original background spectrum of the fresh sample.

The various results of band patterns, sequence of formation, and rates of decline on pumping, indicate that four distinct species were formed, their order of stability being,

$$\text{I} > \text{II} \gg \text{III} > \text{IV}$$

Of these, judging from the results of desorption studies, species I and II (giving rise to the bands of Groups I and II, respectively), were tightly bonded to the sample surface; the behavior of species IV, being easily desorbed, was similar to that of a physically adsorbed species.

The 1336- and 1149-cm^{-1} bands of Group IV are similar to bands at 1332 and 1157 cm^{-1} or 1330, 1308, and 1147 cm^{-1} of aqueous or solid SO_2, respectively (Wiener and Nixon, 1956; Jones and McLaren, 1958), are not greatly shifted from the positions of bands of gaseous SO_2 (Polo and Wilson, 1954), and are very similar to bands found for SO_2 sorption on CaO (Low et al., 1971b). The 1336- and 1149-cm^{-1} bands are consequently assigned to the ν_3 and ν_1 fundamentals of physically adsorbed SO_2.

The Group III bands are attributed to a somewhat more tightly bound species. In SO_2-containing compounds the

S—O stretching frequencies are sensitive to inductive effects (Bellamy and Williams, 1957); and, with a variety of organometallic —SO_2 complexes, ν_3 (the asymmetric stretching fundamental) was found near 1300 cm^{-1} (Braye and Hübel, 1963; Vogt et al., 1965; Vaska and Bath, 1966; Levison and Robinson, 1967). The 1323-cm^{-1} band is consequently assigned to the ν_3 vibration of SO_2 coordinated to the MgO surface. The accompanying 1140-cm^{-1} absorption, indistinct because of overlapping with absorptions of more strongly bound material, is assigned to the ν_1 fundamental (symmetric S—O stretch) of coordinated SO_2.

Some additional experiments were carried out to aid in the interpretation of the Groups I and II bands. Some results are shown in Figures 5 and 6. It was found that one surface species could be converted to another, depending on temperature and surface coverage.

When an SO_2-treated sample was allowed to stand for various lengths of time at 25°C, the weakly bound material giving rise to Group III and Group IV bands converted to the more strongly bound material giving rise to the Group I and Group II bands. Examples of these changes are given by the spectra of Figure 5.

Heating an SO_2-treated sample caused two types of changes to occur, depending on the temperature range, illustrated by the spectra of Figure 6. For example, when a heavily SO_2-treated sample was heated to 100°C in a closed cell, there was a substantial increase in the Group I bands. Results such as spectra A and B of Figure 6 indicate that the relatively high surface coverage coupled with a moderately elevated temperature caused an increase in the amount of species I. Heating at higher temperatures caused a reversal of that process. As indicated by the spectra of Figure 6 and other data, some of the more weakly bound species were formed at the expense of the more tightly bound species. For example, spectrum E of Figure 6 shows small bands of Groups III and IV; after heating to 200°C in the closed cell, the Group III and IV bands were increased (spectrum F, Figure 6). Occasionally, the buildup of the Groups III and IV bands in the 1330-cm^{-1} region was particularly pronounced.

The extent to which the changes were observed was affected by the previous history of the sample—i.e., the surface coverage, temperature, rate of heating, heating time, and relative abundance of the various species. The kinetics were not studied in detail. However, the qualitative observations indicate that the species were interconvertible and point to the order of their stability. The results of the high-temperature degassing experiments (Figure 4) indicate that the material giving rise to the Group II bands is removed at somewhat lower temperatures than the material giving rise to the Group I bands. This is an indication that species I is the more stable of the two. However, the appearance of Group II bands before Group I bands in the initial buildup of surface material (Figures 1 and 2), as well as the results of vacuum and closed-cell experiments (Figures 5 and 6), indicates that the surface processes are complex. Possibly, an activation energy persists which diminishes or prevents the formation of species I at the initial stage of the sorption at very low coverage. As the surface becomes progressively covered by species II, the

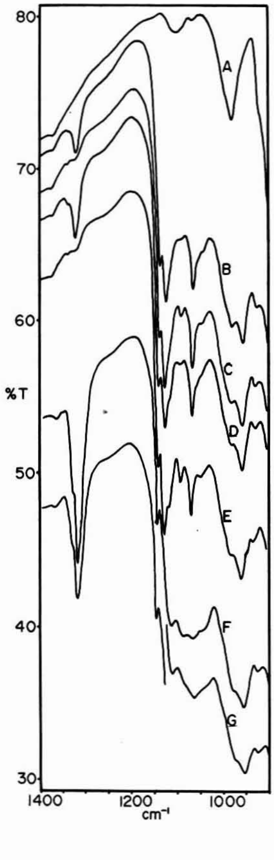


Figure 5. Treatment in static vacuum

A fresh MgO sample was subjected to the standard treatment (A) (see spectrum A of Figure 2), and enough SO_2 was sorbed to cover approximately 90% of the surface. The SO_2 introduced to the cell was taken up by the sample and the pressure within the cell fell to below 1 μ (B). The sample was then allowed to stand for 1.5 hr at 25°C (C). Additional SO_2 was introduced to bring the surface coverage to approximately 100% (D). The sample was then allowed to stand for 15 hr at 25°C (E). Enough SO_2 was added to yield about 1.5 monolayer coverage (F). The sample was then allowed to stand for approximately 18 hr at 25°C

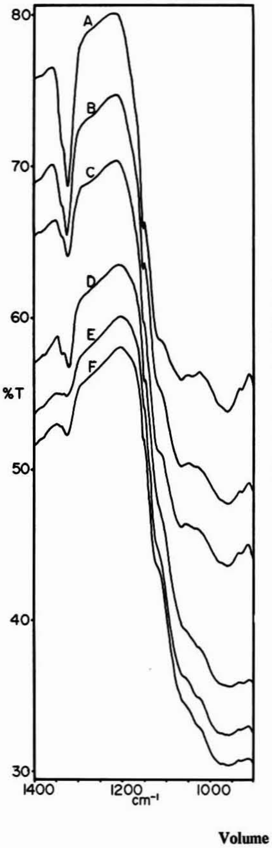


Figure 6. Heating in a closed cell

A degassed MgO sample was subjected to the following sequence of treatments. A: excess SO_2 was added at 25°C, followed by a 15-min degassing at 25°C. The cell was then closed. B: sample was heated for 15 min at 100°C, then cooled to 25°C, the cell remaining closed. C: Sample was degassed for 30 min at 25°C. D: Sample was heated for 1 hr at 210°C, then cooled to 25°C, the cell being closed. E: Sample was degassed for 1 hr at 25°C. F: Sample was heated for 1 hr at 200°C, then cooled to 25°C, the cell being closed formation of species I occurs more readily. Once formed, species I is quite stable and requires elevated temperatures for its removal or conversion to other surface forms.

Although it seems clear that two tightly bound species exist, identifying them is difficult and uncertain because the literature on spectra of inorganic S—O compounds is sparse, and it was not possible for us to observe bands due to the bending modes of sulfite structures or Mg—S stretchings because the MgO samples were opaque below about 750 cm^{-1}. Some similarity between the structures found on CaO and MgO would be expected. In the previous case (Low et al., 1971b), a trio of bands at 973, 925, and 632 cm^{-1} was attributed to the pyramidal sulfite ion formed on the CaO surface. In the present case, however, the positions and patterns of Group I and Group II bands are more like those of monodentate and bidentate sulfito complexes. Newman and Powell (1963) have discussed the ir spectra of several metal sulfites and sulfito complexes, as have Baldwin (1961) and Nakamoto and McCarthy (1968). Based on the similarity between the present bands and those of compounds discussed in the literature, the Group I and Group II bands are respectively attributed to mondentate and bidentate Mg—sulfito surface complexes.

The general fundamental frequencies of the SO_3^{2-} ion in solids appear at 1010, 961, 633, and 461 cm^{-1} (Evans and Bernstein, 1955; Nakamoto, 1963). Cotton and Francis (1960) predicted that the S—O stretching vibration would be shifted to higher frequencies when coordination occurred through the sulfur atom. A search of the literature suggests that for monodentate sulfites the bonding is usually via the sulfur atom, there being few cases where the ligand bonds through the oxygen atom. Based on such considerations, the Group I bands are attributed to a pyramidal SO_3 linked to a surface Mg atom via the sulfur atom (structure I, below). The 1088- and 1041-cm^{-1} bands are attributed to the doubly degenerate ν_3 vibrational mode (asymmetric stretch), and the 956-cm^{-1} band is attributed to the ν_1 vibration (symmetric stretch) of the monodentate surface sulfito complex.

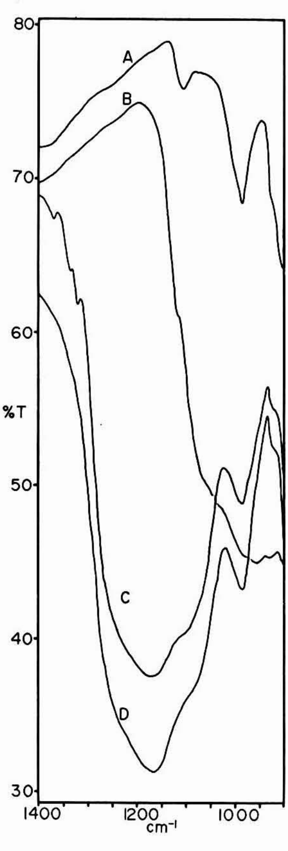
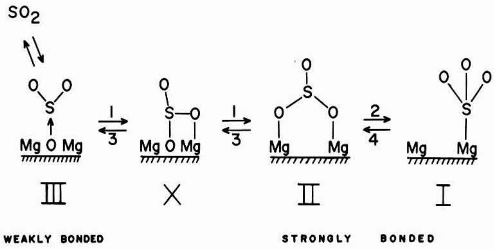


Figure 7. Heating in oxygen

A degassed MgO sample (A) was treated with excess SO_2 and then degassed for 24 hr at 25°C (B). The sample was then heated in 10 torr of oxygen for 1.5 hr at 500°C (C), and degassed for 2.5 hr at 500°C (D). The ordinates are displaced

The Group II bands are difficult to assign because, as pointed out by Sidgwick (1950), two chelating and two bridging types of bidentate structures are possible. It is not possible to distinguish them by selection rules because they all belong to the point group C_s. For bidentate structures, probably bonded through two oxygen atoms of the sulfito group, there are four stretching bands near 1120, 1080, 1030, and 980 cm^{-1}, one of which may be an overtone (Nakamoto and McCarthy, 1968). In the present case, structure II, below, is a reasonable one, and the Group II bands are attributed to its S—O stretching vibration.

It is now possible to suggest a mechanism for the overall reaction, using the above assignments and structures, as follows:



Step 1 always occurs rapidly, and at low coverages species II forms at sites of suitable surface geometry, along with some species I. When the surface is about half covered, steps 1 and 2 become unimportant; most suitable sites are occupied, and the formation of species III becomes dominant. When enough SO_2 has been taken up to cover the surface, physical adsorption of SO_2 (species IV) becomes noticeable, SO_2 adsorbing "on top of" the more tightly bound species. The formation of the strongly bonded species I and II requires the removal of an oxygen atom from the surface, and the reversal of this process would be difficult. Such a surface rearrangement is not necessary for the formation of the weakly bonded species IV and III or for species X. The latter bidentate species, shown in the reaction scheme as a possible intermediate, is consequently unlikely to be responsible for Group II bands. Step 2 is usually slower than step 1 and, with time, there is a slow conversion of species II to species I, accompanied by a rapid conversion of species III to species II. Species IV and III desorb fairly readily when the sample is degassed. Step 3 occurs more readily than step 4, suggested by the faster disappearance of Group II bands than Group I bands. Species I decomposes completely on prolonged degassing at elevated temperatures.

The apparent reversal of the process differs markedly from the behavior of the CaO–SO_2 system, where a large fraction of the surface sulfite was converted to sulfate on heating at 550°C (Low et al., 1971b). Such a sulfite-to-sulfate conversion was not observed with the present MgO–SO_2 system. This observation is in general agreement with those of Foerster and Kubel (1924), who reported that the predominant products resulting from the pyrolysis of $MgSO_3$ were MgO and SO_2; a small amount of sulfate was formed at very high temperatures. It has also been found (Pechkovsky, 1957) that even at temperatures up to 700°C only 4.4% sulfate was formed in the reaction of MgO and SO_2. In the present experiments several degassing steps were carried out at relatively low temperatures, so that most sulfite would have been decomposed before the higher degassing temperatures were reached, so that very little sulfate would have been formed.

The relatively large difference (about 300°C) in the temperatures at which $MgSO_3$ and $CaSO_3$ decompose, and the absence of a significant extent of disproportionation during the decomposition of $MgSO_3$, might be brought about by the existence of a structure such as species II on the MgO surface or on the surface of a partially decomposed $MgSO_3$ crystal. No such structure was observed with SO_2-treated CaO (Low et al., 1971b). Species II is fairly stable and exists in a relatively high surface concentration, and could function as intermediate between species III and I, so that the decomposition-desorption reaction is favored over a disproportion reaction between two species I groups.

While degassing the SO_2-treated MgO samples at temperatures up to 775°C produced no detectable amounts of sulfate, heating the samples in 10 torr of oxygen caused a rapid conversion of sulfite to sulfate. After 1.5 hr at 500°C, a very intense, broad band was observed between 1300 and 1050 cm^{-1}, with shoulders at 1092 and 1250 cm^{-1} (trace C, Figure 7). The region below 1050 cm^{-1} was similar to that of a degassed sample and thus showed that all sulfite species had been converted to the species giving rise to the new bands.

Sulfate ions cause an intense, broad absorption near 1100 cm^{-1} (Ross, 1962). The spectrum of dry $MgSO_4$ shows strong absorption in the 1075–1250 cm^{-1} region with discrete bands at 1240, 1172, 1145, and 1100–1075 cm^{-1}, the 1072-cm^{-1} band being the more intense (Rocchiccioli, 1963; Steger and Schmidt, 1964). The overall band pattern obtained in the present case is very similar to that of magnesium sulfate. Heating the surface sulfites in the presence of oxygen, then, appears to convert almost all of the surface material to a substance very similar to bulk magnesium sulfate. Further degassing of the sample for 3 hr at 500°C caused only very small changes of the spectrum, indicating that the sulfate product was stable (trace D, Figure 7).

In addition to the very intense sulfate bands, three weak bands also appeared near 1369, 1336, and 1323 cm^{-1} after the oxygen treatment. The 1369-cm^{-1} band is assigned to gaseous SO_2. The 1336- and 1323-cm^{-1} bands are attributed to the weakly adsorbed species IV and III. The two additional bands at 1149 and 1140 cm^{-1} associated with these species would be merged with the intense sulfate band centered near 1161 cm^{-1}. It was showed earlier that heating SO_2-treated samples in closed cells caused some desorption and also some transformation of tightly bound to weakly bound species. Such processes would also be expected to occur on heating a sample in oxygen. A part of the surface sulfite would be desorbed to yield gaseous SO_2 and, when the cell was cooled, would be adsorbed as species IV and III, possibly forming some species II and I. It was observed that, on allowing the sample to stand for 1.5 hr at 25°C subsequent to the oxygen treatment, the 1369-, 1336- and 1323-cm^{-1} bands became almost imperceptible, pointing to a slow adsorption of SO_2 and a slow conversion of weakly bound to strongly bound material. The corresponding Group I and Group II bands were not observed, however, probably because the amount of material was very small. Also, these adsorption and conversion processes were much slower than the sorption of SO_2 on fresh MgO, probably because regions of the surface suitable for sulfite formation were occupied or made inaccessible by the stable sulfate species.

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Mercury Pathways in a River and Estuary

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■ A method for measuring total mercury in water, suspended particulate matter, and bottom sediments has been evaluated. Some data have been applied to a study of the geochemical pathways of mercury in a rural river and estuary system. Concentrations of mercury in the LaHave River (Nova Scotia) are related to the proximity of a small rural town. The dissipation of mercury in solution appears to be through dilution, as well as by adsorption on suspended particulate matter which raises the level in particulate matter to the range of 2.04–34.4 ppm. Bottom sediments in the LaHave River are affected by sedimentation of particulate matter containing high levels of mercury, but the mercury concentration in the bottom sediments ranges from 0.09 to 1.06 ppm. Mercury released to the natural environment from industrial waste effluents appears to be discharged mostly in the dissolved form but may be quite rapidly adsorbed as shown by analyses of suspended particulate matter and bottom sediments.

Accurate and precise analyses of trace elements in the marine environment have become essential as a result of the recent interest in toxic metal pollution. Part of the aim of this laboratory was to evaluate and apply an existing technique for total mercury analyses (Hatch and Ott, 1968) of water and sediment to a nonindustrial river, estuary, and open marine environment.

The LaHave River system (Nova Scotia) (Figure 1) was studied as a background area because it is navigable and no large amount of industrial effluent is released into it. A study of mercury pathways was undertaken to evaluate the importance of water and suspended particulate matter as a transport mechanism, because the movement, chemical form, and mobility of mercury entering the sea is important in the study of biological uptake (Bligh, 1970).

Field Sampling

The estuary of the LaHave River is a narrow, relatively shallow reach of water that extends about 24 km inland from the headlands of the Atlantic coast of Nova Scotia. Tidal water extends inland to the residential and commercial town of Bridgewater, population of about 6500. Rural dwellings and small villages are scattered along both sides of the river from Bridgewater to the coast. A narrow navigation channel averaging 7 meters deep is maintained from Bridgewater to the mouth of the river.

Water samples from the LaHave River system were taken either by pumping with a nonmetallic bilge pump and plastic hose or by a large-volume Teflon-lined water sampler (Buckley, 1970). Large volumes of water were passed through a constant-flow centrifuge on board ship to concentrate all suspended particulate matter greater than 0.2 μ in diam. At each station, 4 liters of uncentrifuged water, 4 liters of centrifuged water, and the concentrated suspended particulate matter were poisoned with $10^{-4}M$ sodium azide and returned to land-based laboratories. Bottom samples were obtained by grab samplers and scuba divers inserting cores by hand.

Water samples from other locations were obtained by surface samplers taken in 20-liter polyethylene containers. They were centrifuged and stored in the same manner as the LaHave samples.

Analytical Techniques

Reagents and Standards. All reagents are certified reagent grade chemicals. Mercury standards are prepared from $HgCl_2$ dissolved in deionized water (18 MΩ-cm resistivity). Stock solutions of 1 mg/ml Hg are used to prepare 0.01 μg/ml standards. A working curve is established by analyzing varying amounts of 0.1 μg/ml standard (0 to 0.20 μg Hg range). Each standard contains 50 ml of water, 20 ml of concd H_2SO_4, and 10 ml of concd HNO_3.

Sample Preparation. Water samples are prepared by measuring 250 ml of sample into a 500-ml Erlenmeyer flask and adding 20 ml of concd H_2SO_4 and 10 ml of concd HNO_3. The solution is heated for 1 hr at 90°C. Smaller sample volumes are used for water containing mercury concentrations greater than 0.8 ppb.

Sediment samples are oven-dried at 60°C and weighed into 125-ml Erlenmeyer flasks. Ten ml of water, 20 ml of concd H_2SO_4, and 10 ml of concd HNO_3 are added, and the solution is heated for 1 hr at 90°C. The amount of sediment used varies from 1 gram to 10 mg depending on the concentration of mercury. Extremely high-concentration samples are diluted to maintain the absolute amount of Hg in the system below 0.2 μg.

Sample Analyses. The sample or standard is transferred to a 500-ml round-bottom aeration flask and diluted to 400 ml with deionized water. Ten ml of 3% w/v NaCl–3% w/v hydroxylamine sulfate solution is added, followed by 10 ml of 10% w/v $SnSO_4$. The aeration apparatus (Hatch and Ott, 1968) is then assembled and magnetically stirred.

An atomic absorption spectrophotometer (Perkin-Elmer Model 303) is coupled with an automatic null recorder readout and a linear strip chart recorder to measure the mercury vapor absorption. All instrumental settings are those recommended in the Perkin-Elmer analytical methods book (1971). In addition to the mercury analyses described in this paper, 18 other elements and particulate organic carbon were determined in water and sediments.

Results

The minimum value for confident mercury analyses for this laboratory was 0.002 ppm in 1 gram of sediment or rock and 0.010 ppb in 250 ml of water. Table I contains the analyses of several standard rocks which were carried out to evaluate the precision and accuracy of the method. The significance of the difference between our results and published results is difficult to evaluate because there are few published values in the literature.

Low results might be accounted for in cases where interfering elements were either oxidizing the tin(II) more readily

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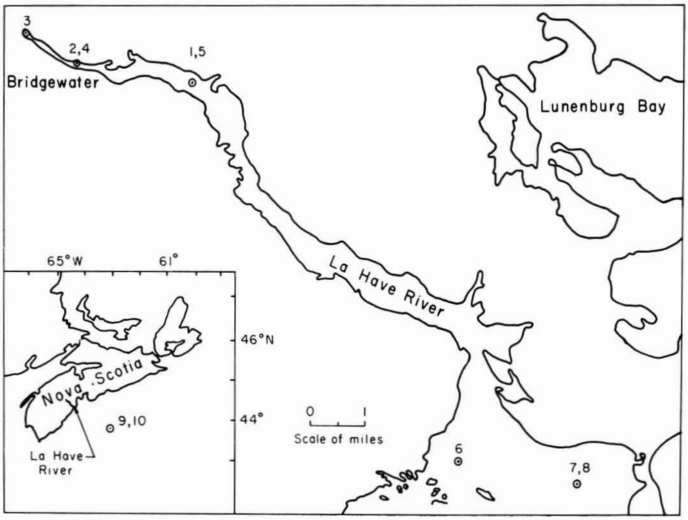

Figure 1. Location map of LaHave River and Estuary, Southeast coast of Nova Scotia, Canada

Table I. Standard Rock Samples

			Published values[b]		
Sample	Hg, ppm[a]	Mean deviation	NAA[c]	AA[d]	Flameless AA[e]
W-1	0.240	0.002	0.17	0.34	0.18
G-2	0.064	0.0006	0.039	0.050	...
DTS-1	0.010	0.0004	0.004	0.007	...
GSP-1	0.019	0.002	0.021	0.015	...
PCC-1	0.006	0.0006	0.004	0.010	...
AGV-1	0.024	0.0000	0.004	0.015	...
BCR-1	0.005	0.0005	0.007	0.005	...
Illite No. 35	0.158	0.0000	...	...	...

[a] Results from duplicate analyses, this laboratory.
[b] Values for W-1 from Hatch and Ott (1968). Remaining literature values from Flanagan (1968).
[c] Neutron activation analyses.
[d] Atomic absorption analyses.
[e] Flameless atomic absorption analyses.

than mercury, or amalgamation was occurring and the mercury was prevented from being vaporized. The interference due to amalgamation was not significant because the elements (Ag, Au, Pt) were present in low concentrations. The process of other elements—e.g., Fe, Mn, Cu—oxidizing the tin was minimized by the oxidizing acid medium which left these elements in an oxidized form. Even though the amount of Fe, Mn, and Cu in the standard rocks is large, no interferences appeared to be related to these elements.

Since the method is very selective for mercury, it is difficult to reason how enhancement of mercury absorption could occur. Volatile organic compounds and dissolved gases could absorb energy in the uv region (2537Å), but the standard rocks contain very little of these materials. In addition, no correlation was noted for mercury concentrations and particulate organic carbon values in the river samples. In general, there was no indication of enhancement caused by organic compounds.

Tables II and III list analytical results for samples taken in the LaHave River and estuary, and Table IV contains mercury determinations for samples from industrial areas.

Discussion

LaHave River and Estuary. Measurements of total mercury in solution, in suspended particulate matter, and in bottom sediments of the LaHave River and estuary give some indication of the variability and complexity of the occurrence, transportation, and dispersal of this trace element. We have found that concentrations of mercury in solution at several stations in the river vary from 0.036 ppb to 0.380 ppb while analyses of mercury on dry suspended particulate matter gives concentrations of 3.59 to 34.4 ppm. Bottom sediments from the same locations varied from 0.09 to 1.06 ppm.

Dissolved mercury content in the river suggests that an injection occurs near the center of the town of Bridgewater (Stations 2, 4) where a sewer outlet enters the river (Figures 2*C* and 3*B*). Klein and Goldberg (1970) found mercury concentrations in surface sediments up to 0.82 ppm near a Los Angeles sewer outfall. One source of mercury in sewage is from commercial chlorine bleaches which contain up to 200-ppb mercury (Jonasson, 1970). The Bridgewater injection was not indicated by other dissolved trace elements (Co, Pb, Cd, Mn, Fe, Ni, Mo, Cu, Zn); however, particulate organic carbon values were highest at stations 2 and 4.

The major processes involved in reducing the dissolved mercury content are adsorption on suspended particulate matter followed by subsequent flocculation and deposition, and dilution by tidal flushing. Salinity profiles for the river (Figure 2*A*) show that tidal mixing occurs in the estuary up to the town of Bridgewater. The effect of these processes is the reduction of dissolved mercury content from 0.201 to 0.108 ppb between stations 2, 4 and stations 1, 5, respectively. The water at stations 6, 7, and 8 has a salinity of 28 parts per thousand (av), and the dissolved mercury content approaches that which was found in continental shelf seawater.

The determination of mercury in suspended particulate matter is important in considering all aspects of mercury transport and mobility. Fine-grained suspended matter may adsorb and exchange ions from solution and transport them

Table II. LaHave River and Estuary Analyses

Station	Depth, meters	Salinity, ppt	Dissolved Hg, ppb	Total particulate matter, g/l.	Hg in suspended particulate matter, ppm (dry wt)	Particulate Hg, ppb
3 (mean)	0	0.0	0.036	0.001	8.05	0.008
2,4	0	1.9	0.090	0.001	10.9	0.01
2,4	1.5	16.2	0.380	0.003	3.93	0.01
2,4	6.5	26.6	0.134	0.007	7.12	0.05
2,4 (mean)		14.9	0.201	0.004	7.32	0.03
2,4	Bottom Sediments 0.27 ppm					
1,5	0	5.4	0.175	0.002	3.59	0.01
1,5	1.5	8.8	0.057	0.002	6.39	0.01
1,5	7.5	28.4	0.091	0.017	7.58	0.13
1,5 (mean)		14.2	0.108	0.007	5.85	0.04
1,5	Bottom Sediments 1.06 ppm					
6	0	24.9	0.057	0.003	6.32	0.02
6	2.0	29.0	0.056	0.003	20.2	0.06
6	6.0	28.4	0.058	0.003	7.05	0.02
6 (mean)		27.4	0.057	0.003	11.2	0.03
6	Bottom Sediments 0.12 ppm					
7,8	0	26.5	0.054	0.002	14.0	0.03
7,8	2.0	28.7	0.076	0.002	30.2	0.06
7,8	10.5	29.6	0.046	0.002	34.4	0.07
7,8 (mean)		28.3	0.059	0.002	26.2	0.05
7,8	Bottom Sediments 0.09 ppm					
9,10	2.0	30.0	0.071	0.002	20.2	0.04
9,10	20	30.3	0.088	0.002	5.12	0.01
9,10	240	34.0	0.058	0.003	2.04	0.01
9,10	Bottom Sediments 0.14 ppm					

through the estuary or to deposition sites within the estuary. The significant aspects of the suspended particulate matter are therefore the size and nature of particles, the concentration in suspension, and the rate of flocculation and sedimentation. With the exception of the freshwater lense at Bridgewater, the average concentration of mercury in dried suspended particulate matter from stations in the upper estuary is $^1/_2$ to $^1/_4$ that found from stations in the lower estuary (Figure 3*C*). This increase in mercury concentration is probably due to increased adsorption on finer particles that remain in suspension. The general decrease in quantities of suspended particulate matter is probably due to flocculation and deposition at various sites within the estuary. The processes of flocculation and size fractionation are related to salinity. This is illustrated by the data from stations 6, 7, and 8 where low quantities of particulate matter were found in high-salinity water, while the highest values for mercury in particulate matter were also found (Figure 2*A*, *B*). The ratio of particulate mercury to the dissolved mercury changes from the head of the estuary at Bridgewater where it is 0.2, to the seaward end of the estuary at stations 7 and 8 where the ratio becomes 0.8. This suggests that only the finest grained particles having high adsorbed mercury persist in the higher salinity waters.

To test the hypothesis that the adsorption of mercury on particulate matter is dependent on the adsorption capacity and the specific surface area of the particles, a sample of bot-

Table III. Mercury in a Size-Fractionated Bottom Sediment[a] from LaHave River

Diam, μ	Mean specific surface area,[b] cm²/g	Size fraction in sample, wt %	Hg, ppm	Total concn, %
>60	400	2	0.51	1
20–60	600	20	0.44	12
4–20	2,000	49	0.68	44
<4	12,000	29	1.12	43

[a] Size fractionation by sedimentation based on settling times of equivalent spheres in deionized water (Stoke's Law).

[b] Specific surface area calculated on basis of spheres having density of 2.5 g/cm³.

Table IV. Industrial Effluents

Sample	Dissolved Hg, ppb	Hg in suspended particulate matter, ppm (dry wt)	Hg in bottom sediments, ppm (dry wt)
Paper mill (settling pond)	0.080	10.0	. . .
Paper mill (effluent)	2.0–3.4	5.6	1.16
Fertilizer plant	2.6–4.0	32.0	0.56
Smelting plant	2.0–4.0	. . .	0.71
Chlor-alkali plant	80–2000	14.0	2.02

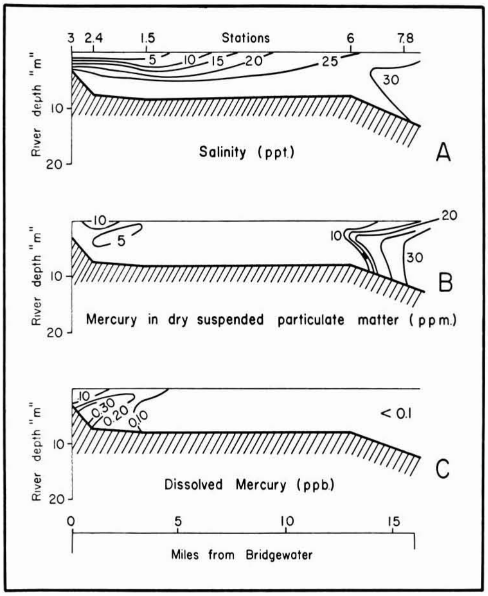

Figure 2. *A.* **Salinity profile for LaHave River and Estuary (Town of Bridgewater is located at stations 2, 4);** *B.* **Contoured concentrations of mercury in dried suspended particulate matter;** *C.* **Contoured concentrations of dissolved mercury in river and estuary waters**

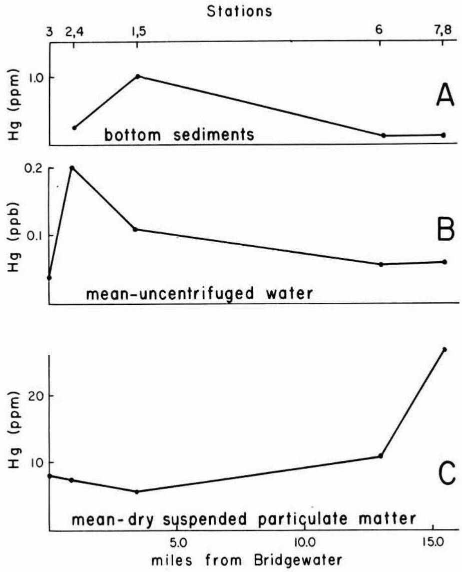

Figure 3. *A.* **Mercury concentration in bottom sediments;** *B.* **Mean dissolved mercury content in water column;** *C.* **Mean mercury content in dried suspended particulate matter for the water column at each station**

tom sediment from the LaHave River was fractionated into four size ranges. The amount of mercury in each size fraction is given in Table III, which shows that the mercury content in each fraction less than 60 μ increases linearly with the log of the mean specific surface area of the particles. Thus, the hypothesis seems to be valid in that the adsorption of mercury is related to the specific surface area. Cation exchange capacity of medium and coarse sand may be higher than that of fine sand and coarse silt (Kennedy, 1965). The largest fraction in Table III displays this characteristic. From consideration of these test results, it may be concluded that the particles in suspension in the estuary are either extremely fine-grained or that the adsorption capacity is enhanced by various mechanisms which would allow mercury concentrations to be as high as 34.4 ppm.

The data from stations 9 and 10 cannot be genetically related to the stations in the LaHave estuary, because the former stations are located some 60 miles seaward from the mouth of the river. These data compare with the river data only in that the surface particulate matter content is quite similar to those of the lower LaHave River. The mercury content of the particulate matter obtained from deep water on the continental shelf was considerably less than the surface, but still remained above 2 ppm. This value was more than 15 times higher than the bottom sediments at the same location.

Mercury content of bottom sediments in the LaHave estuary range between 0.09 and 0.27 ppm, except for stations 1 and 5 where the level is 1.06 ppm. The exceptional values at stations 1 and 5 may be attributed to generally finer-grained sediments which were deposited as a result of less transport competance and flocculation. The decreased transport competence is caused by generally slower current speeds as the estuary becomes broader below Bridgewater. Flocculation would be caused by reduction of electrostatic surface potentials or fine-grained particulate matter as it comes in contact with the higher salinity water.

It may be noted that even the finest fraction of bottom sediments (Table II) contain much less mercury than the suspended particulate matter. Methylated mercury can be formed by bacteria in bottom sediments (Jensen and Jernelove, 1969), and because it is soluble in water it would be released from the sediments. This might be the reason for the lower level of total mercury in bottom sediments compared with that found in suspended sediments.

Coastal Industrial Sites. Industrial and agricultural sources of mercury pollution (catalysts, slimicides, fungicides, electrolyses cells) are introduced directly in ionic or metallic form or as organo-mercury compounds. Airborne mercury may be released in significant amounts in the burning of coal and oil, from industrial plant stacks and in the dust from open pit mining. No attempt was made in this study to examine air-water interactions of mercury, but possibly this aspect has a significant effect on mercury in surface waters of lakes and coastal areas.

Measurements of mercury from several industrial waste disposal sites in the Atlantic Provinces were made to determine the quantity and form of injection into the natural environment. The samples for these determinations were collected at various times on a random sampling basis without regard for temporal variations which may occur with production schedules of the plants. In all cases, samples were taken directly from the outfall pipes or in the marine area adjacent to effluent discharge. The amount of dissolved mercury varied over a wide range (Table IV), but only in the case of the settling pond of a paper mill were the levels comparable with the average value for the LaHave River. Few data exist for the quantitative determination of mercury in industrial settling ponds. However, it appears that the relatively low mercury level in the water from the paper mill settling pond may be due to adsorption on suspended sediment. The levels for a fertilizer plant, paper mill, and smelting plant effluents were an average of 43 times higher than the dissolved level for the LaHave River. The discharge of the chlor-alkali plant was up to 28,500 times higher than the LaHave River.

The nature of discharged particulate matter from the industrial sites varied with the type of manufacture or processing and in no case could the inorganic content of the particulate matter be considered similar to natural suspended sediments. The amount of mercury found in the particulate matter at all sites was less than the maximum level found in the particulate matter from the LaHave. This observation was especially noteworthy at the chlor-alkali plant. Here, although the concentration of dissolved mercury was up to 28,500 times higher than the average for the LaHave River, the particulate mercury was only slightly higher than the average for the LaHave. Bottom sediments collected from areas up to 800 meters from these effluent outlets contained mercury concentrations higher than those from the LaHave but are still considerably lower than average suspended particulate matter.

Acknowledgment

The authors wish to thank J. M. Bewers, D. Loring, and A. Walton of the Bedford Institute for reviewing the manuscript and making helpful suggestions in the manner of presentation of the data.

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COMMUNICATION

Solubilization of Lead in Lake and Reservoir Sediments by NTA

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■ The proposed replacement of phosphate by nitrilotriacetic acid (NTA) in detergent formulations could result in the latter compound finding its way into public water supplies. Reservoir bottom sediments frequently contain insoluble lead deposited from automobile exhausts. The possibility of NTA solubilizing significant amounts of lead into drinking water was investigated by shaking suburban reservoir and lake sediments with water containing NTA. A concentration of soluble lead 12 times the maximum permitted level was observed in certain experiments.

Since nitrilotriacetic acid (NTA) has been under consideration as a replacement for phosphates in laundry detergents, and hence could be used in amounts ranging from 200–500 million lb/year, some of the possible effects of this compound on the environment have received attention. Significant amounts of this compound could, under certain circumstances, be released into water supply systems. Our concern in this study was the possible solubilization of reservoir lead by NTA.

NTA is a well-known complexing agent, having first been characterized by Schwarzenbach et al. (1945). Its biodegradation in sewage treatment was studied by Swisher et al. (1967), who added NTA at different dosages to laboratory-activated sludge units. They concluded that there was substantially complete biodegradation in a short time, since NTA was reduced from initial levels of a few hundred ppm down to about $^1/_{10}$ of that in periods of time ranging from 5 to 10 hr. The analysis for NTA was through the formation of its complex with an excess of ferric ions, precipitation of unchelated iron, and a colorimetric Fe determination after filtration. Accordingly, the direct determination of NTA itself was not employed in these studies.

In many parts of the United States, particularly in suburban areas, there is considerable automobile traffic near and directly around main water reservoirs. An appreciable lead fallout from traffic is deposited in the soil adjacent to the highways in various insoluble forms, largely as carbonates and salts of soil anions (Motto et al., 1970; Daines et al., 1970). Because these compounds are both insoluble and heavy, they settle out to the bottom of bodies of water. A detectable amount of lead

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Table I. Solubilization of Lead by NTA

	Lead concn, ppm^a		
	Mamaroneck Reservoir bottom	Crystal Lake bottom	Rt. 80 shoulder
Total Pb	36	120	160
After 1 hr			
0 ppm NTA^b	<0.02	0.03	<0.02
2	0.02	0.05	0.05
20	0.07	0.61	0.40
After 24 hr			
0 ppm NTA	0.02	<0.02	0.02
2	0.08	0.05	0.04
20	0.03	0.43	0.15

[a] Lead reported as mg/kg of sediment or as mg/kg of solution.
[b] NTA as trisodium salt.

thus does not ordinarily find its way into domestic water supplies. The maximum permissible concentration of lead in public water supplies is set at 0.05 ppm by the Public Health Service.

Metal solubilization from various sediments by NTA has been studied and has been the subject of several studies available to this author only in preliminary and draft form. In certain of these studies, it was observed that 10 ppm of NTA could solubilize Cu, Cd, and Zn but not Fe or Pb. However, these sediments were taken in rural areas, presumably far from highways so the lead could have been in a refractive form as contrasted to that originating from automobile emissions.

Experimental

A sample of reservoir sediment was collected from the Westchester Joint Water Works Mamaroneck Reservoir (New York State), at a point approximately 20 ft from Mamaroneck Avenue at two separate locations in the spring of 1971. A second sample was collected from the bottom of Crystal Lake in Englewood, N.J. approximately 30 ft from Rt. 80 at the same time of year, and a third sample was taken from the shoulder of Rt. 80 adjacent to Crystal Lake.

Experiments were carried out as follows: 30-gram samples of the sediments were shaken for varying periods of time with 100 ml of reservoir or lake water to which had been added different amounts of NTA. The total lead content of the sediments was determined by shaking the sediments with $1M$ nitric acid for a few days. Lead concentrations were determined with a Perkin-Elmer Model 303 atomic absorption spectrophotometer by direct analysis of the nitric acid extracts using aqueous lead nitrate standards.

The lead content of NTA-treated solutions was determined by the procedure of Willis (1962) employing ammonium pyrrolidine dithiocarbamate to sequester soluble lead and concentrate it in a small quantity of methyl isobutyl ketone. The standards here were aqueous lead nitrate solutions extracted into the ketone using the same method. The detection limit of this procedure is 0.02 ppm, with an average deviation of about ±0.01 ppm.

It was observed that these latter analyses should be performed within a few hours after the samples are extracted; overnight standing apparently led to appreciable loss of detectable lead in both unknown and standard solutions. That NTA does not interfere in the determination of lead by this procedure was shown by carrying out analyses of known solutions with and without NTA being present; 20 ppm of NTA did not affect the analysis of a 0.05-ppm standard lead solution.

Results

Table I summarizes the results obtained. It is evident that as little as 2 ppm of NTA can raise lead up to and exceeding the 0.05-ppm maximum permissible level. A concentration of 20 ppm of NTA raised the level of soluble lead to approximately 0.6 ppm from the Crystal Lake bottom and to nearly the same levels from the Rt. 80 shoulder. Comparable results were obtained from the Mamaroneck Reservoir, although the concentrations of lead were not as high, perhaps due to the lower total lead content of the sediment at that spot; a sample taken a few weeks earlier from the same region showed 80-ppm total lead.

Conclusions

It is evident that the lead emanating from automobile fuel exhausts can indeed be solubilized rather rapidly by NTA present at relatively low concentrations. Whether these concentrations will be found in reservoir waters is not known, but the paucity of sewage treatment in so many parts of this country coupled with our over use of water resources suggest that the problem merits serious study.

Acknowledgment

The author acknowledges with thanks the assistance of S. C. Chang and H. P. Gregor of the Department of Chemical Engineering and Applied Chemistry, Columbia University, where the experimental work was carried out.

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CORRESPONDENCE

Fate of Phosphorus in Waste Treatment Processes: Enhanced Removal of Phosphate by Activated Sludge

SIR: The article by Menar and Jenkins [ENVIRON. SCI. TECHNOL., **4** (12), 1115 (1970)] purporting to show that phosphate removal by activated sludge is due largely to chemical precipitation is impressive, but we wish to emphasize that their data are not universal in application.

In our own studies (Levin, 1963; Levin and Shapiro, 1965; Levin and Shaheen, 1967; Shapiro, 1967; Shapiro et al., 1967), we showed that the uptake of phosphate by activated sludge is inhibited by poisons such as 2,4-dinitrophenol, or mercuric chloride, and is thus far more likely to be a biological phenomenon than a chemical one. Similarly, the release of phosphate by anaerobic sludge is affected by poisons, being inhibited at low concentrations and stimulated at high concentrations of, for example, cyanide.

Furthermore, whereas Menar and Jenkins claim that bubbling of an anaerobic sludge with nitrogen will cause apparent uptake of phosphorus due to calcium phosphate precipitation brought about by the stripping of CO_2 from the system, we have actually used nitrogen bubbling to create and maintain anaerobic conditions to favor phosphate release. In fact, both vigorous bubbling with nitrogen and anaerobic mechanical stirring resulted in identical rates of phosphate release.

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SIR: I have no objections to Levin and Shapiro's letter except to say that I do not claim that bubbling nitrogen gas has any significance with respect to removing soluble phosphate from activated sludge. It is the bubbling with CO_2-free gas that is significant; argon, methane, helium, neon, or oxygen, etc., would be just as effective as long as they were CO_2-free.

David Jenkins

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industry trends

Nalews, Inc. and **Roy F. Weston, Inc.** have joined forces to form jointly owned Nalews-Weston to market turn-key solutions to industrial pollution control problems.

M. W. Kellogg Co. has been awarded a coal gasification feasibility study contract by the Panhandle Eastern Pipeline Co. (Houston, TX) and Peabody Coal Co. (St. Louis, MO) to determine practicality of producing 250 million standard ft^3 per day of substitute natural gas (SNG) using Lurgi gasifier technology.

Envirotech Corp. will consolidate the major portion of its research operations in a new research center in Salt Lake City, UT. The 72,000-ft^2 facility will house the mechanical, sanitary, and continuous-process R&D efforts of the company's Process Equipment group as well as interrelated projects.

Envirogenics has purchased Brooks Chemical (Cleveland, OH) for an undisclosed amount of cash. Brooks makes chemical specialties for water and waste treatment and had 1971 sales in the million dollar range.

Wheelabrator-Frye is supplying six electrostatic precipitators for three Ideal Cement Co. plants. The units are part of a $22 million pollution abatement effort by Ideal begun in 1971 to be completed by 1974.

Combustion Engineering, Inc. has received a $3.4 million contract from the City of Hamilton, OH for a field-erected steam-raising electric generator.

Continental Can Co. has started construction on a $2.4 million secondary water treatment facility at it's Port Wentworth, GA paper mill site, northwest of Savannah. The system will accommodate up to 23 million gpd of waste discharge.

Automatic Burner Corp. (Chicago, IL) has been awarded a contract by the National Oil Fuel Institute to develop an ultrasonic oil burner. The unit will use Sonic Development Corp.'s patented Sonicore atomizing nozzle.

Dow Chemical Co.'s Imbiber Beads have been licensed by the California State Water Resources Control Board for use in controlling oil spills in California.

Bolt Beranek and Newman has formed a new Environmental Systems Group to provide government and industry with engineering services and related skills in solving pollution problems.

AJAX International (Santa Barbara, CA) says its 800,000-gpd reverse osmosis water treatment plant—the largest of its kind in the world—is now in operation in Kashima, Japan at Sumitomo Metal Industries, Ltd.

National Sanitation Foundation has purchased a $1.5 million office and laboratory building in Ann Arbor, Mich. which expands the foundation's research, office, and test areas by 170%.

Boeing Computer Services, Inc. has received a contract from the City Council of Riverside, CA to implement a computerized management control system for collection of solid waste.

General Testing Laboratories Washington, DC has opened an exhaust emission testing lab for independent evaluation of engine performance for the transportation industry.

Continental Steel Corp. (Kokomo, IN) says that the final stage of its pollution control effort at the company's Kokomo plant will be completed by the end of 1972 and will meet all federal and state requirements for stream pollution control. The total system will cost about $1.2 million.

Reynolds Metals Co. is expanding its line of recycled aluminum products to include recycled alloy ingot for sale to the casting industry. Reynolds' can recycling program is operating in 31 states.

General Utility Equipment, Inc. Jacksonville, FL) is in the process of tripling production and office space for marketing its line of self-contained potable water, waste water, and tertiary treatment plants.

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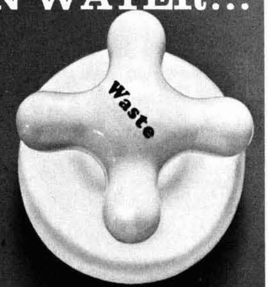

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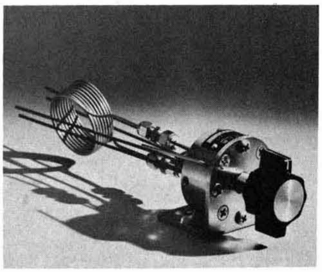

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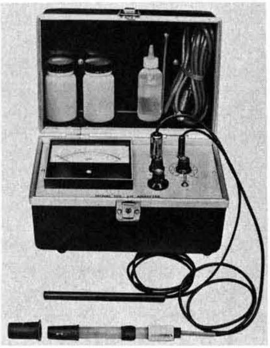

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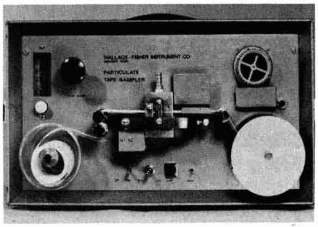

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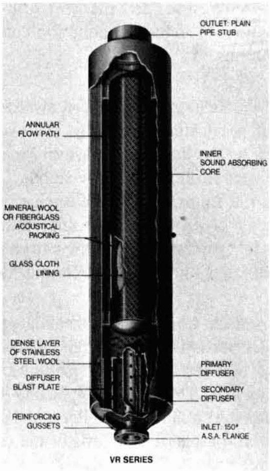

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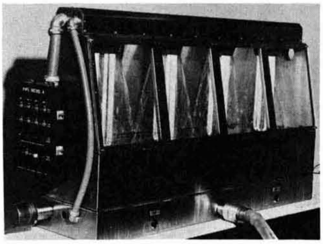

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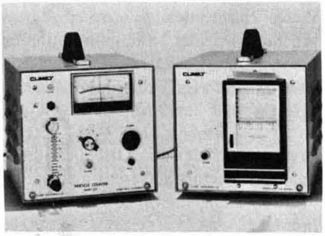

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Boiler upgrading. Pamphlet tells of company's service in upgrading outdated boilers to help meet pollution standards. Literature has charts, photos, and data tables that show cost of modernizing is often less than cost of replacement. North American Manufacturing Co. **95**

Air supply. Bulletin describes self-contained, gas-fired packaged air supply systems in several sizes to meet most industrial requirements. Application data, installation photos, performance charts, options, and construction details are given. Aerovent Fan Co., Inc. **96**

Sludge conditioning. Brochure is available on conditioning sludges from sewage plants, petrochemical wastes, and paper and pulp processes using the Dynamic Sludge Conditioner. Unit can chop difficult materials in-line, and conditioning can be done without an open pit. Franklin Miller, Inc. **97**

Filtering aids. Bulletin describes line of diatomaceous earth filtering aids and applications to oil, chemical, food, and beverage industries. Witco Chemical Corp. **98**

Paper mill deposits. New literature covers treatment programs for control of inorganic salt deposits, slime, pitch, oxalate, rosinate deposits, and scale in paper mills. Betz **99**

Gas mixtures. Flyer lists available calibrated mixtures and several ancillary pieces of equipment for air pollution and emissions measurement. Matheson Gas Products **100**

Fluidizing media. Brochure gives data on operating characteristics of Poroflo fluidizing media for several applications. Bendix Corp. **101**

Water height gauge. Specifications for Envirogauge water height gauge are given in new data sheet. Beckman Instruments, Inc. **102**

Computer service. Literature describes pollution monitoring system which includes comprehensive computer reports that give empirical data with which to examine pollution problems and trends. Environmental Measurements, Inc. **103**

Corrosion control. Literature covers advantages and applications of Magna Corrosometer which uses electrical resistance to measure corrosion. Guide includes performance specs and gives data on various electrodes. Magna Corp. **104**

Water clarification. Illustrated 8-page brochure provides basic information on advanced water clarification systems tailor-made to individual needs. Rheem Mfg. Co. **105**

Dry wastes. Publication lists line of dry waste compactors and front-loading dry waste containers. Rollins International, Inc. **106**

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.

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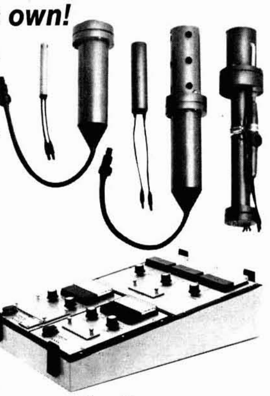


When you think sensors or measurement, think Martek first! For further data write to: Martek Instruments, Inc., 879 West 16th Street, Newport Beach, Calif. 92660.

MARTEK INSTRUMENTS, INC.

Circle No. 20 on Readers' Service Card

Processes for Air Pollution Control. G. Nonhebel, Ed. 736 pages. CRC Press, 18901 Cranwood Pkwy., Cleveland, OH 44128. 1971. $35, hard cover.

Reference for chemical engineers responsible for design and operation of manufacturing plants which include gas purification processes. Methods for minimizing air pollution are covered in 11 of the 19 chapters. ■

What Every Business Firm Should Know About Pollution Control—And Penalties. Chicago Association of Commerce & Industry, 130 S. Michigan Ave., Chicago, IL 60603. 1971. $29.95.

Five cassette tapes cover the 1971 Midwest Environmental Pollution Control Conference and Exhibition. Sessions taped include: the law, solid waste disposal, industrial water treatment, air pollution control, and public relations and finance. Recommended for business executives involved with specific pollution problems. ■

Proceedings of the Second International Clean Air Congress. H. M. Englund, W. T. Berry, Eds. 1380 pages. Academic Press, 111 Fifth Ave., New York, NY 10003. 1971. $85.

Compendium of information from 33 countries on the scientific, technological, and administrative aspects of air pollution control. Volume consists of six basic sections—introduction, administration, engineering, meteorology, chemistry and physics, and medicine and biology. Publication is of reference value to research workers, engineers, and administrators involved in air pollution, environmental chemistry, ecology, and meteorology. ■

Chemurgy—For Better Environment and Profits. vi + 134 pages. Chemurgic Council, 350 Fifth Ave., New York, NY 10001. 1971. $11, paper.

Publication is comprised of 14 papers given at the 32nd Annual Conference of the Chemurgic Council (an organization dedicated to upgrading agricultural products and other renewable resources through chemical technology). Topics in three main areas—better environment, everybody's concern; food values from heated water; and chemurgy lowers cost in agriculture. ■

Environmental Legislation. William D. Hurley. ix + 81 pages. Charles C Thomas, 301–327 E. Lawrence Ave., Springfield, IL. 62700. 1971. $6.50, hard cover.

The publishers describe this text as written for scholars inquisitive about the framework of laws which constrain polluters, and for those industry, state, and municipal officials accused and accusing others of polluting, as well as for educators and news media officials. ■

Our Dirty Air. Sarah M. Elliott. 64 pages. Simon & Schuster, Inc., 1 W. 39 St., New York, NY 10018. 1971. $3.95, hard cover.

Informs young readers about the serious air pollution problem and enlists their aid to fight against it. Says the author, "... young children ... need to know how to clean up the world we live in. After all, young children have to breathe dirty air just as much as anyone else." ■

Toward a New Environmental Ethic. 24 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. 1971. 60¢, paper.

Booklet discusses the federal Environmental Protection Agency and its functions in air pollution control, water pollution control, solid waste management, radiation, pesticides, and noise. ■

Pesticide Biochemistry and Physiology, Vol. 1, No. 1. R. D. O'Brien, Ed. 122 pages. Academic Press, Inc., 111 Fifth Ave., New York, NY 10003. 1971. $15 per annum. Published quarterly.

Journal publishing papers dealing with the biochemistry and physiology of pesticides and their effects. Deals with research in these areas. ■

The Nation's Environment—Problems and Action. 99 pages. Research Advisory Council, East Tennessee State University, Johnson City, TN 37601. 1971. $2.50, paper.

Consists of papers presented at an Environmental Forum conducted on the campus of East Tennessee State University. Featured speakers from HEW, TVA, Department of the Interior, University of Georgia, University of North Carolina, U.S. Bureau of Mines, and Appalachian Region Commission. ■

Pollution Control in Metals Industries. 23 pages. American Society for Metals, Metals Park, OH 44073. 1971. $15, paper.

Computer-generated bibliography which cites all references to pollution control in the metals industries for the period January 1967–May 1971. Survey covers methods of pollution abatement such as treating effluents, waste disposal, fume control, dust control, exhaust gas purification, regeneration of solvents, removing poisonous materials from industrial water, and reclamation practices. ■

No Further Retreat. Raymond F. Dasmann. vii + 244 pages. Macmillan Co., 866 Third Ave., New York, NY 10022. 1971. $6.95, hard cover.

Beginning with a chapter on natural history, the author describes the climate, land formation, vegetation, and animal and vegetable life of Florida. He then examines the environmentally threatened areas and the efforts that have been made or can be made for their preservation. ■

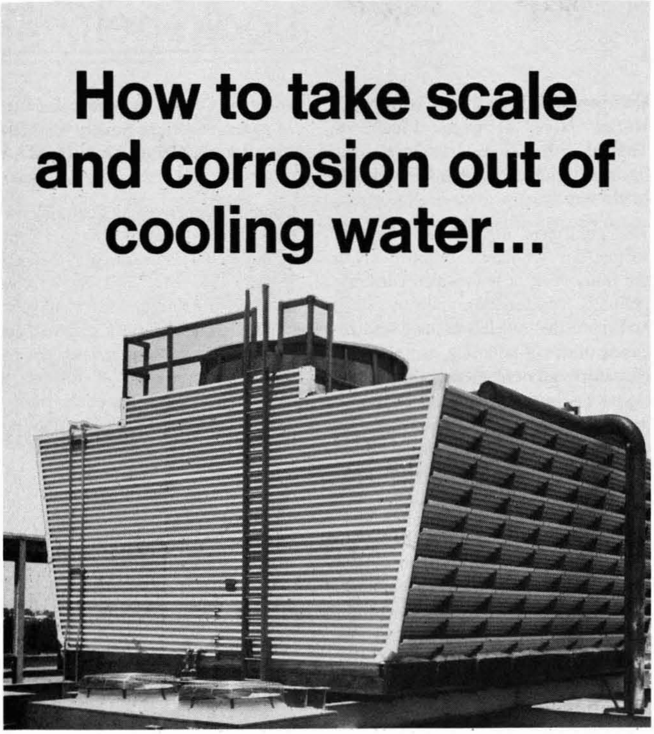
Part 23 of the 1971 Annual Book of ASTM Standards. 954 pages. ASTM, 1916 Race St., Philadelphia, PA 19103. 1971. $31.00, hard cover.

Part 23 contains all of the ASTM standards on water and atmospheric analysis. New or revised standards included are: method for sampling stacks for particulate matter, test for arsenic in water, and evaluation of air assay media by the monodisperse DOP smoke test. ■

Liquid Waste of Industry: Theories, Practices, and Treatment. Nelson L. Nemerow. viii + 584 pages. Addison-Wesley Publishing Co., Inc., Reading, MA 01867. 1971. $22.50, hard cover.

Suitable for researchers as well as graduate courses in sanitary or environmental engineering, this book covers the theory, art, and practice of eliminating the pollution characteristic of industrial liquid wastes. Economic, social, and political factors affecting proper waste treatment are considered. A general knowledge of chemistry, bacteriology, mathematics, and treatment of water and sewage is prerequisite. ■

(Continued on p 286)



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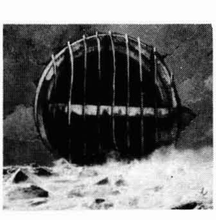

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Organic Compounds in Aquatic Environments. Samuel J. Faust, Joseph V. Hunter. xxii + 638 pages. Marcel Dekker, Inc., 95 Madison Ave., New York, NY 10016. 1971. $20.75, hard cover.

Deals with organic compounds—especially those resulting from man's technology—and how they influence and pollute the environment, affect the water supply, and represent potential toxic, carcinogenic, and genetic hazards. Of particular interest for graduate students, teachers, and researchers. Biologists, microbiologists, chemists, sanitary and environmental engineers, geologists, geophysicists, and oceanographers working in the area of organic pollution will find this helpful. ■

Managing the Environment—International & Economic Cooperation for Pollution Control. Allen V. Kneese, Sidney E. Rolfe, Joseph W. Harned, Eds. xxxvii + 356 pages. Praeger Publishers, 111 Fourth Ave., New York, NY 10003. 1971. $15, paper.

This report is the result of an international conference on "Goals and Strategy for Environmental Quality Improvement in the 1970's," organized by the Atlantic Council of the United States and Battelle Memorial Institute. Industrialists from North America, Europe, and Japan participated, and officials from the U.S. and Canadian governments, the United Nations, OECD, NATO, and the European communities lent their full cooperation. ■

Interbasin Transfers of Water: Economic Issues and Impacts. Charles W. Howe, K. William Easter. xiv + 196 pages. Johns Hopkins Press, Baltimore, MD 21218. 1971. $9.50, hard cover.

The authors consider large-scale transfers in terms of regional demands for water and alternative means available to meet those demands. Concentrates on the western U.S., which is the locale of most large-scale transfer proposals, and on agriculture, which would be the principal user of the water. ■

Environment for Man. William R. Ewald, Jr., Ed. ix + 308 pages. Indiana University Press, Bloomington, IN 47401. 1971. $2.95, paper.

American Institute of Planners sponsored a study to look into the next 50 years (1967–2017) and the future environment. Papers deal with physiological, psychological, and sociological impact of the physical environment. ■

meeting guide

March 20

Society of Plastics Engineers, Inc.

Buffalo Section Meeting

Depew, NY

Will cover the plastics and pollution problem. Contact: Charles Ball, State Univ. of New York at Buffalo, 1300 Elmwood Ave., Buffalo, NY 14200

March 20-24

Ohio State University

Midwest Workshop in Environmental Science

Columbus, Ohio

Contact: John Lindamood, Dept. of Food Science and Nutrition, Ohio State University, Columbus, Ohio 43210

March 21-23

Environmental Protection Agency and University of Houston

National Conference on Control of Hazardous Material Spills

Houston, Tex.

Write: H. Nugent Myrick, Associate Professor of Civil and Environmental Engineering, University of Houston, 3801 Cullen Blvd., Houston, Tex. 77004

March 26-28

Environmental Mutagen Society

1972 Meeting

Cherry Hill, N.J.

Write: Warren Nichols, Program Committee Chairman, Environmental Mutagen Society, Dept. of Cytogenetics, Institute for Medical Research, Copewood St., Camden, N.J. 08103

March 26-28

National Petroleum Refiners Assoc.

70th Annual Meeting

San Antonio, Tex.

Contact: National Petroleum Refiners Association, 1725 DeSales St., N.W., Suite 802, Washington, D.C. 20036

March 26-29

Environmental Division of American Institute of Chemical Engineers and American Society of Mechanical Engineers

Environmental Water Technology Conference

New Orleans, La.

Theme is "Process Wastewater Reuse in Industry." For more information: J. K. Rice, General Conference Chairman, Cyrus Wm. Rice Div., NUS Corp., 1910 Cochran Rd., Manor Oak Two, Pittsburgh, Pa. 15220

April 3-4

American University

12th Annual Washington Conference on Business-Government Relations

Washington, DC

Discussion of the present and future role of EPA in a dynamic business-government relationship. Fee: $100. Contact: Jimmy D. Johnson, Dir., Private Enterprise Center, School of Business Administration, American Univ., Washington, DC 20016

April 3-4

Oklahoma State University

Industrial Wastes and Advanced Water Conference

Stillwater, Okla.

Conference will bring together those responsible for producing wastes and those responsible for disposing of wastes to attempt to solve problems associated with both operations. Fee: $12. Contact: Engineering and Industrial Extension, Oklahoma State University, Stillwater, Okla. 74074

April 5-7

International Association for Great Lakes Research

15th Conference on Great Lakes Research

Madison, Wis.

Contact: Gregory D. Hedden, Director, University Extension Sea Grant Program, 610 Langdon St., Madison, Wis. 53706

April 6

Clemson University

Environmental Systems Engineering Spring Seminar

Clemson, SC

Topic is computer control of waste water treatment. Contact: Environmental Systems Engineering Dept., 401 Rhodes, Clemson Univ., Clemson, SC 29631

April 6-7

Research Triangle Universities and several national societies

National Symposium on Costs of Water Pollution Control

Raleigh, N.C.

Sessions include: Economic implications of national goals for water pollution control, economic incentives for pollution control, and economics of industrial waste management. Contact: F. E. McJunkin, Assoc. Director, Water Resources Research Institute, 124 Riddick Bldg., NCSU, Raleigh, N.C. 27607

April 9-14

American Chemical Society

163rd ACS National Meeting

Boston, Mass.

For details: A. T. Winstead, ACS, 1155 Sixteenth St., N.W., Washington, D.C. 20036

April 10-12

North Carolina State University and others

Fourth Annual Air Pollution Workshop

Raleigh, N.C.

Program presents current and future goals concerning research on the effects of air pollution on vegetation and ways of communicating these goals between and among scientists and program planners at governmental levels. Contact: William A. Feder, Suburban Experiment Station, Univ. of Massachusetts—Waltham, 240 Beaver St., Waltham, Mass. 02154

April 17-19

Springfield (IL) Sanitary District

Illinois Annual Wastewater Conference

Springfield, IL

For information: G. L. Peters, Secretary-treasurer, Springfield Sanitary District, Rt. No. 5, Springfield, IL 62707

April 18-19

Water Quality Research Council

1972 International Water Quality Symposium

Washington, D.C.

Symposium will explore the role of water quality in disease. Contact: David X. Manners Co., Inc., 237 E. Rocks Rd., Norwalk, Conn. 06851

April 18-20

Illinois Institute of Technology and others

34th Annual Meeting of the American Power Conference

Chicago, IL

Program will cover seven general categories: mechanical, nuclear, electrical, industrial, and hydroelectric power; water technology; and general interest. Write: R. A. Budenholzer, Dir., American Power Conference, ITT, Chicago, IL 60616

April 19-21

Houston Junior Chamber of Commerce

5th Annual National Pollution Control Conference & Exposition

Houston, TX

Write: Aubrey Lafargue, Junior Chamber of Commerce, Houston, TX 77000

(Continued on p 288)

SOLID WASTES

A new publication of the American Chemical Society puts the nation's solid waste problems in perspective.

A 96-page book entitled "SOLID WASTES" contains 26 articles that first appeared in Environmental Science & Technology.

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- Federal government programs
- Fly ash utilization
- Auto hulk disposal

and many others

The book can only be obtained from the Society and is not available in any bookstore. It costs just $2.00.

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April 20-21

International Association for Pollution Control

Annual Conference on Pollution Control and the Marine Industry

New Orleans, La.

Conference will cover legislation, regulations, standards, enforcement procedures, research and technology, and future concepts for environmental conservation. Contact: Carolyn Bloch, International Association for Pollution Control, Suite 700, 4733 Bethesda Ave., N.W., Washington, D.C. 20014

April 20-21

Univ. of Tenn. Dept. of Civil Engineering and APCA Southern Section

Second Annual Industrial Air Pollution Control Conference

Knoxville, TN

Topics include foundry furnace, chemica processes, wood products, mining and manufacturing, and combustion process control; emerging rules and regulations for stationary sources; emission inventory, point source monitoring; and emergency episode plans. Contact: Kenneth E. Noll, Conference Director, Dept. of Civil Engineering, UT, Knoxville, TN 37916

April 24-25

American Medical Assn.'s Council on Environmental and Public Health

1972 Congress on Environmental Health

Los Angeles, CA

Contact: Diane Dale, Dept. of Environmental, Public, and Occupational Health, AMA, 535 N. Dearborn St., Chicago, IL 60610

April 24-25

Du Pont Instruments

Second Annual Symposium on Mass Spectrometry

Wilmington, DE

Directed at pollution, food, and drug analysis. Write: T. R. Garrett, Symposium Director, Du Pont Instruments, 1500 S. Shamrock Ave., Monrovia, CA 91016

April 27-29

American Congress of Expositions

ACE WEST II

Los Angeles, CA

Environmental air management show and meetings along with four other shows. Contact: ACE WEST II, 77 Jack London Sq., Oakland, CA 94607

May 1-4

Institute of Environmental Sciences

18th Annual Technical Meeting and Equipment Exposition

New York, NY

Will review the status of environmental sciences, integrate all aspects of environmental problems, and investigate problems associated with educating those involved in environmental decisions. Contact: Institute of Environmental Sciences, 940 E. Northwest Hwy., Mt. Prospect, IL 60056

May 1-5

Navy Industrial Environmental Health Center

Workshop in Environmental Health

New York, NY

Of interest to the medical profession, safety officers, industrial hygienists, and managers. Contact: W. A. Redman, Jr., 3333 Vine St., Cincinnati, OH 45220

May 2-4

Purdue University

27th Purdue Industrial Waste Conference

Lafayette, IN

For more information, contact: David W. Hawkins, Civil Engineering Bldg., Purdue Univ., Lafayette, IN 47907

May 7-12

Electrochemical Society

Electrochemical Contributions to Environmental Protection Symposium

Houston, TX

Contact: Ernest G. Enck, Executive Secretary, ECS, P.O. Box 2071, Princeton, NJ 08540

May 8-10

American Society for Quality Control

26th Annual Technical Conference

Washington, DC

Topics will include nuclear power and environmental control. Write: American Society for Quality Control, 161 W. Wisconsin Ave., Milwaukee, WI 53203

May 8-11

American Mining Congress

1972 American Mining Congress Coal Convention and Exposition

Cleveland, OH

Subjects include water treatment, sulfur reduction, dust control, and reclamation programs for surface mining. Contact: American Mining Congress, Ring Bldg., Washington, DC 20036

May 11-12

Chemurgic Council

33rd Annual Conference

Washington, DC

Sessions on agricultural wastes, municipal wastes, and waste heat. Contact: John Ticknor, Chemurgic Council, 350 Fifth Ave., New York, NY 10001

May 11-12

International Association for Pollution Control

Second Annual Conference on Pollution Control and the Marine Industry

Washington, DC

Conference will provide vessel owners, operators, port authorities, oil drillers, manufacturers, and legislators a total view of all present and proposed activities in marine pollution control. Write: Thomas Sullivan, IAPC, 4733 Bethesda Ave., NW, Washington, DC 20014

Call for papers

April 1 deadline
American Water Resources Association

Eighth American Water Resources Conference

St. Louis, Mo.

Papers invited in the following areas: water quality considerations (surface water and groundwater); water supply interactions; modeling interactions, social, legal, and economic interactions; and data techniques. Contact: D. L. Warner, Technical Program Chairman, Geological Engineering Dept., University of Missouri—Rolla, Rolla, Mo. 65401

Courses

April 15, 22, 29, and May 6, 13, 20
American University

Community Environmental Management Series Short Course

Washington, DC

Sessions identify and discuss the role of systems tools and techniques in confronting: air and water pollution, solid waste disposal, and other areas. $250. Contact: Martha Sager, Director of Environmental Science Programs, American University, Washington, DC 20016

April 17-21 and 24-28
University of Texas at Austin

Advanced Water Pollution Control Short Course

Austin, TX

First week covers biological waste treatment, and the second week covers physical and chemical waste treatment. Contact: Engineering Institutes, P.O. Box K, Univ. of Tex. at Austin, Austin, TX 78712

University of Colorado

Water Resources Graduate Training

Boulder, CO

Interdepartmental program provides in-depth training in water quality control and management and broad-based studies in water management and engineering. For students with backgrounds in engineering, chemistry, biology, or related sciences. Write: J. Ernest Flack, Dir., Water Resources Training Program, Engineering Center, OT 4-34, University of Colorado, Boulder, CO 80302

May 15-18
University of Massachusetts—Amherst

Environmental Quality Control—Monitoring & Analysis Procedures Short Course

Amherst, MA

Concurrent sessions measuring air, water, and noise pollution and solid wastes. Fee: $160. For details: Course #CE 72-54, Continuing Education, Univ. of Mass., Amherst, MA 01002

May 22-26 and May 30-June 2
Manhattan College

17th Summer Institute in Water Pollution Control

Bronx, NY

Stream and Estuarine Analysis or Biological Waste Treatment offered the first week, and Advanced Topics in Mathematical Modeling of Natural Water Systems the second week. Total fee: $425. Limited number of grants available. Write: Donald J. O'Conner, Environmental Engineering & Science Program, Manhattan College, Bronx, NY 10471

May 22-26
University of Missouri—Rolla

Water Pollution Control/Waste Treatment and Disposal Short Course

Rolla, MO

Will present the fundamental concepts and discuss physical, chemical, and biological treatment of waste water. Fee: $250. Write: Ju-Chang Huang, Dept. of Civil Engineering and Environmental Research Center, Univ. of Missouri — Rolla, Rolla, MO 65401

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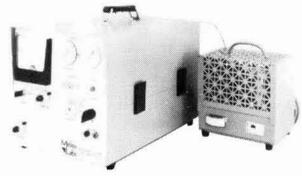

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