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SQUELCHING THE NOISE GREMLIN

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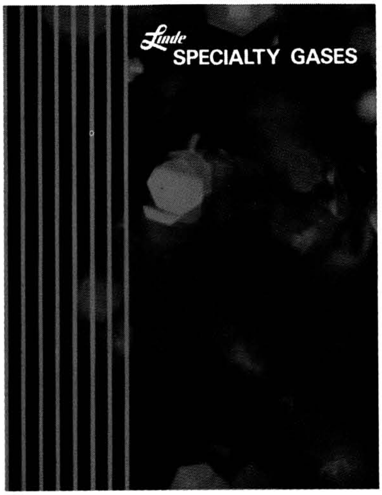
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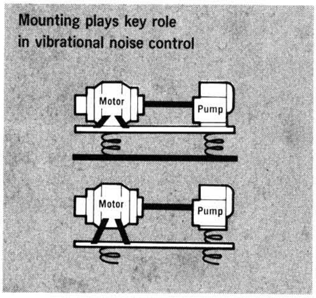

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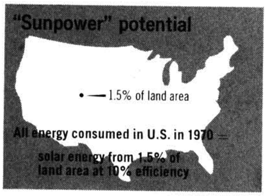

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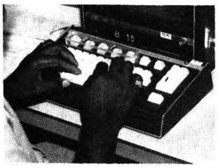

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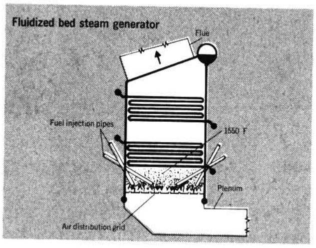

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CONTENTS

International

PAT report

Features

Outlook

Departments

Current research

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CURRENT RESEARCH

Modified cellulose adsorbent for removal of mercury from aqueous solutions 993

W. N. Marchant

Inorganic mercury was selectively removed from aqueous solution over a pH range of 1–9 using a modified cellulose adsorbent containing vicinal thiol groups. Amounts of mercury removed from solution were dependent on flow rate.

Selective absorption tubes and emission technique for determination of ambient forms of mercury in air 996

R. S. Braman* and D. L. Johnson

Detection and quantitation of levels of particulate and volatile mercury compounds were achieved using sequential selective absorption tubes and a dc discharge spectral emission detector. The lower limit of detection was 0.01 ng Hg.

Distribution of atmospheric mercury species near ground 1003

D. L. Johnson* and R. S. Braman

A recent method for measuring "volatile" and "particulate" mercury was used to study background levels for mercury compounds in the Tampa Bay area. Most of the mercury detected was "volatile," and the results suggested a wide variety of sources and transport processes.

Acute effects of outboard motor effluent on two marine shellfish 1009

R. C. Clark, Jr.,* J. S. Finley, and G. G. Gibson

Mussels and oysters showed physiological stresses when exposed to diluted outboard motor effluent in a running seawater system. Mussels showed an immediate response with delayed mortality, while oysters were much less affected.

Treatment of aqueous effluents from $UF_6(g) \rightarrow (NH_4)_4[UO_2(CO_3)_3](s) \rightarrow UO_2(s)$ conversion 1014

H. Z. Dokuzoguz* and H. M. Muller

A four-step process is developed for the treatment of aqueous effluents generated during the manufacture of UO_2 fuels. CO_2, NH_3, H_2O, and U are recovered and returned to the conversion process, while $CaF_2/Ca(OH)_2$ can be safely discarded.

Characterization of organics in secondary effluents 1017

Josepha Manka, Menahem Rebhun,* Asher Mandelbaum, and Arie Bortinger

Gel permeation chromatography was used to determine that most of the humic compounds isolated from secondary effluents are within a molecular weight range of 1000–5000. A number of specific compounds were identified using mass spectrometry and gas chromatography.

Determination of permeability profile of surface terrain 1020

T. N. Smith and C. R. Phillips*

A method for determining the permeability profile of a liquid through the surface cover in a permafrost region was developed and tested. Permeability to oil is unaffected by the initial moisture content of the surface cover.

Thermal and photochemical reactions of NO_2 with butyraldehyde in gas phase 1024

S. Jaffe* and E. Wan

The thermal rate constant for the reaction of NO_2 with butyraldehyde and the rate constant for the photochemical oxidation of butyraldehyde were determined. The values were close to those for the lower molecular weight aldehydes.

NOTES

Cation solubilities of lignite fly ashes 1026

D. G. Shannon* and L. O. Fine

Water extracts of four lignite fly ashes were analyzed for concentrations of Ca, Na, Mg, and Fe. As the H_2O:ash ratio increased, the relative concentrations of Ca, Mg, and Fe also increased. About 50% of the cations solubilized from dust collector ash appeared to exist as sulfate.

Inhibition of photochemical smog reactions by free radical scavengers 1028

C. W. Spicer,* D. F. Miller, and Arthur Levy

Several free-radical scavengers, proposed as photochemical smog inhibitors, were investigated in smog chamber experiments. It was concluded that while some smog reactions are inhibited, other serious side effects also result.

CORRESPONDENCE

Air quality control using minimum pollution dispatching algorithm 1031

P. G. Friedmann* and B. F. Wollenberg

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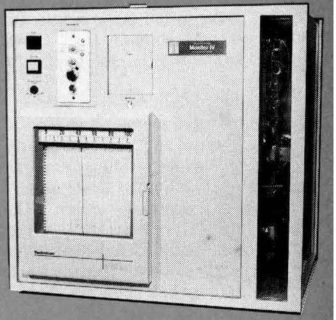
* To whom correspondence should be addressed.

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

Credits: 972 (upper), Smithsonian Institution; 972 (lower), Zweig Photo Studio (Washington, D. C.); 974,975, Exxon Co., U.S.A.; 991, Ted W. Johnson

Cover: Gerald M. Quinn


Monitor IV

LETTERS

Sulfur gas cleanup

Dear Sir: With regard to the news item carried under Currents (*ES&T,* July 1974, p 599), I would like to clarify the status of IFP technology for cleaning up sulfur-containing gases.

Actually there are two different IFP cleanup processes, one for Claus unit tail gas and one for stack gas from power-generating and similar large installations. Both are liquid phase processes in which SO_2 and H_2S form a complex with a proprietary catalyst dissolved in a polyethylene glycol solvent. There are important differences beyond the basic chemistry, however, but this is not the place to go into detail.

What I would like to set straight for the record, though, is the fact that both IFP processes are far past any development stage. Twenty-two Claus tail gas cleanup plants have been licensed by IFP in the U.S., Canada, Europe, and Japan, of which 14 are already operating. Four stack gas cleanup plants have likewise been licensed. One in Japan started up last month and a second in France is scheduled for startup in September.

Pierre Bonnifay
Institut Francais du Petrole
New York, N.Y. 10022

Gravel beds: Who was first?

Dear Sir: We agree with all the statements made in the PAT report (*ES&T,* July 1974, p 600) except one which is quite misleading.

The first gravel bed filter on this continent went in operation early in 1972 in our plant here in Mississauga. It was supplied by Lurgi and Gesellschaft für Entstaubungsanlagen (GfE, Munich, Germany) for dedusting the exhaust air on a clinker cooler of a 3000-ton-per-day cement kiln.

C. Zulauf, V-P Operations
St. Lawrence Cement Co.
Mississauga, Ont., Canada

All about chemicals

Dear Sir: We found Mr. Gross's article, "Markets for Chemicals Grow and Grow," (*ES&T,* May 1974, p 414) very interesting, and we concur with many of his observations. We were surprised, however, that his projections appeared not to include the use of precipitant/coagulants in existing wastewater treatment plants for phosphorus removal and improved reduction in BOD and suspended solids. Also, polyelectrolytes are used where needed as coagulant aids with both alum and ferric salts. However, there are many examples where metal salts work satisfactorily without the aid of polyelectrolytes. Incidentally, the list of billion dollar companies should have included Allied Chemical. Allied is the largest producer of aluminum sulfate but does not produce ferric chloride.

M. O. Ericson
Allied Chemical Corp.
Morristown, N.J. 07960

More on Four Corners

Dear Sir: Our staff has reviewed, with interest, the recent article on the scrubber system installed at the Four Corners Power Plant (*ES&T,* June 1974, p 516). The article was factual and well written; but, in my opinion, reflects a lack of understanding of the problems facing state regulatory agencies, particularly those in undeveloped and lightly industrialized states such as New Mexico.

I do not see that the problems of "moving targets" and available technology are behind us. This statement may come as a surprise to those who believe the federal new source performance standards define the limits of technology, that the federal ambient air standards provide the criteria for control design, and that the environmental movement died giving birth to the energy crisis.

New Source Performance Standards (NSPS) suffer from the flaw of being irretrievably tied to a compromise definition of available technology. While this may be necessary on a national basis to prevent large-scale economic and societal dislocations, it has obviously resulted in nationally required controls for new sources which are less restrictive than the degree of control currently being achieved by existing sources. For example, the NSPS for particulate emissions from coal-fired generating stations is 0.1 lb per MBtu's and yet there are four large coal-fired boilers in New Mexico which are presently emitting less than half that amount. Because of the environmental necessity, many western states will be requiring new sources to control to a level better than is required by NSPS—certainly this is currently the situation in New Mexico.

The overwhelming reason why I believe ambient air standards do not provide adequate design criteria, however, is one to which our society has traditionally been responsive and that is economics. It has not been generally recognized that one of the effects of recent federal and state legislation is that before a construction permit can be obtained for a new source the permitting agency must first determine that neither state nor federal standards or regulations will be exceeded. Should regulatory agencies adopt emission regulations for existing sources that allow emissions of such magnitude that resulting ambient concentrations are at or near the level of ambient standards, they will have created a zone inside which no new industry emitting the same pollutant can be located. The principle of no significant deterioration if it continues as a legal requirement will act as a further limitation.

In review, there are strong economic as well as environmental pressures in New Mexico and, I believe, in other western states for the best possible air pollution controls. These pressures are operating presently to require better pollution control than is required under the Clean Air Act, and in my opinion will continue to operate into the future. Unless industry both new and existing recognizes this situation the problem of moving targets will continue to haunt us.

The additional problem for industry of having to wrestle with technology that is newer and better than that which can be obtained "off the shelf" is also a way of life in much of the West. It seems appropriate for a publication such as *ES&T* to be aware of these factors when discussing the problems of air pollution control in New Mexico or other western states, and to include these considerations so as to provide proper balance.

Cubia L. Clayton, Chief
State of New Mexico Environmental
Improvement Agency
Santa Fe, N.M. 87501

Ember joins ES&T

Lois R. Ember joined the publication in September 1974. Mrs. Ember has degrees from the University of Illinois (BS in zoology) and the University of Chicago (MS in physiology) and several years of experience at Meloy Laboratories (Springfield, Va.) and Commonwealth Services, Inc. (Washington, D.C.). She will be contributing to the staff-written portions of *ES&T* and coordinating features.

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For author's guide and editorial policy, see June 1974 issue, page 549, or write Katherine I. Biggs, Manuscript Reviewing Office, *ES&T*

Has anyone been listening?

The environmental plans of man often go astray. Well-intentioned though they are, the plans for air, water, and solid waste cleanup have run into deadline difficulties, energy constraints, and are now caught up in the economic spiral of increasing costs. When one hears of a stretchout in deadlines, one can only ask how long it will be before a request for such a stretchout is made to the Congress. It seems inevitable.

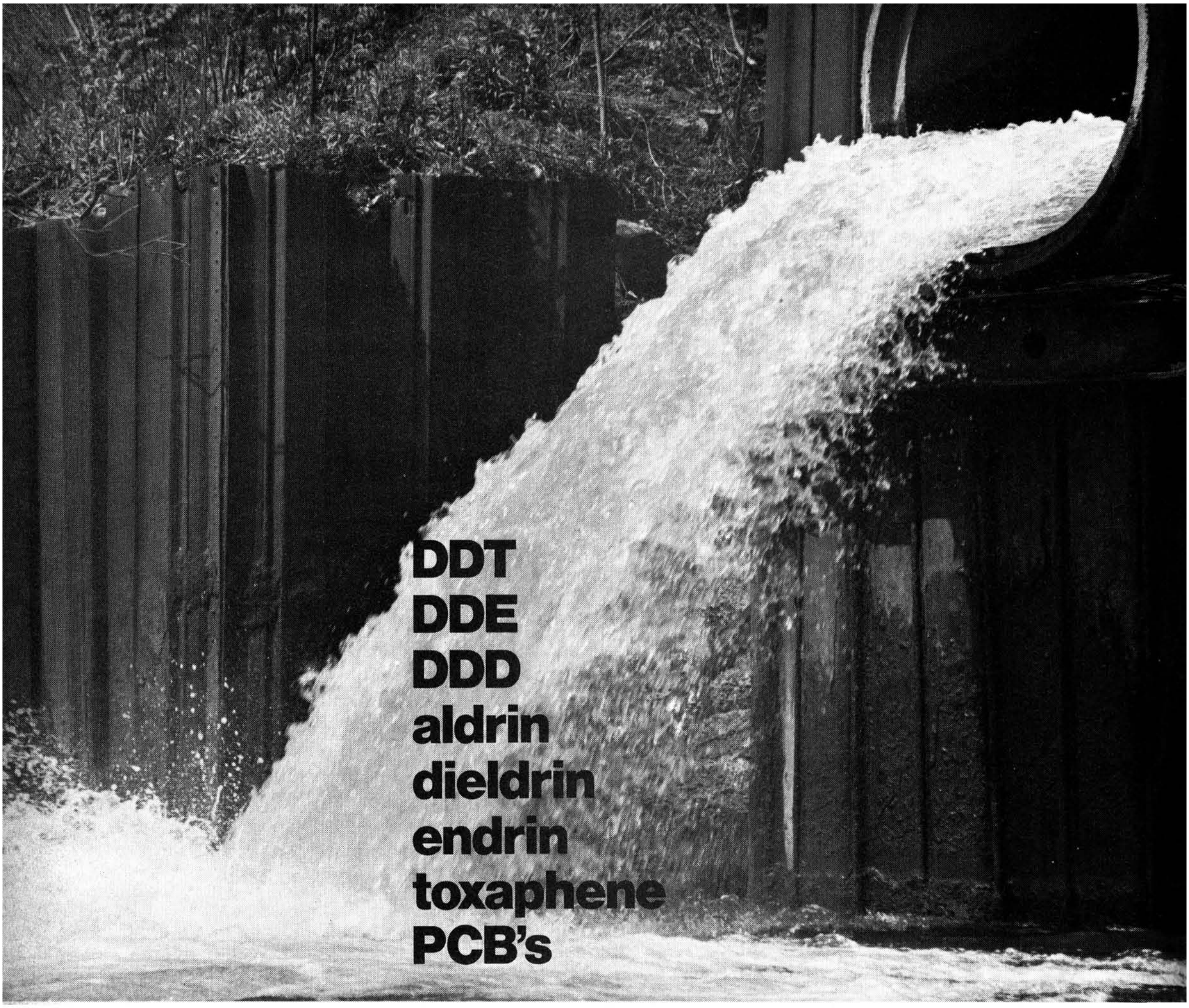
Consider, for example, another dilemma—this time with noise, the fourth form of pollution. At the federal level, control efforts in the EPA stemmed from an authorization (title IV of the Clean Air Act of 1970) to establish a noise control office; it was followed in October 1972 with the enactment of the Noise Control Act, P.L. 92-574.

From a mere beginning—two people in April 1971 to approximately 100 today, and a funding level of $4.7 million in fiscal 1974 and a proposed level of $6 million this fiscal year—much has been achieved. By July 1, 1973, three reports mandated by legislation were submitted to the Congress. This March, EPA came out with its "Levels Document" which set forth the levels of noise that are not to be exceeded to protect the health and welfare of the public. It points out that the beginning of hearing impairment begins at 75 decibels [dB(A)]. At 90 dB(A), the level prescribed by OSHA for the U.S. workplace, there would be a 10–20% permanent hearing impairment. All point out that to reduce the decibel din from 90 to 85 would be costly; estimates range from $15–45 billion for the U.S. industrial workplace.

EPA is also in the process of identifying various products as sources of noise. This June, the agency identified the first two—medium and heavy-duty trucks, and portable air compressors—for which regulations will subsequently be issued. Another 20 products have been identified as sources of noise—an additional eight transportation and 12 construction equipment items. Ideally, some 40–50 will be regulated in the next 5–10 years.

Although this may all sound like more noise, only by decreasing the decibel din can this nation return to a safe and healthy exposure to noise in our workaday and leisure environments.

Stanton Miller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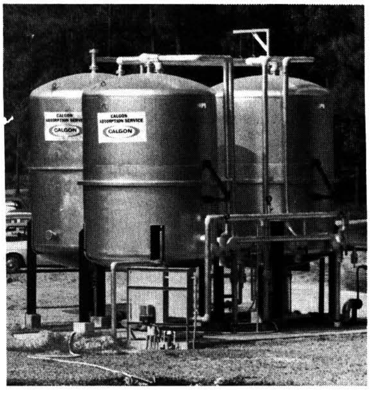
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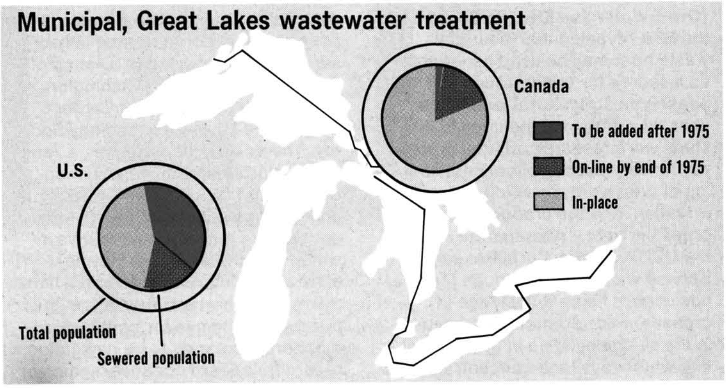

Municipal, Great Lakes wastewater treatment

INTERNATIONAL

The accelerated rate of degradation of Lake Erie apparently has been halted, so reports the International Joint Commission in its second annual report to the governments of the U.S. and Canada. The Commission concluded that the treatment plant construction programs of both countries will be completed or in the process of implementation by the end of 1975. The Commission recommended that the U.S. formulate legislation restricting the phosphorus content in detergents (limitations in effect in Canada since 1970), that the two governments increase research on the effects of waterborne viruses, and of PCB's on fish in the Great Lakes, and that the effects of chemical techniques for purifying water supplies be further studied.

WASHINGTON

EPA issued its first annual National Water Quality Inventory and the 1974 "Needs" Survey. The water quality report, the first systematic analysis of the impact of water pollution nationwide, pointed out that levels of coliform bacteria and oxygen-demanding organic compounds have decreased in the past 10 years, while nitrogen and phosphorus levels have increased. The preliminary "Needs" survey listed cost estimates submitted by the states for waste treatment facility construction to meet the 1983 goals of P.L. 92-500. Total costs for traditional programs, excluding treatment and/or control of stormwaters increased by $54 billion. The stormwaters estimate amounted to $235 billion.

The NRC report on the effects and control of automotive emissions was submitted to the U.S. Senate Committee on Public Works. The study by the National Research Council revealed "no substantial basis" for altering present federal ambient air quality standards. Only a small fraction of the total health hazard posed by air pollution may be related to automotive emissions; studies to measure the effects of sustained exposures of individuals to combinations of air pollutants should be undertaken. Achieving current standards with present technology could cost $12 billion annually. These costs should decrease with technological advances in automotive design, with decreases in the average car size, and with certain changes in emission control policies.

AEC's proposed ruling would prohibit commercial burial of transuranic waste in soil. Under the proposed amendment, transuranium waste would be solidified, if liquid, packaged, and transferred to the AEC for storage and ultimate disposal. Upon delivery, the Agency would levy a charge to the waste generator to cover the cost of further treatment and disposal procedures. Under a program outlined in a draft environmental impact statement, the AEC would develop retrievable surface storage facilities for long-lived transuranium-contaminated and commercial high-level wastes, until methods and locations for permanent disposal of such wastes become available.

The feasibility of floating electric power plants using ocean temperature differences to generate electric power has been funded by the National Science Foundation under the Research Applied to National Needs (RANN) program. Two California firms will analyze the design concepts for plants of 100 MW or larger, plants large enough to satisfy residential customers in a city of 300,000–400,000 population.

Using underwater parachutes or propellers may permit the harnessing of a section of the Gulf Stream known as the Florida Current. The practical possibility of reaping the power of ocean currents was discussed in a workshop organized by the National Oceanic and Atmospheric Administration.

Expanded government research on the health hazards posed by industrial and household chemicals was retained by the U.S. Senate in the amendments to the FY 1974 Labor-HEW appropriation bill. One amendment would fund a 3-year study of health problems resulting from the drinking of asbestos-contaminated water, and the other would extend research on health effects of possible carcinogenic chemicals. The amendments would provide a 25% increase in funding and research capacity to the National Institute of Environmental Health Sciences and the National Institute for Occupational Safety and Health.

STATES

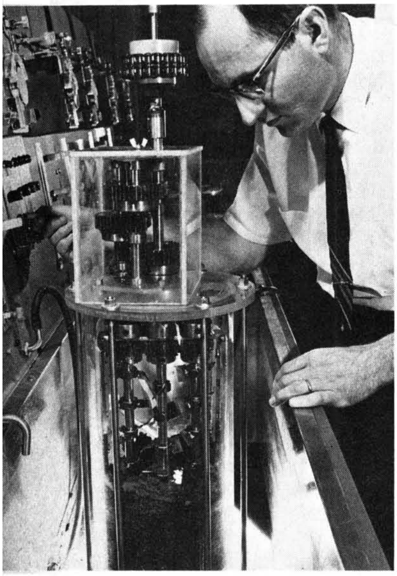
A California Supreme Court decision, requiring motorists owning 1966–70 automobiles to retrofit their cars with NO_x emission control devices, was overturned by Senate Bill 2471 and signed by Gov. Reagan in early September. The legislation limits the mandatory device installation schedule, keyed to license plate numbers, to the six counties within the South Coast Air Basin, effective January 1, 1975. The requirement for installation of devices with change of ownership for all vehicles is unaffected by the law. These devices increase gasoline consumption up to 10%, and the mandatory installation program was originally delayed by the Air Resources Board in December 1973.

This year's tussock moth spraying operation has been completed and more than 400,000 acres of timber forests in Washington, Oregon, and

Idaho were sprayed with DDT. The pesticide killed 95% of the moths in the areas sprayed and thousands of acres of forest were not defoliated. But, alternatives to DDT were not tested under field conditions simultaneously with the pesticide. The tussock moth outbreak subsided before such testing could be undertaken.

Pennsylvania's Dept. of Environmental Resources reported erratic results from spraying against the gypsy moth with the biological spray Bt. Egg mass reduction occurred, but this was accompanied by a high level of defoliation.

Eleven of New Jersey's 567 municipalities compost leaves on a sizable scale, according to D. V. Arent and M. S. Finstein of Rutgers, the state university. Leaf composting is regulated by the state of N.J. Administrative Code 7:26-Rules of the Bureau of Solid Waste Management.



Composting of leaves

N.J.'s Public Service and Electric Gas Co. will be the first utility to burn fuel made from municipal waste. Eco-Fuel briquettes, developed by Combustion Equipment Associates, Inc., of New York, N.Y., are odorless and low in sulfur content. The utility plans to burn 200 tons per day of the briquettes mixed with oil (see *ES&T*, March 1974, p 210).

A study sponsored by the Eugene, (Ore.) Water and Electric Board and the EPA revealed that industrial waste heat may be used beneficially as a source for underground soil heating on agricultural land. Other uses for waste heat included in the study were research on frost protection, greenhouse applications, cooling of crop plants, humidity control, irrigation, and the production of two crops per year. In a separate report, the USDA's Agricultural Research Service warns that, although fertilization of corn fields with sludge increases yields dramatically, metals in the sludge build up in the soil, pollute waterways, and concentrate in the plants.

Termites occasionally attack Hawaii's local communication network. More difficult than gophers or squirrels to apprehend because of their small size, these termites tax the sleuthing skills of Hawaiian Telephone Co.'s repair crews. Recently, five nests of termites were uncovered along a 60-ft section of cable near Pearl Harbor. The determined insects had chomped their way through a ⅛-in.thick polyethylene outer sheath, a ⅛-in. solid lead inner sheath, and a $^1/_{16}$-in. layer of polyethylene covering the coaxial cables and individual wires. All this to get to the thin-paper insulation surrounding each wire in the cable. As the paper was eaten away, the wires shorted out and service was interrupted for 12 hr.

MONITORING

Man-made fluorocarbons are showing up in remote areas of the world, as well as in atmospheres over populated lands, according to data gathered by the U.S. Naval Research Laboratory (NRL, Washington, D.C.). During extensive surveys aboard ships and aircraft, NRL found that the highly biostable trichlorofluoromethane (CCl_3F), widely used in cooling systems and aerosol propellants, was also appearing in surface seawater. For 200 air samples taken on a Los Angeles-to-Antarctic cruise, November–December 1972, for example, NRL found an average of 61 parts per trillion (ppt) of CCl_3F. In January 1974, 120 ± 18 ppt of CCl_3F were found at 80° N near Spitsbergen, Norway.

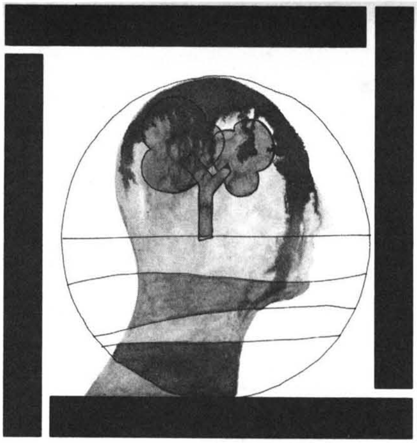
Spot-checking of scheduled ocean disposal of acid industrial waste is possible by airborne remote sensor surveillance, reported M. Champ of American University, Washington, D.C., at the Tenth Annual Conference of the Marine Technology Society. The acid waste produces a zone of discoloration visible on uv imagery; at night, however, this technique does not work. In addition, the present sensors may not be effective in winter months when the thermocline breaks up. Because of the limitations of airborne surveillance, the principal technique for continuous monitoring appears to be navigation recorders aboard oceanographic vessels.

TECHNOLOGY

Reduction of NO_x emissions by catalytic means, exceeding the very rigid Japanese 0.25-g/km requirements for 1976, equivalent to U.S. 1978 requirements, was announced by Gould, Inc. (Chicago, Ill.). The Gould catalyst uses a "Getter system" that catalytically removes oxygen from exhaust gas before it goes through the NO_x catalyst. The NO_x catalyst, tested on a 1973 Datsun, using the Federal Durability Driving Schedule and unleaded gasoline, showed no signs of deterioration after 60,000 km of driving. Catalysts controlling hydrocarbon and carbon monoxide emission were deteriorated only minimally. The Datsun averaged 22 mi/gal of gasoline.

Odor elimination with wet scrubbers and granular activated carbon (GAC) adsorption was achieved at the Sacramento, Calif., Main Wastewater Treatment Plant. This system, using a 3-ft thickness of Calgon Corp.'s "BPL" GAC, removes pollutants which remain after secondary biological treatment effluent is passed through sodium hypochlorite scrubbers. These scrubbers remove the bulk of hydrogen sulfide. The total system, designed and engineered by DeWante and Stowell Consulting Engineers (Sacramento), is effective even when local food canneries, whose effluents are a strong odor source, are at peak production.

Efficient removal and recovery of chrome from plating rinse waters was announced by R&D Chemical Co., Inc., Dayton, Ohio. The compa-



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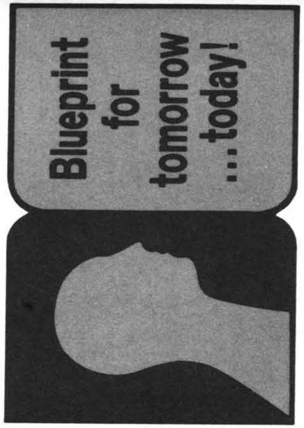

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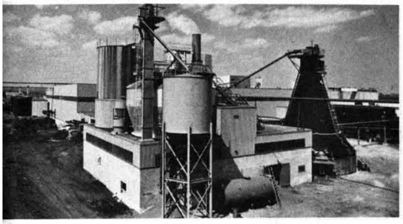
ny's "RD-343" process has been shown in field tests to remove total chrome and to provide simple recovery and regeneration of the chrome in a form suitable for direct reuse in chromium plating or dipping. Removal is effected in one cycle, and all wastewater may be continuously reused as primary plating rinse water. The practically sludge-free system requires far less capital investment and incurs much lower operating costs than do evaporation, destruction, or ion exchange systems.

Incineration of unshredded municipal garbage was demonstrated on a full-scale basis with a fluid bed system made by Copeland System, Inc., Oak Brook, Ill. The garbage, which contained organics, glass, metal, plastic, paper, and other materials, was burned at 1200–1450°F. No smoke or odor appeared at temperatures as low as 1200°F. The garbage, introduced at 16,000 lb/hr, also contained "tramp items," such as oil filters, inner tubes, motors, and other miscellaneous items. The City of Thunder Bay, Ont., Canada, and The Great Lakes Paper Co., Ltd., cooperated in the tests.



Solid waste disposal plant

Recycling of 90% of a brass foundry's waste is now possible, and a major pollution source becomes a company profit. At the 3rd International Pollution Engineering Congress & Exposition, held in Chicago in September, the U.S. Bureau of Mines, University, Ala., said that 75% of brass and 83% of molding sand used for manufacture could be reclaimed and recycled. The reclaimed sand seems better than the original because less binder, a costly item, is required. According to the Bureau, a 42-tpd operation could achieve credits of $0.50/day for copper and $6.00/ton for sand, with a gross profit, after capital and operating costs, of about $19/ton of sand.

INDUSTRY

Dames & Moore, Los Angeles, Calif., has prepared an environmental impact statement (EIS) on LNG terminals and vaporization plants planned for Los Angeles Harbor, Point Conception, and Oxnard, Calif. These major facilities would be built by Western LNG Terminal Co., a subsidiary of Pacific Lighting Corp. Each terminal would be able to handle up to 4 billion ft^3 of gas daily, with a peaking capacity of 5 billion ft^3. According to Jack Yaghoubian, a Dames & Moore partner and principal-in-charge for this EIS study, the EIS "represents the most extensive study conducted in this field."

UOP's president John Logan said that catalytic convertors present no danger to public health. He also said that catalytic convertors add no more sulfur to the air than is already in the gasoline cars burn. Logan predicts that use of catalytic convertors will eliminate other harmful chemicals while saving money for motorists and conserving energy resources. Addressing fears that the convertors may create sulfuric acid mist, and recalling that gasoline accounts for less than 1% of atmospheric sulfur emissions, Logan wanted to "clear the air" about the convertors' effects, since they will be used on 1975 model cars.

Jerome Klaff, chairman of the National Commission on Materials Policy during its existence, said that Congress and the Administration did nothing to meet today's and the future's economic crisis and energy and environmental needs, despite "noble-sounding rhetoric" which greeted its conclusions. He told the National Association of Recycling Industries (NARI), New York, N.Y., that it was "unconscionable that present economic policies make it cheaper for a municipality to collect waste and bury it in landfills or burn it than to recover these valuable resource assets." Klaff said that such policies are "at complete variance with sound socioeconomic and environmental needs and demands."

Jerome Klaff

The Conference Board, New York, N.Y., expects corporate pollution control (PC) spending to continue rising, despite the energy crisis. A Board survey of 212 firms revealed that about 65% of these firms feel that PC spending will not decline, despite the 1973–74 winter's fuel shortage, energy conservation, or higher energy prices. Indeed, overall PC expenditures should climb by 55% over 1974, as compared with 28.1% between 1972 and 1973. In dollar terms, the 1974 PC expenditures would exceed $2.7 billion, of which electric utilities would spend over $900 million, and the petroleum industry about $43.9 million. Of the total to be spent, the paper industry could account for 15.2% in its PC capital program.

David Marcus & Co., Inc., Kentfield, Calif., is building a recycling plant to convert 500,000 lb/mo of waste polyethylene film into new plastic products. The company is also working on showing waste collectors and refuse haulers how to obtain far greater profits from waste than those collected from mere hauling and dumping fees. The firm believes that vast quantities of needed materials are lying in dumps or in obscure corners of thousands of manufacturing facilities throughout the U.S. The company's "avowed purpose," as stated by David Marcus, founder and president, is to regenerate useful raw materials from such waste and continuously to seek markets for these materials.

The American Petroleum Institute, (API), Washington, D.C., and 11 oil companies are suing the EPA for relief from effluent controls and guidelines set up in May. The suit charges that the rules, with compliance deadlines of 1977 and 1983, impose hardships and inequities on refineries, and usurp states' authority to issue discharge permits. The suit also charges that the EPA "improperly and illegally" ignored Congress' mandate of the plant-by-plant approach, and instead purported to issue binding nationwide effluent discharge standards to be mechanically "cranked" into permits issued by states and regional administrators.

PAT REPORT
PRACTICAL, AVAILABLE TECHNOLOGY

Fluidized bed steam generators for utilities

Pope, Evans and Robbins' unit will burn a variety of U.S. coals; continuous operation at a West Viriginia utility starts next July

Fluidized beds have been used for many years in the chemical industry to enhance reaction rates, but their use in steam generators is a relatively new concept. More recent is the development of the fluidized bed combustion technique to produce utility boilers at a fraction of their present size. Such boilers would burn almost any fuel, including low-quality coals such as lignite. Although the basic principles of fludizied bed combustion of coal have been known for 50 years, little progress has been made on a commercial design.

Pope, Evans and Robbins (PER), consulting engineers, will complete installation of the first boiler at the Rivesville Power Station (Fairmont, W.Va.) in the first quarter of 1975. Continuous operation of the unit is scheduled to begin in July 1975.

Mr. C. G. McKay, Vice-President—Operations of Allegheny Power Service Corp., says, "We were interested in the fluidized bed boiler project because it shows great promise of being able to use high-sulfur coals to meet the standards of power plant emissions that have been established by EPA and cut the overall cost of generating electricity without the use of stack gas scrubbers that still have not been perfected. Our Rivesville Station, operated by Monongahela Power Co., an Allegheny subsidiary, was selected as the site for this project because of the availability of local high-sulfur coal, appropriate operating and supportive facilities for this test, and steam conditions of 1270 psig, 925°F, with no reheat, that can use existing turbine generating equipment. Also, the 300,000 lb/hr packaged unit, the highest capacity factory-assembled boiler in transportable size, can be accommodated in space available in the present building."

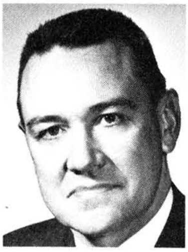
Fluid bed combustion has the eyes and ears of high government officials. For example, in a February 15, 1974, letter to the President of the U.S., Secretary of the Interior Rogers C. B. Morton wrote, "We believe the fluidized bed combustion boilers offer the best prospects for providing large volumes of clean energy from coal at an early date. Current pollution controls allow only limited use of high-sulfur coal in conventional boilers. The early demonstration of a low-cost, pollution-free combustion technique would help alleviate this undesirable situation and stimulate the production and utilization of Eastern coal."

In 1965, PER began active development work on atmospheric fluidized bed boilers in their Alexandria, Va., laboratory using a unit capable of burning 100 lb of coal/hr. In 1967, a small boiler (5000 lb of steam generation/hr at 300 psig) was built by PER under contract to the Office of Coal Research (OCR) for development of the start-up technique, turndown method, and pollution control. By the end of 1973, about 5000 hr of test operation were performed by PER on this unit, using crushed limestone as bed material for sulfur capture. Combustion intensity of 1.2 million Btu/hr/ft^2 bed surface was achieved, equivalent to 480,000 Btu/hr/ft^3 within the oxidizing fluidized bed.

In fact, two general approaches are being taken in development work and in construction and operation of such boilers. In France and Czechoslovakia, fluidized bed furnaces have been developed for steam generators in which there is no direct contact between the inert fluidized particles and the heat transfer surfaces, the boiler tubes. On the other hand, work involving direct contact heat exchange has been actively pursued in England and in the U.S. In the boilers without direct contact, the hot off-gases generate all the steam in conventional fashion, and no appreciable size or cost advantages are attained.

How it works

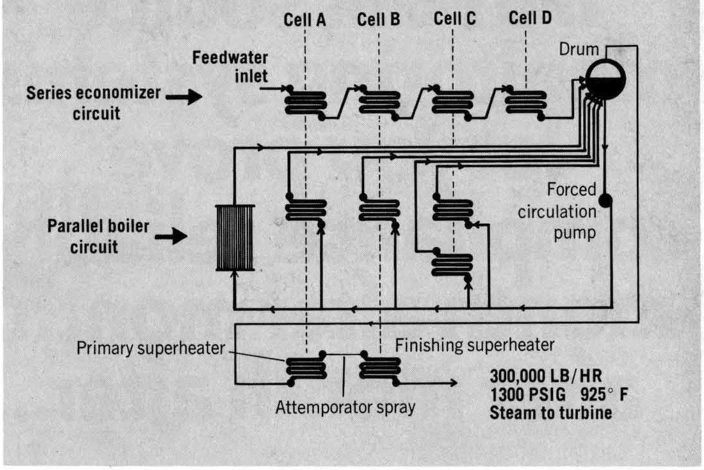
Basic design for direct-contact heat transfer units involved inert granular material supported by fluidizing air from a distribution grid. The grid contains horizontal boiler tubes immersed in the fluidized bed and surrounded by heat exchange surface membrane walls. Combustion within the fluidized bed is very intense. The granular bed material is limestone or ash, and very high volumetric heat release and heat transfer rates are obtained. As a result, there is no need for a large space-wasting furnace, and the amount of surface required is reduced.



Allegheny Power's VP McVay
"to use high sulfur coals . . . without use of stackgas scrubbers"

John E. Mesko, vice-president of PER, explains that start-up of an atmospheric fluidized bed boiler requires heating a portion of the bed to 800°F, hot enough to ignite bituminous coal. After coal ignition, the temperature of the bed rises rapidly until the system achieves thermal equilibrium. At equilibrium, the energy released in the bed equals the energy absorbed by the boiler tubes, plus the energy contained in the hot gases leaving the bed. The desired bed temperature is obtained by setting the proper ratio of heat transfer surface to heat release volume.

PER-Foster Wheeler steam generator



Operating characteristics of the bed dictate an optimum design temperature range of 1500–1600°F, with excess oxygen at about 3%. At these conditions, about 50% of the heat released by the burning coal is absorbed in the immersed tubes.

Coal burns rapidly in a fluidized bed, even at 1500°F. The rate is so high that at any point the bed is composed almost entirely of the inert particles that were added before combustion began. Typically, a sample of bed material would analyze at less than 1% carbon. Based on bed volume, the heat release is 300,000–400,000 Btu/hr per ft^3. Counting the open furnace space above the bed, the rate is 100,000–200,000 Btu/hr/ft^3. The wide range in this overall furnace release rate follows from the fact that the furnace volume is set by design considerations other than heat release—i.e., tube arrangement, access for maintenance, water circulation. In either way of calculating, the heat release rate is much higher, as much as a factor of 10 more than the release rate in conventional coal-fired furnaces.

The heat transfer coefficient is also higher, 50–60 Btu/hr/ft^2/°F. But the important advantage is in the uniformity of the heat flux. The peak and average fluxes are equal; there is no danger of burnout as long as the feedwater treatment is intelligently handled. A typical riser has a heat flux of 50,000 Btu/hr/ft^2.

Tubing length is reduced because most of the steam is generated in tubes heated on both sides. Actually, effective projected radiant surface (EPRS) is a concept not used in designing an atmospheric fluidized bed boiler. Superheater surface requirements are also reduced because of the high heat transfer coefficient and the fact that fireside deposits do not form.

Fireside corrosion is also avoided, apparently because the sodium, potassium, and vanadium in the coal are not released, or if released, are picked up by the bed particles instead of the tubes. The ratio of bed-particle-surface area to heat-transfer-surface area is about 15–1. Condensing vapors are thus more likely to deposit on a bed particle than a tube.

Unlimited coal type

Unlike a pulverized coal-fired boiler, ash properties are not significant to the design of an atmospheric fluidized bed boiler. The same basic design applies for all coals. The bed temperature is too low for the ash to soften or change chemically in any detrimental way. All fuels are burned at a heat release rate equivalent to 110,000 Btu/hr/ft^2 of EPRS. In a pulverized coal-fired unit, this value may be as low as 40,000 with a high alkali coal.

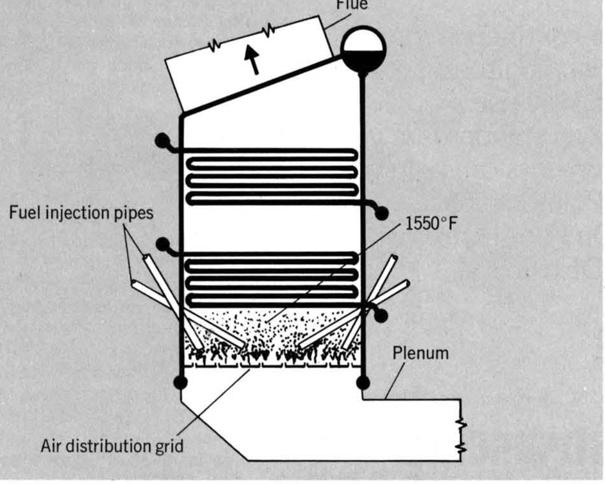
The boiler designed and developed to date could not be used if the coal were very fine and dry, since the coal is difficult to feed uniformly, and successful operation depends on even fuel distribution. With current mining and transport methods, a ½–¾ in. top size is easy to get.

Keeping low emissions

Tests performed recently bv the Bureau of Mines, Department of the Interior, on the Pope, Evans and Robbins unit in the Alexandria, Va., laboratory established that both NO$_x$ and SO$_2$ emissions were held below EPA emission standards for new coal-fired plants. The conclusion reached by the Pittsburgh Energy Research Center of the Bureau of Mines indicates that "Test data obtained during the two 4-hr tests on the fluidized bed boiler showed emissions of 0.80–1.20 lb SO$_2$/10^6 Btu and 0.11–0.17 lb NO$_x$ (calculated as NO$_2$) per 10^6 Btu, compared with EPA Standards of 1.20 lb SO$_2$/10^6 Btu and 0.70 lb NO$_2$/10^6 Btu for new coal-fired plants," while burning coal with 4.5–4.8% sulfur content.

The coal fed to a fluidized bed boiler is crushed to a 1.4-in. or 3.4-in. top size, not pulverized. A good fraction of the ash stays in the fluidized bed, or if carried out with the products of combustion, is separable in a low-pressure drop cyclone dust collector. Little, if any, metal oxide or sulfate fume is formed, and the quantity of very fine particulate is relatively low. Sulfur trioxide has also not been detected when limestone is

Fluidized bed steam generator



used as the bed material. Plume opacity and particulate emissions may be low from a fluidized bed boiler without a precipitator. However, due to current EPA regulations, provisions for electrostatic precipitator are recommended.

Sulfur dioxide in the fluidized bed is actually controlled by the use of limestone as bed material, based on the following reactions:

$$CaCO_3 + heat \longrightarrow CaO + CO_2$$

$$CaO + SO_2 + {}^1/_2O_2 \longrightarrow CaSO_4$$

The limestone is kept reactive either by the addition of fresh limestone, in a once-through system, by regeneration to recover sulfur dioxide in useful concentrations,

$$CaSO_4 + CO \longrightarrow CaO + SO_2 + CO_2$$

or by adding a low-cost catalyst (common salt) with the coal.

Current material balances indicate that for 2000 lb (1 ton) of 5.6% sulfur coal, 400 lb of limestone is required to remove over 90% of the sulfur. Studies are now being undertaken by EPA to develop alternate plans for calcium sulfate ($CaSO_4$) disposal. Since the temperature in the fluidized bed boiler is relatively low, NO_x emission is considerably below the value that EPA's rules would allow. A clear stack is readily achievable, inasmuch as there are relatively few micron-sized particles and there is virtually no sulfuric acid mist even at exhaust temperatures of 250°F.

Building the unit

The design of the 300,000-lb/hr unit, as a cell, for a 800-MW fluidized bed steam generator was developed by Foster Wheeler Corp. (Livingston, N.J.). Their design consists of four modules, each containing seven vertically stacked fluidized beds, called cells.

During the latter part of 1973, the 300,000-lb/hr capacity unit was released for fabrication. Based on competitive price bidding, the award went to Foster Wheeler. Final dimensions of the boiler are 12 ft wide, 25 ft high, and 38 ft long.

The atmospheric fluidized bed boiler is seen as the necessary first step on a long path toward better use of coal, the only major fossil fuel resource in the U.S. If and when the successful performance of the first 30-MW unit is demonstrated, then other utilities will commit funds for the installation of such boilers in the 200–800 MW capacity range.

The environment in sub-Saharan Africa

Certain countries may build environmental protection into their development plans, but such moves may not come quickly

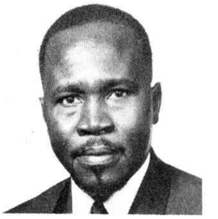
"Clean water is of higher priority than clean air initially; however, attention certainly will be given to clean air," says Gaston Banda-Bafiot, the Central African Republic's ambassador to the U.S. He believes that his government will eventually require that in the design of a factory, for example, water pollution control (WPC) will be totally incorporated in the factory's engineering, equipment, and operations.

As a professional electrical engineer who was his country's minister of energy before assuming his Washington post last year, Ambassador Banda-Bafiot has a strong appreciation of environmental matters. He points out that the necessity for resource conservation is well recognized in the Central African Republic, and expects that when resource recycling begins in ernest, it will proceed more rapidly in his country than it has in the U.S., given equal time frames.

The priority question

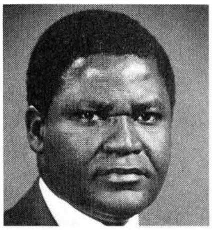
Raimi Ojikutu, who was a fellow of the Woodrow Wilson International Center for Scholars (WWICS, Washington, D.C.) for about 1½ years, as well as head of the faculty of anthropology and human biology, and environmental research, University of Lagos (Nigeria), has raised some cogent points. He told *ES&T* that the environmental protection issue is clearly understood by many African countries and governments, but that economic, political, and social issues intervene, and these often undermine the desire of any of those governments to place priorities on environmental issues as against issues of economic development. The reason, Ojikutu said, is that the importance of the environment is less appreciated among policymakers and economic development planners in those countries, who wonder why environmental matters need not take a "far back seat" to economic development.

However, environmental issues may stubbornly refuse to take that back seat. As Ojikutu said, "For any long-term benefits of economic development, environmental matters become a clear issue, particularly when such development will affect not only the ecology or physical environment, but the society itself for which development is meant. Such development's damage becomes irreversible if the resource base of the development is not properly planned. The environment is the most important component of this resource base."



Ambassador Banda-Bafiot

"Controls should be built in plans"



Raimi Ojikutu

"Environment cannot take 'back seat'"

Overcoming monumental obstacles—not the least of which was suspicion of the intent and motives behind the effort—Ojikutu organized a "highly successful" seminar, sponsored by the WWICS, on problems of human environment in the sub-Saharan African countries, held in Washington, D.C. in March 1973. Response elicited by the seminar (48 delegates from 13 countries attended; six more countries indicated interest) indicated that many of these countries are, in fact, considering how best to approach the task of setting up environmental "machinery" within their governments, and tackling the multitudinous environmental problems in these countries. This effort would deal not only with the question of poverty, but also with problems resulting from development—particularly in each country's urban areas.

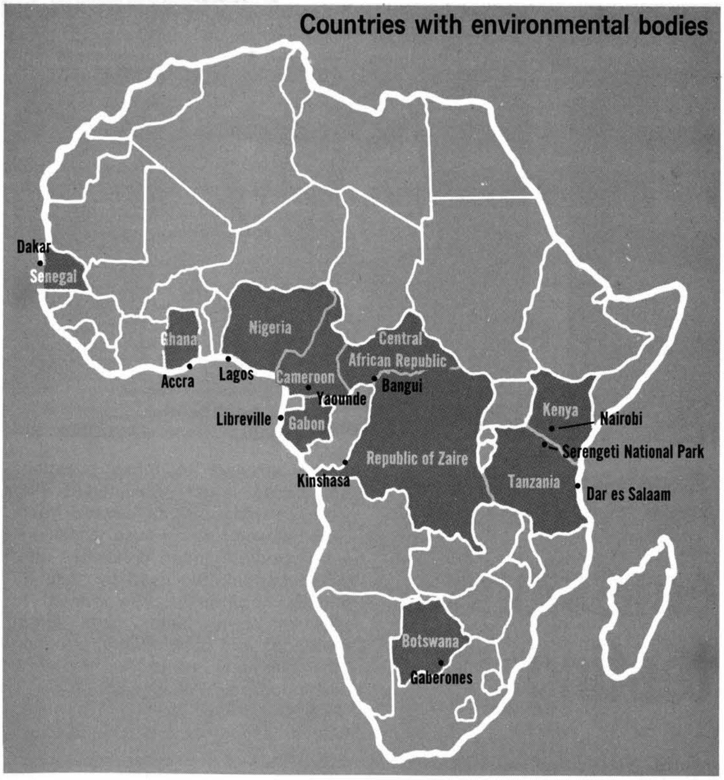
While Ojikutu found this response encouraging, he made it plain that economic, political, and social issues are major stumbling blocks to the development of an environmental effort. There are budget and financial problems, as well as technical uncertainties. Thus, in addition to conducting in-country efforts, these African nations may seek assistance and action through cooperation with international or United Nations agencies, or through bilateral agreements.

Some national initiatives

Countries which already plan active environmental efforts include Botswana, Cameroon, Ghana, Kenya, Nigeria, Senegal, Tanzania, and Zaire. As of mid-1974, the Gabonese Republic (Gabon) was added to the list. Ojikutu believes that up to now, none of these countries have reached the point at which, through the necessary legislation, they could enforce environmental guidelines or measures among any of the ministries responsible for such activities as economics, industry, and social welfare, to any appreciable extent.

Nevertheless, guidelines and enforcement might not take too long to come, at least in certain countries. Nigeria, for example, has regulations on some aspects of environmental protection as part of her town and country planning laws and other laws relating to mining and industry. However, these laws are neither comprehensive nor adequately enforced, according to cognizant authorities in Lagos, the Nigerian capital.

To change this situation, the Nigerian government organized the National Coordinating Committee on Human Environment (NCCHE). The NCCHE is an interministerial advisory committee which operates under the aegis of the Nigerian Federal Ministry of Economic Development and Reconstruction in Lagos. The NCCHE will review environmental laws with the aim of making them much more


Countries with environmental bodies

comprehensive than they are at present, and strengthening their enforcement. It is expected that any penalties resulting from such enforcement would be civil.

The NCCHE advises the Nigerian federal government on action programs and control measures necessary for protection of the nation's physical environment. It also coordinates activities of all bodies concerned with such programs on a national basis. The NCCHE has neither a full-time director nor executive machinery which it directly controls; rather, it relies heavily on the executive capacity of existing agencies. The NCCHE was authorized by the Nigerian government in February, and held its first meeting in early September.

Committees similar to the NCCHE are being formed in each Nigerian state to provide local links to Lagos. However, the NCCHE is not set up to have direct relationships with the United Nations Environment Program (UNEP, Nairobi, Kenya), or any other international agency.

Nigerian environmental priorities are expected to be, over the near and intermediate term,

- proper planning of human settlements—layout, housing, transportation, and related efforts
- waste disposal, covering domestic and industrial wastes
- water pollution control, covering domestic and industrial wastes
- protection of productive land from degradation through erosion and desert encroachment.

Tanzania is very active in wildlife conservation through work being done at the Serengeti Wildlife Research Center and the Tanzanian College for Wildlife; through setting aside generous wildlife preserve areas such as Serengeti National Park; and through heavy punishments for poachers. Other environmental preservation missions include a forestation program and a soil erosion prevention project, both being in Tanzania's five-year plan.

Water pollution control is apparently an emerging priority in Tanzania, especially with respect to offshore areas. For example, Tanzania's East African Harbors Corp. is empowered to impose fines on cargo ships which deliberately pollute the ocean water within the country's 50-mile territorial boundary.

What others are doing

Other sub-Saharan African countries are now setting up or planning governmental environmental machinery. Botswana, in southern Africa, has commenced environmental planning in its Ministry of Mining and Ministry of Wildlife. In addition to wildlife preservation, Botswana also hopes to avoid environmental degradation which so often results from mining, and to restore land which has been mined.

The United Republic of Cameroon, which is noted for carefully planned development, has not forgotten about the environment. Environmental matters are handled by the Ministry of Equipment, Environment, and Land, with assistance from the Ministry of Plan and Territorial Management. Paul Tessa is the Minister of Equipment, Environment, and Land; his ministry is located in Yaounde, Cameroon's capital.

Ghana organized the National Environmental Protection Council (NEPC), located at Accra, Ghana's capital. The NEPC's head is E. A. Boateng who heads a 15-member council. The Ghanian NEPC has the job of formulating policy with regard to environmental matters, coordinating national and international liaison with respect to these matters, and advising the government on all such issues.

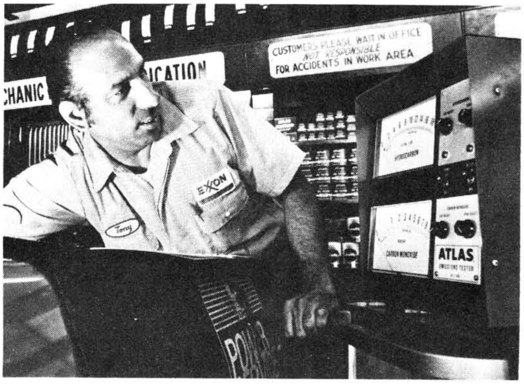
As host nation to UNEP in Nairobi, Kenya has established its own Environmental Secretariat. The Republic of Senegal has created the position of Secretary of State for Protection of Environment at Dakar, and the Republic of Zaire now has an Environmental Service which is in the Office of the President, and is located at Kinshasa.

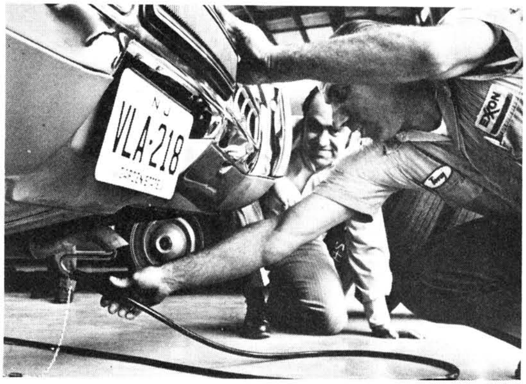
Environment and development

In about mid-1974, Gabon, an associate member of the Organization of Petroleum Exporting Countries (OPEC), created a ministerial-level office at Libreville, devoted to environmental protection. Gabon is rich in natural resources, and heavy mining, and oil exploration and drilling activities are in that country's immediate future.

The Gabonese ambassador to the U.S., Vincent Mavoungou, and members of his embassy, say that Gabon does not want to see great damage done to the human environment by runaway, uncontrolled oil and mineral exploration and economic development. The feeling in Gabon seems to be that the time for environmental planning is during economic development's early stages for maximum enhancement of human welfare and conservation of natural resources.

Hopefully, the Gabonese approach will be shared by the other developing nations of Africa. Should this happy state of affairs indeed materialize, the pace of environmental protection activity in these African countries south of the Sahara could one day equal or surpass that of pollution-laden nations which refer to themselves as "developed." JJ





Automotive emissions testing

Three years in the making, Exxon's diagnostic, repair procedure is quick and reliable for reduced car emissions and improved engine performance

If you are looking for a way to check car tailpipe emissions to minimize air pollution, and at the same time to check on the tuning of cars, then your search may be over.

For now, a simplified inexpensive diagnostic and repair procedure has been developed. It uses only emissions at idle and points a mechanic directly to those factors that are most likely to be responsible for high emissions. It was designed to avoid wasting a mechanic's time and to provide him with an efficient method of getting to the problem.

The procedure was developed by the Products Research Division, Linden, N.J., one of five divisions of the Exxon Research and Engineering Co. For the past three years, Jerome Panzer, a research associate with more than 18 years of industrial experience at Exxon, has spearheaded the development of this program.

"We got into the vehicle emissions inspection area because our marketing people were concerned with providing technical assistance to service people," Panzer says. "The basic objective was to come up with service procedures for the car mechanic, procedures he could use to correct those vehicles that might be rejected by a state emissions inspection program. Such programs are being considered by many states."

But Panzer is quick to point out that one of the key messages to get across is that the great value of this procedure is not just in terms of correcting car emissions to pass state tests but in the actual repair, the tuning, of car engines.

Start-up

In the early phase of the program, his team evaluated about 12 of the 20 commercially available emissions analyzers that would be used by automobile dealers, the garage industry, or by state inspection agencies. "At first, many instruments had deficiencies but our suggestions to the equipment manufacturers contributed to the development of better equipment," he says. "Ultimately, we developed a set of criteria for instruments for service station use which has been published and discussed with equipment manufacturers. Exxon Company, U.S.A. uses these criteria to select emission analyzers for its Car Care Centers and many of its service stations." Panzer says an emissions analyzer costs approximately $1600–2000.

In addition to developing a new diagnostic and repair procedure and evaluating emissions analyzers, the Exxon team needed to learn:

- What kinds of emissions tests are most effective?
- How should Exxon's service station people be prepared to repair cars with high emissions?
- What percentage of cars are likely to fail state emissions tests?
- How would emissions change with time after repairs are made?

The answers to these questions are based largely on studies that were carried out with several fleets of employee cars whose emissions were studied under conditions that would normally be used by state inspection programs. "We wanted to look at some factors that affect emissions and to develop information that ultimately would be helpful in servicing cars," Panzer says.

Dynamometer testing, so-called loaded testing, of the type used by the EPA in its certification of new cars requires not only expensive equipment but the procedure requires about 12 hr and several trained operators. Because of the cost and time involved, this procedure is not suitable for a routine state emissions inspection program.

Two types of test procedures have been considered for such routine inspection. The first is a short loaded test, still using a costly dynamometer and skilled operators, but requiring only about 3–5 min to run. The second is an idle emissions test that can be performed in 30 sec without a dynamometer and with less skilled operators.

One key finding was obtained when the Exxon researchers compared the two types of test procedures. The group discovered that repairs based on idle emissions testing were just as effective in reducing actual car emissions as the more expensive and time consuming dynamometer procedure.

Leading the nation

In February 1974, New Jersey became the first state to require maintenance of passenger cars which fail an emissions test (*ES&T*, September 1972, p 785). Several other states including California and Massachusetts have been working on programs.

Exxon has been conducting training sessions for its service station dealers and mechanics in New Jersey to enable them to repair cars rejected by the state inspection stations. More than 500 people have attended the training course to date and preparations are under way to take it to other parts of the country.

The training is held at a service station or some location where garage-type facilities are available. Class size is from six to 20 people, with the ideal number being 12.

At the start of the one-day course, the dealers are briefed on the New Jersey emissions inspection program and their role and the company's in it. Following that, they hear a more detailed discussion on the subject of harmful automotive emissions, an explanation of how the emissions analyzer works and then, a description of the Exxon-developed emissions-oriented repair technique.

Next, the class goes to the adjacent garage where the participants are able to use the emissions analyzer themselves. Since service mechanics are oriented to working with their hands, the training is designed to provide them with as much hands-on experience as possible. Three automobiles are used. Each one has a different intentionally caused engine malfunction—which may be a misset carburetor idle, a fouled spark plug, a bad ignition wire, or some similar problem.

The group is divided into teams told to use the emissions analyzer and diagnostic procedure to identify the malfunctions in the cars. Each team will work on the three cars.

"This part is very dramatic because it shows exactly what happens to the emissions with many of the tune-up problems that they are likely to encounter," Panzer explains. "By using the different automobiles, the analyzer and the diagnostic procedure, they discover they can do a very effective job in identifying the problem quickly." At that point, the dealer will either be able to make the adjustments or repairs himself or have them done at other places of business where such work can be done.

Finally, since emissions-oriented repairs represent a new aspect of automotive repair and service, the dealers are given pointers on how they can explain to their customers what emissions-oriented repairs are, and how the car is being serviced to ensure a combination of low emissions and good performance.

Other findings

Other factors affecting emissions have been studied by Panzer. First, how do emissions correlate with the distribution of cars by age, make, size, number of cylinders and the like? Not surprisingly, emissions increased in proportion with vehicle age and use. Among pre-1968 cars, emissions varied with vehicle make.

Servicing. The use of an emissions analyzer is explained by Panzer

In examining another factor affecting emissions, Panzer states, "We found that published emission standards, those developed by various state air pollution control agencies or other research works, would reject up to 60% of the car population. Our studies show that the practical upper rejection limit is 50%. Above this, a large percentage of the rejected cars could not be made to pass emission standards without overhauling or replacing the engine at great expense to the car owner."

A third item was the concern that occurs in a state that has its own inspection stations and where cars are required to wait in line for a lengthy period of time up to 2–3 hr until they can be inspected.

Most of the time, their cars are idling while they wait. This idling increases the under-hood temperature of the engine, which, in turn, causes higher emissions. These emissions increase the percentage of cars rejected by the state test. Waiting in line on a hot summer day with the air conditioning running further increases emissions.

To overcome this problem, one action some motorists have taken before being inspected is to race the engine at high speeds for a couple of minutes. In many cases, this tends to cool the engine enough to pass.

Further insight

On the average, about 40% of all cars have driveability problems within a year after tune-up; these problems are usually discovered by the motorist himself during normal driving. Such problems include stalling, engine hesitation, rough idling, and loss of power, to mention a few. Many of these cars show a substantial increase in hydrocarbon emission levels over their original tune-up levels.

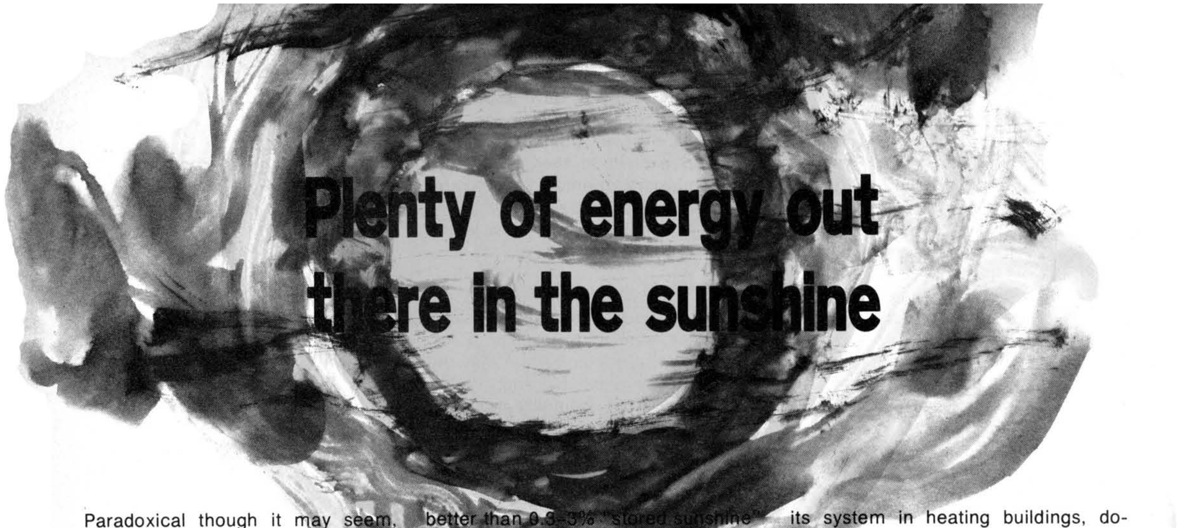
"In our work with employee cars, we started with all the cars being tuned," Panzer says. "In following the change of emissions with time we found that CO emissions remain relatively constant for 10 months and then rise sharply. With hydrocarbon emissions, we have a different picture. After tune-up, average HC emission levels rise very sharply within the first two or three months but then tend to fall off a bit and level out.

"These results show that emissions do not deteriorate linearly as had been expected," he explains. "Linear deterioration predicts that the effective emissions reduction of an inspection/maintenance program (the change in emissions from before tune-up to the average level during the year following tune-up) will be one-half the reduction occurring during the tune-up. The Exxon research shows that the actual effective emissions reduction will depend on whether motorists voluntarily have their cars serviced when they run into drivability problems," Panzer says. "If such repairs are made with an emissions-oriented procedure, the average effective CO reduction is roughly the same as the initial reduction right after tune-up, while the average effective HC reduction is only one third that of the initial reduction."

The highlights of the three years of idle mode testing at Exxon have been described in technical papers presented to the Society of Automotive Engineers and the Air Pollution Control Association.

Looking ahead

Certainly, the New Jersey experience is noteworthy and serves as an example for other states and areas of the U.S. that are contemplating emissions inspection programs. There is a very significant economic incentive in going to nonloaded idle-type testing since loaded testing takes highly trained personnel and expensive equipment. With the above program's success, it simply is not necessary to use dynamometers to perform routine emissions inspections. One simply can do as good a job in less time and at less expense with Exxon's test and repair procedure. SSM



Plenty of energy out there in the sunshine

Paradoxical though it may seem, virtually the whole U.S. economy runs on solar energy. Over mind-boggling periods of time, this solar energy was captured and stored through photosynthesis and later metabolism of plants and animals; the metamorphosis of their organic remains burns today as coal, oil, and gas. Unfortunately, this "stored sunshine" has a near-zero replacement rate and, often, a high pollution potential. Efficiency of such sunshine storing is 0.3–3%.

One object of the national and world solar energy development effort, therefore, is to shorten the solar energy collection time from eons to instants. Another is to obtain a renewable, nonpolluting "fuel" which can help the U.S. and other nations reduce their dependence on fossil hydrocarbons, and provide a measure of relief from the economic consequences of such dependence.

Solar energy arrives at the surface of the U.S. at about 1500 Btu/ft^2/day on the average. This represents 42 billion Btu/mi^2/day, or 15 trillion Btu/mi^2/yr. In 1970, the U.S. consumed 65 quads (one quad = one quadrillion Btu) of energy. Thus, 4300 mi^2 of U.S. territory receives solar energy equivalent to the U.S. energy consumption for 1970. If useful conversion of solar energy could be accomplished with 10% efficiency, 43,000 mi^2, or about 1.5% of the land area of the 48 contiguous states would have provided collection facilities for all the energy consumed in the U.S. in 1970.

Heating and cooling

Goetz Oertel, NASA's chief of solar physics, told *ES&T* that a 30% average efficiency for solar heating units is possible. This efficiency can sometimes be greater or less (as low as 10%, or as high as 55%), depending upon materials, design, construction, and application. Be that as it may, even a 10% efficiency is far better than 0.3–3% "stored sunshine" efficiency of fossil fuels. Moreover, systems and materials are probably more readily available at this time for solar heating than for electric generation. Thus, it can be expected that solar heating will move the fastest, with solar cooling close behind (about 2–5 yr), and pumping and electric generation further "down the pike."

Solar heating and cooling prospects were brightened when President Ford signed the Solar Heating and Cooling Demonstration Act (P.L. 93-409) on September 3. P.L. 93-409 allocates $60 million for demonstrating practical solar heating technology within 3 years and developing and demonstrating combined heating and cooling systems within 5 years. Primary responsibility will be shared by NASA and the Department of Housing and Urban Development (HUD).

Terrence Caster, president of Energy Systems, Inc. (ESI, El Cajon, Calif.), predicts that solar energy in U.S. homes will eventually be a $77 billion industry. He estimated that heat and not water bills could be cut up to 95% through use of solar units. With strictly private funding, Caster is providing refined, wet-type solar systems for space and water heating, integrated into custom ($135,000–300,000) homes in the Vista del Colinas subdivision near San Diego, Calif., an industry first. The total value of a contract to provide the systems for the subdivision of 23 fancy homes is $149,000.

Revere Copper and Brass Inc. (New York, N.Y.) is marketing a solar energy collector for heating and cooling. Revere uses a blackened copper surface to absorb radiant heat and transfer it to a fluid circulated through tubes fastened securely to the absorber surface. The collector plate is covered with transparent material so that solar energy may be admitted and re-radiated energy trapped. Revere sees applications of its system in heating buildings, domestic water, and swimming pools, and operating absorption-type air conditioning units.

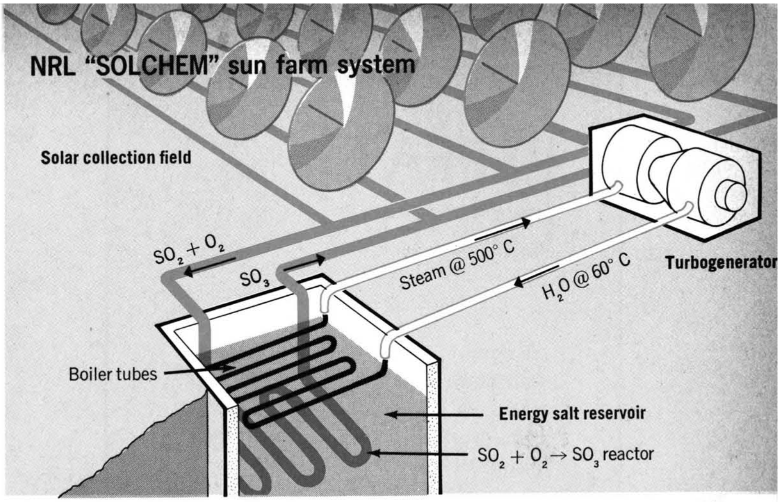
PPG Industries is now producing solar energy collector cells commercially. Each cell is over 6 ft long and nearly 3 ft wide, and consists of two tempered glass panels plus an insulated black aluminum absorber plate enclosed in a stainless steel frame. A $1\frac{5}{16}$-in. thick air space separates the two glass panels from each other and the absorber plate. Glass fiber, $2\frac{1}{2}$ in. thick, insulates the back of the absorber plate. A liquid circulates through tubing built into the plate.

The cells would be used for heating and hot water. PPG Industries estimates that for a family of four or five, in a typical home with 2000 ft^2 of floor space, a 20-cell system would provide about 80% of heating needs, as well as all hot water needs. In some sunny climates, for hot water, perhaps four cells would suffice.

Solar air conditioning or refrigeration is similar to conventional refrigeration, except that pressure is produced by heating a very concentrated solution of salt in liquid ammonia in a compartment. The solution's vapor pressure becomes greater than the vapor pressure of pure liquid ammonia as the ammonia goes into the concentrated solution of salt and dilutes it. Solar regeneration drives pure ammonia from the dilute solution and reconcentrates the solution. A similar system runs with water and lithium bromide. Rankine cycle engines, using organic fluids, can also be employed.

To be competitive on an economic basis with other energies, solar heating installations must be priced at about $6.00/ft^2, Charles Hauer, director of the public technology project office of the National Science Foundation (NSF), finds. Hauer feels that the solar energy industry, even now, is close to direct competition.

It will be used for heating and cooling before it is harnessed for electricity. Whatever its application, solar energy does not pollute


NRL "SOLCHEM" sun farm system

Pumping

A type of pump, actuated by solar energy, has been in use at Chinguetti, Islamic Republic of Mauritania (West Africa), since early 1973, as reported in *Jeune Afrique* (*Young Africa*), July 20, 1974. This pump is actually helping to furnish water to 2000 inhabitants of that town, and is located in a school building. In the near future, similar pumps will be installed in Algeria, Chad, Libya, Mali, and Upper Volta. The pump system consists of a battery of solar collectors, an expansion motor, a water pump propelled by the motor, and a water reservoir with its distribution system.

In the Chinguetti pump, the sun heats water to 70–80°C. The warm water, in turn, heats a liquefied gas which expands to produce the pressure necessary to drive the motor and make the pump work. The gas is condensed, decompressed, and cooled by water from a well. The cycle then recommences. The pump, specially adapted for tropical desert zones, needs one kw of power, can supply 50–80 m^3/day of water, needs little maintenance, and can be handled on a day-by-day basis, even by one who is illiterate.

"Sunpower"

Electric generation by solar energy, whether by direct or indirect routes, is much further in the future. In general, the technology needs considerable additional improvement. Capital costs for land, materials, equipment, and installation will be very high; however, these high initial costs could be sharply offset by long equipment life, low operation and maintenance costs, and extremely low, or even zero expense for fuel.

One approach to "sunpower" consists of photovoltaic cells of silicon "doped" with traces of arsenic, boron, phosphorus, and other elements of similar properties. NASA's Oertel noted that one might achieve 10% efficiency with photovoltaic system under present technology. He also said that while the doped silicon components comprising voltaic systems were very expensive (a 28-V voltaic cell array costs $7000, for example), a breakthrough earlier this year could reduce the cost of these components by perhaps 90%.

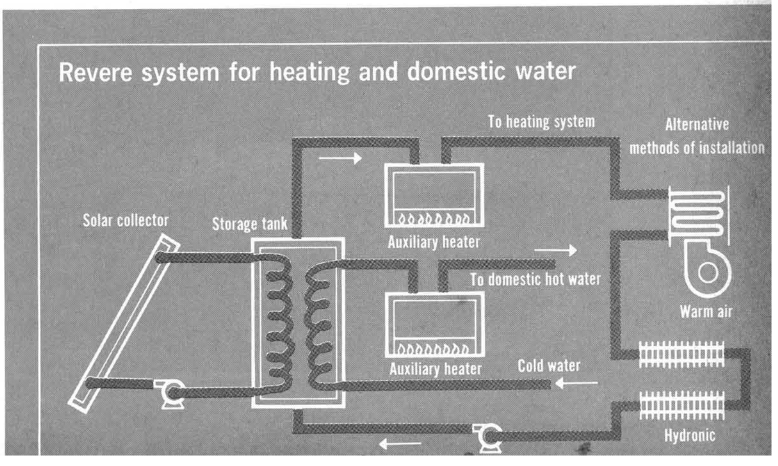
George Hamilton, president of Solar Energy Co. (Washington, D.C.), said that a technology capable of producing electricity directly actually exists, and needs no further research and development (R&D). Hamilton spoke of a 1-MW array or set of echelons of doped silicon, which would cover 16 acres. With an average "working sunshine" day of 6.67 hr, one system could give 6.67 MWH of electricity each day (the average home uses about 9000 KWH/yr). The system's orientation and construction would be a function of latitude.

Hamilton estimates that an array system network across the U.S. could contribute materially to meeting peaking demand for electricity. He believes that the first array may cost about $20–35 million, but that costs could fall to $4.5 million/array with increased production. Hamilton also estimates that the first array installed could furnish power at $0.07/KWH, all totaled, and that the high initial array cost is quickly offset by durability, minimal maintenance needs, nonpollution, and zero fuel cost.

Other approaches to "sunpower" involve an indirect route—that is, using the sun to produce heat, steam, hydrogen from water electrolysis, or other means of obtaining energy not by direct conversion to electricity. A heat approach is readily visualized when one thinks of the large solar collector at Odeillo, southern France, where temperatures of up to 7000°F have been recorded. A similar collector, capable of up to 5000°F, has been installed by the U.S. Army at Los Alamos, N.M. With such heat, electricity could perhaps be generated by the high-pressure superheated steam method or some other means.

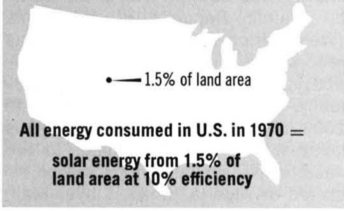
Another secondary fuel route involves hydrogen. Here, the sun would power a photovoltaic system which would electrolyze water. The hydrogen would then be collected and utilized as a clean-burning fuel which produces very high temperatures.

Talbot Chubb of the U.S. Naval Research Laboratory (NRL), Washington, D.C., uses a gas, such as sulfur trioxide (SO_3), for high-tem-


Revere system for heating and domestic water

perature endothermic gas phase reactions in an energy transfer fluid. The SO_3 can be passed through a solar furnace to collect energy to produce electricity. The SO_3 "SOLCHEM" system is closed, and thus poses no environmental danger. Temperatures of 450–600°C could be made available—high enough not only to make superheated steam for electric power, but to allow for oil shale processing without using much product fuel to provide heat. Chubb estimates that a full-scale SOLCHEM "sun farm" system could furnish a 24-hr, 100-MW electrical output. Perhaps initial SO_2 needed for SO_3 production could be "harvested," concentrated, and purified from what would otherwise be stack gas emissions.

"Sunpower" potential



All energy consumed in U.S. in 1970 = solar energy from 1.5% of land area at 10% efficiency

Support

Sen. James Abourezk (D-S. Dak.) says that the U.S. now has a movement going on solar energy. However, Sen. Abourezk wants to see solar energy R&D kept separate, so that it would compete with other energy R&D. He is convinced that electric power from solar sources can become a major factor in the foreseeable future, though he felt that it is impossible, at present, to estimate the number of years in which this would happen. He does not want to see solar energy R&D slowed down or stopped by virtue of turning it over to an agency such as the Atomic Energy Commission which "has no interest in promoting solar energy over and above its own interests." His belief is that solar energy R&D should be led by NASA.

It looks as though NASA, together with HUD, will indeed have a share of the R&D pie, thanks to P.L. 93-409. Other funding and support will be handled by the NSF's Research Applied to National Needs (RANN) program, and other public and private agencies. Perhaps further practical support may come from federal, state, and local tax incentives; indeed, this is now in the works. Nevertheless, as Sen. Abourezk said, the momentum is there for the development of a renewable, nonpolluting energy "fuel" which will give America a real push in the direction of badly needed energy diversification.

JJ


Marv Rubin

FEATURE

Hydraulically operated machine noises

Pumps, valves, and air and water bubbles trapped in a fluid—the sources of these noises—are controllable. Noise reductions can be achieved without necessarily increasing the cost

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Sperry Vickers, Troy, Mich. 48084

Keeping the noise level of hydraulically operated machines within OSHA limits is a job for the hydraulic system designer, machine designer and builder, and the end user. The main objective is to wind up with a machine that is within these limits without unnecessarily increasing its cost.

Pump noise

Pumps are one source of noise energy in hydraulic systems. Pump-induced vibrations or pulsations can cause other system elements to radiate audible noise greater than that coming from the pump. Pumps, being relatively small, are poor noise radiators, whereas reservoirs, electric motors, and piping have large surface areas and are good radiators of noise. To effectively control noise, it is necessary to consider the three forms of pump noise—structureborne, airborne, and fluidborne.

In engineering noise controls, it is useful to think of noise as being made up of many single frequency components. Unbalance in the pump, its drive motor, or the coupling that joins them produces noise energy at shaft frequency. The largest noise energy component is at the pumping frequency, which is the shaft frequency times the number of pumping elements (vanes, pistons, gear teeth).

The human ear is not very sensitive to frequencies below about 500 Hz. This is recognized in setting legal and contractual noise limits by expressing these limits in terms of "A" weighted levels. This "A" weighting may discount sound at pumping frequency significantly. Because of this, and the fact that pump sound peaks in the middle frequency range, the most effort must be directed to controlling sound in the frequency range of 500–2000 Hz.

The rating frequently used is in terms of "A"-weighted sound pressure levels, 3 ft from the pump. Actually, this is a computed figure from a mathematical model that assumes all the sound power emanating from the pump is radiated from a single point. While this is not exactly true, it is close enough to give practical values.

When a pump is installed as part of a simple tank-type power supply in accordance with proper installation practices, the sound level 3 ft from the tank will be about equal to the sound level rating for the pump. This gives a rough rule of thumb useful in preliminary planning.

Proper selection of pump operating parameters provides another noise control opportunity. Pump speed has a strong effect on noise, while pressure and pump size (displacement) have about equal, but smaller, effects. Since these three factors determine horsepower, they provide a basis for a trade-off with noise. To achieve the lowest noise levels, the lowest practical speed is used and the most advantageous combination of size and pressure is selected to provide the needed horsepower. Another option that may be available is to select a pump that is the quietest for the longest portion of the duty cycle.

Fixed displacement pumps are usually quieter than variable displacement units at comparable operating conditions because their construction is more rigid. However, fixed pumps in such circuits always produce maximum flow, and are not well suited for machines where the duty cycle calls primarily for low flows. In mobile vehicles where such duty cycles are often encountered, variable pumps operate at reduced displacement most of the time. In this environment, they are generally quieter and more efficient than fixed displacement pumps.

Valve noise

Valves are another source of noise energy in hydraulic systems. But, compared to pumps, valve noise is not too objectionable. However, as pumps get quieter, it's anticipated that valve noise will be of greater concern.

There are several types of valve noise. The most common is a hissing sound caused by cavitation. Another type is a single tone noise that can be described as a whistle or squeal. Luckily, it does not occur often. Sometimes it is due to imperfections or wear, and the cure is to replace the valve seat, poppet, or spring with a new one of the same design. In other cases, the noise is due to an interaction with the rest of the circuit. This calls for replacing the valve with one of a different design. Direct-acting or single-stage pressure control valves are relatively susceptible to this difficulty. If such trouble develops, they should be replaced with pilot-operated or compound valves which are relatively immune to this type of trouble.

A third type of valve noise occurs only at very low flows. In this condition, pump pulsations sometimes cause valve poppets to rattle against their seats. This occurs at pumping frequency and is best described as a very loud buzzing. A smaller valve should then be used so that the poppet will open wider at the low flow. In some circuits, it may be necessary to change from a poppet-type to a spool-type valve.

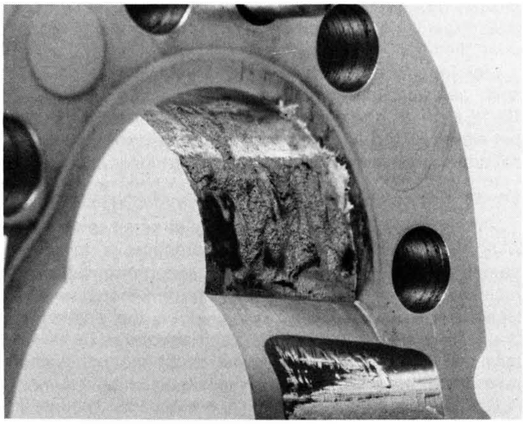
Fluid factors

In most hydraulic systems, air and water in the fluid can aggravate the noise problem. Quiet hydraulic components are designed to work on "solid" fluid. Entrained air bubbles, even though they may be only a fraction of 1% by volume, change the compressibility of the fluid so much that it can cause a normally quiet pump or valve to become intolerably noisy. When pressure is applied to entrained air bubbles, they collapse violently and produce enough energy to make considerable noise.

Dissolved air by itself is not considered a problem because it does not change the viscosity or compressibility of the fluid. However, it can become a factor when it is released by changes in atmospheric pressure or an increase in fluid temperature. The amount of air that can be held in solution with a hydraulic fluid is proportional to the pressure the air exerts on the surface. A petroleum-based fluid can absorb about 9% of air, by volume, at atmospheric pressure and room temperature. Subjecting a fluid saturated with air at atmospheric pressure to, say, 5-in. Hg vacuum when it can hold only 7$^1/_2$% of air, would cause it to become supersaturated. It would then begin to release air, forming entrained bubbles.

Temperature is an independent variable in bubble formation because an increase in temperature tends to liberate dissolved air. Thus, a fluid column marginally saturated with air at pump inlet pressure could release air bubbles at increased temperatures.

Oil temperatures should be maintained between 120–150°F (50–65°C). Lower oil temperatures can raise oil viscosity to a point where excessive separation time is required. Because of this, some systems are noisy for a period after start-up. Where heat exchanger water is not thermostatically controlled, the system will heat up slowly, permitting this noisy condition to persist for long periods and causing extensive cavitation damage as well. If a thermostatic control is not practical, it may be advisable to install an electric heater in the reservoir to shorten the warm-up period.

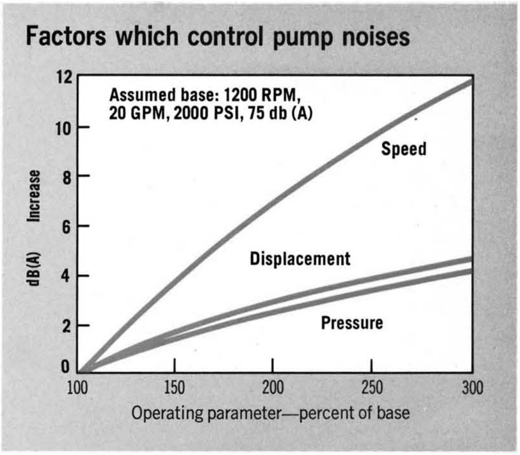


Pump's trapped air bubbles cause wear as well as noise

Pump cavitation can be controlled by engineering its suction line to minimize pressure drop. Some good rules to follow are:

- maintain suction line velocities below 5 ft/sec or 1.5 m/sec
- keep pump inlet lines short
- minimize bends and joints in the inlet line
- locate the reservoir as high as practical in relation to the pump to provide a flooded inlet
- use low-pressure drop inlet filters or strainers
- use an oil that has a low viscosity, but above the minimum recommended by the pump manufacturer, at the operating temperature of the system.

There are other sources of air bubbles carried in the hydraulic fluid. One is air sucked into the pump inlet line through a loose fitting, valve stem packing, or another part of the circuit that is under vacuum. This can occur even when a joint is oil tight. In mobile hydraulics, pressurized reservoirs are used so that inlet lines are above atmospheric pressure. This completely eliminates such sources of ingested air. Remember, however, that pressurized reservoirs raise the fluid saturation pressure so that high-inlet-line-pressure drop can still cause cavitation.

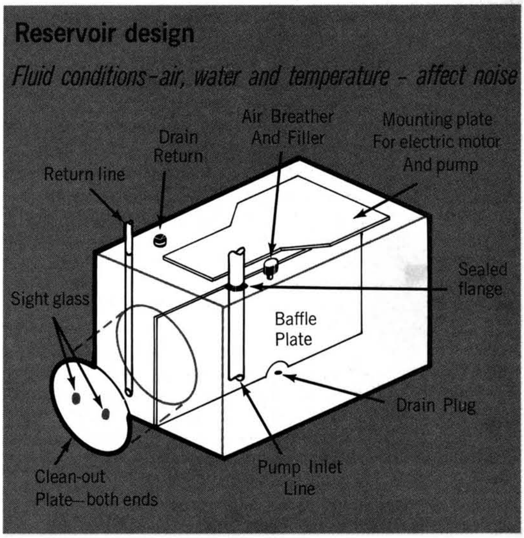


Water in hydraulic fluids can be as troublesome as air. At temperatures above 180°F (85°C), vacuum causes steam bubbles to form. These are more violent than air bubbles. Steam formation can occur whether the water is there intentionally (as in water–glycol or water-soluble oil fluids are used) or unintentional (as a pollutant in oil or phosphate esters). With water-based fluids, fluid temperatures and vacuums must be controlled to prevent steam-induced noise.

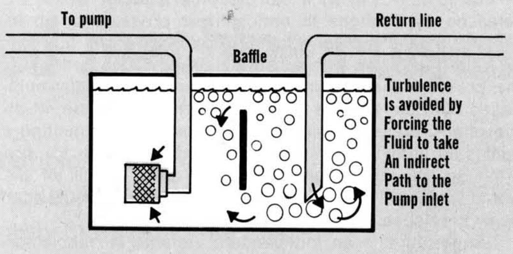
Reservoir condensation is a principal source of water pollution in hydraulic systems. This can be minimized by maintaining high oil levels that minimize the airspace above the oil.

Reservoir design

Considerable control over fluid condition is possible through proper reservoir design. For example, the best place to remove entrained air bubbles is the reservoir. Return fluid often contains bubbles that will separate out if given enough time. Thus, the reservoir should be large enough and have sufficient baffles to provide this time.



Diffusers decrease turbulence, reducing noise



A volume equivalent to 2 min of maximum system flow capacity generally is considered adequate. Lower capacity reservoirs can be used, but baffling then becomes critical to maximize the dwell time of the oil in the reservoir for bubble dissipation. When adequate size or baffling cannot be provided, sloping screens can be used to assist in the separation process. Experiments have shown that a 60-mesh screen installed at a 30° angle from the horizontal is effective in removing up to 90% of the air bubbles.

Fluid returning to the reservoir must be introduced below the fluid surface to minimize air entrainment. The return line should terminate a few inches below the lowest oil level that will occur. Also, a diffuser will help break up the returning fluid into a number of small, low-velocity jets to reduce surface turbulence and whirlpooling.

Similarly, the end of the reservoir outlet or pump inlet line opening should not be located near the reservoir fluid surface. Even when it is several inches below, flow into the line can induce a whirlpool that will entrain air.

Airborne noise control

Large, flat sheet metal panels are particularly responsive to pump-induced vibrations because their continuous surfaces act as good sound radiators. Where these surfaces cannot be avoided, rigid braces may prove effective. Rectangular panels should be broken into three different-sized triangles.

Sound can be shielded in a manner similar to light. Locating noise sources behind machine members or a sheet metal shield can sometimes provide nominal noise reductions at very little cost. Totally enclosing a noise source is one of the most effective noise controls. Noise reductions of 20 db, or more, can be made by using enclosures. This not only requires that the enclosure be carefully engineered, but also that the enclosed unit be vibration-isolated from the rest of the machine.

Enclosures often have surfaces that are better sound radiators than the noise sources they are quieting. For this reason, they should be mechanically isolated from hydraulic lines or other machine elements that can transmit noise vibrations to them. Often the rubberlike materials used to seal openings can also be used to mechanically isolate the enclosure as well.

Hydraulic lines are a major source of airborne sound. Lab tests, which include evaluating pumps with associated inlet and return lines of approximately 12 ft (3.5 m) each, show that noise levels are increased by 2–3 db (A) just from line noise. Now that quieter pumps and valves are being used, line noise is increasing in importance and is sometimes the major source of noise. In such cases, most of the noise controls applied to other components will be ineffective unless the line noise also is controlled.

Line lagging or wrapping is effective. A barrier material such as filled vinyl can be used. A layer of $^{1}/_{4}$–$^{1}/_{2}$ in. (6–12 mm) of fiberglass or polyurethane foam should be put between the line and the barrier to provide airborne sound absorption and vibration isolation.

Vibration noise control

Vibration noise control is primarily directed toward isolating pump vibrations. Common practice is to mount pumps and their drive motors on a common base and resiliently mount this subassembly on the machine. Most isolation theory, however, is based on the assumption that isolators are mounted on a stiff structure. The theory may not hold in cases where the pump–motor assembly is resiliently mounted on, say, a flexible tank top.

It is also common practice to use resilient mounts so that the assembly will have a natural frequency of one half to one quarter the pump shaft rotational frequency. This provides a maximum of isolation but, in some cases, such a mounting will be too flexible to be acceptable.

Additional control sometimes can be achieved by resiliently mounting only the pump in the pump–motor subassembly. If a soft mounting system is used for this purpose, the torque reaction that must be carried through the mounts will shift the pump centerline whenever the pump is loaded. This causes shaft misalignment and a shifting of the hydraulic lines attached to the pump. Using a natural frequency 2.5–3.5 times the shaft frequency will minimize these difficulties. Where an independent pump isolation is used in addition to a resilient pump–motor subassembly mounting, the latter system should have a natural frequency that is one half the shaft frequency or less.

Drive couplings must serve two noise control purposes. One is to provide vibration isolation between the pump and its drive. The other is to extenuate the effect of pump misalignment. Couplings providing rubber-like materials in the drive train are favored for isolation purposes.

Pump misalignment can cause noise by producing high loads that must be carried by the pump and motor bearings. Almost any commercial flexible coupling will accommodate the misalignments that occur without such loading, if good alignment practices are followed. Where good alignment cannot be provided, or in some cases where the pump alone is resiliently mounted and the torque reaction causes misalignment, two couplings separated by a short shaft should be used.

Hydraulic lines frequently provide the primary path for transmitting noise energy from the noise source to components that, in turn, react to this energy and radiate sound. One method for preventing noise energy in the form of line vibrations from reaching machine elements is to isolate the line from the rest of the machine. This is done by using commercially available resilient line supports.

Line isolation is also accomplished by using flexible hose. Hose must be used when the noise source is resiliently mounted, otherwise stiff lines attached to the noisemaker will interfere with the isolating action of the mounts. Flexible lines can cause trouble, however, if they are not used correctly. Since hose is so responsive to fluid pulsations, it can be a strong sound radiator if long lengths are used. It also acts like a bourdon tube when bent, so that pressure generates forces to straighten it. Pressure pulsations, therefore, are converted into cyclic forces than can cause lines and other machine elements to vibrate.

Similarly, pressure changes the length of hose. If such changes are restrained, forces proportional to the pressure are generated. This mechanism, then, converts pressure pulsations into vibration forces. Unless hose is used properly, it can increase rather than decrease noise.

The best isolation is achieved when two short flexible hoses, either parallel or at right angles to each other, are joined by rigid line or fittings. In straight run line, a single flexible hose at the noise generator is usually sufficient, but one at each end may be better.

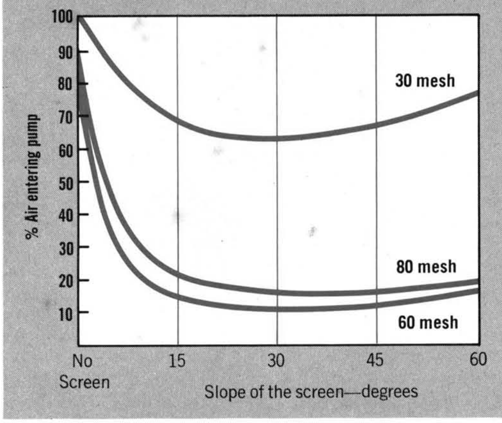
Pulsation noise control

Pumps do not deliver a perfectly constant flow. Instead, the flow changes slightly as each pumping element discharges, and this causes pulsations in system pressure. The range of these pressure pulsations is generally only a few percent of the mean pressure. If a fraction of 1% of the energy of these pulsations is converted to sound, it may be intolerable. Fortunately, this degree of conversion does not occur often.

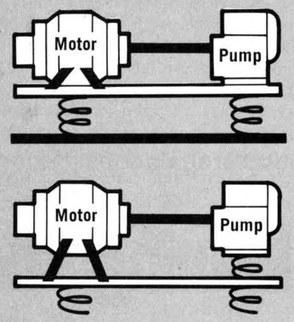
One method for reducing fluid pulsations is to provide a large oil volume at the discharge port of a pump and let the compressibility of the fluid absorb the flow variations. Flexible hose, because it expands, also helps smooth pump flow. Attenuations from these sources tend to be small, but can be significant in some cases.

Gas-loaded accumulators, used as a side branch to the pump discharge line, can also reduce pulsations, although they tend to be less effective than flow-through types. These tend to be low-frequency devices that greatly reduce the low-frequency components of the pulsations without having much effect on the critical midfrequency components.

Screens remove trapped air, reducing noise



Mounting plays key role in vibrational noise control



Bladder-type accumulators tend to be more effective than piston types. Only 1 in.^{3} of gas at system pressure will produce the attenuations needed in most cases. Simply using a larger accumulator may not provide more attenuation. Acoustic filters that work like an automotive muffler are as effective as flow-through, gas-loaded accumulators and do not require maintenance. These are sometimes referred to as tuned filters. They must be selected on the basis of pumping frequency and flow capacity. Like flow-through, gas-loaded accumulators, they tend to be bulky and expensive.

Reducing fluid pulsations will only be effective in reducing the airborne noise of an entire machine in those cases where the pulsations excite some machine component into being the predominant sound source. Such cases do not occur often. For cost reasons, all pulsation attenuation devices should be evaluated in a given machine before deciding to include them in the system.

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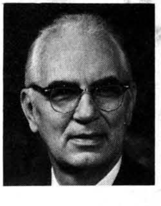

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FEATURE

Water pollution regulations, becoming more stringent, are strong motives behind efforts for

Cleaning the animal farm environment

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At present, the average American farmer produces enough food for about 50 people, whereas 30 years ago, he could produce enough for only 10 people. Unrestricted availability of energy, technological advances, and a favorable climate have allowed U.S. farmers to become perhaps the most efficient in the world. However, food prices are now escalating because of increased production costs which have recently come to include pollution controls.

In general, animal agriculture should be able to comply with the no discharge effluent limitation guidelines as set forth in the *Federal Register,* February 14, 1974. Land, the medium for crop production and terminal disposal of animal wastes, is sufficient because more fertilizer components are required for the production of foodstuffs than are available in animal wastes. Thus, all manure could be profitably and safely recycled to the land if certain serious logistic problems could be solved, or production unit size and location regulated. This approach and corresponding considerations are graphically illustrated by a visit to any productive agricultural area in which total return of animal manures to the land is the most commonly applied "best practicable technology."

In their manure, the approximately 1.2 billion head of livestock in the U.S. produce about 20 billion pounds of nitrogen annually. If this manure were spread equally on the approximately one billion agricultural acres, the annual nitrogen fertilization rate would be only about 20 lb per acre, which is much less than necessary for most crops. However, what nitrogen the manure can furnish should not be applied to crops faster than these crops can assimilate this nitrogen. For this reason, while nitrogen is so vital to agricultural production, the rate at which it can be applied becomes a limiting factor in animal waste disposal.

Animal production industry

Waste management is only one component of the overall animal production system. However, waste management in itself can be viewed as a system consisting of one or several pretreatments prior to final disposal. Regardless of the particular animal type under consideration, the waste management alternatives are similar. Research efforts can be accelerated, and implementation of solutions expedited if the commonality of unifying principles of all animal wastes is fully appreciated.

Animal production facilities vary widely. Low-density pasture units represent a zero level of waste handling and pretreatment, along with the recovery of full fertilizer value. The waste volume from high-density confined operations approaches the excreted load and thus calls for considerable further pretreatment. Recent trends toward larger production units reflect the impact of current economics, technology, and labor considerations in animal production. However, environmental protection and effluent regulations may eventually become the most important factor determining the size, location, and type of animal production unit that is both economically practical and environmentally acceptable.

Waste handling systems

Many wet and dry waste handling systems now exist, and numerous innovations are being introduced. Wet systems use water to reduce labor and facilitate transport, but they have the potential disadvantage of increasing the amount of polluted water. Dry systems, by contrast, decrease the waste volume to be handled.

Current liquid systems ranged from hand hosing to automated flushing techniques. Dairies were among the first to use flushing water that carries the waste from housing areas to a collection tank prior to direct land irrigation or further treatment and land disposal. An automated hydraulic swine waste handling system has been developed by the Iowa Agricultural Experiment Station. Anaerobic lagoon effluent is recirculated hourly in a 700-head growing building through flushing gutters. It is reported that the system's success is ascribed to pigs that learn quickly to defecate in the gutter, keeping the remainder of the pen dry and clean. A few commercial egg producers are using undercage waterwash systems. Waste falls through cage bottoms into a channel periodically flushed into a lagoon.

Some housing units for beef and dairy cattle, and many for swine, have slotted floors for waste passage into underhouse storage pits. Partially slotted installations have a solid concrete portion that requires periodic cleaning by dry scraping or waterwash. Totally slotted floors eliminate hand labor to clean pens, and therefore are responsible for continuing trends to enclosed houses with totally slotted floors. The storage pit slurry can be pumped into a tank vehicle for surface or subsurface field spreading or discharged to a lagoon.

The underfloor ventilation system for houses with manure storage pits provides a totally controlled environment in which air is uniformly exhausted from the manure pit. Moisture is evaporated from the floor, and gases and odors are exhausted from the building before they can enter the animal atmosphere above the slats. Over 200 new swine houses with underfloor ventilation have been constructed in North Carolina during the last several years. This is an example of the trend to environmentally controlled growing conditions currently being recommended as most important for optimal animal performance.

Pretreatment and utilization schemes

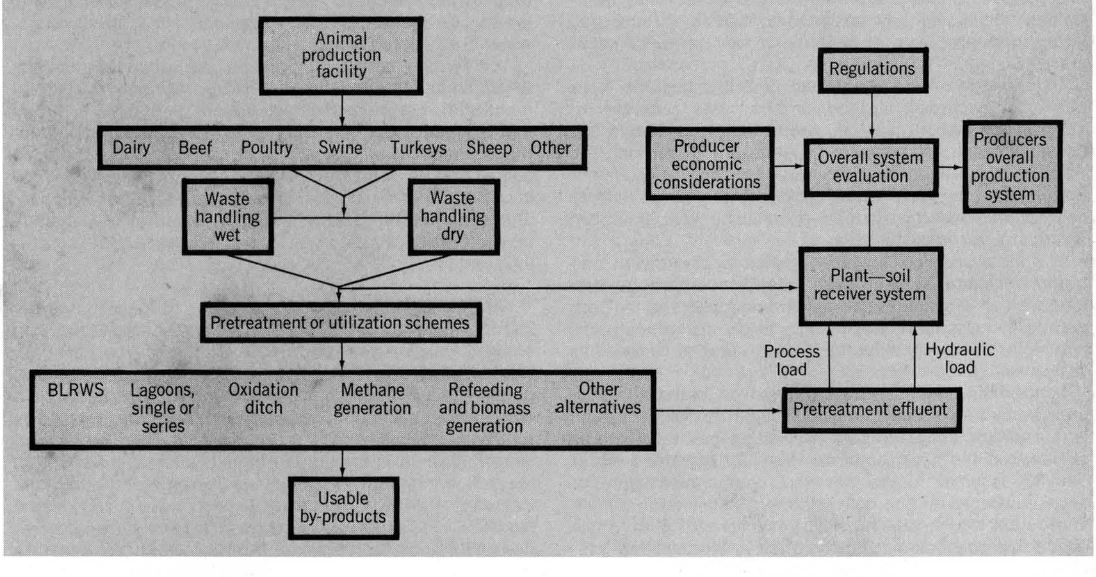
Many alternative pretreatment or utilization schemes, in-house or extramural, may be employed prior to terminal disposal. Although it is impossible to describe all available pretreatments, concepts are similar and the commonality of all animal waste allows general implementation for the feedlot industry.

Unaerated lagoons are the simplest and most commonly employed pretreatment units for swine waste. Aerators have been installed in a few lagoons for odor control and greater biochemical stabilization. In-house treatment systems, such as oxidation ditch, air injectors, or mixers have been incorporated into the manure storage pit design to enhance pretreatment and control odor prior to terminal land application. However, some malfunctions resulting in animal death have motivated many producers to separate mechanical treatment systems from the housing facilities. Discharge or overflow from aerated or unaerated lagoons and oxidation ditches is not sufficiently treated for stream discharge.

The barriered landscape water renovation system (BLWRS) represents a modified soil plot that can reduce both the organic and nitrate content of wastewater. Organic materials are oxidized and nitrogeneous materials converted to nitrates in the aerobic zone, while in the anaerobic zone, nitrates are converted to nitrogen gas by biological denitrification. The carbon or energy required to maintain anaerobic conditions in the saturated area, and necessary for biological denitrification, can be injected into this zone in some convenient form, such as molasses. Climatic effects must be taken into consideration if this system is not totally covered, because rainfall may use up the hydraulic capacity for any particular day of operation, and icing of the spray nozzle or freezing of the surface precludes waste disposal. Researchers with the Michigan Agricultural Experiment Station report that BLWRS is ready for application in large feedlots.

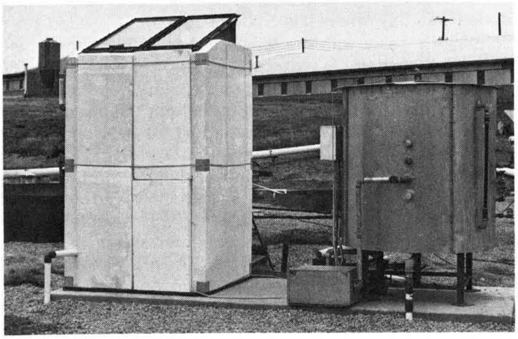
A solar still-type reactor for the mesophilic fermentation of swine waste, incorporating condensate removal and methane recovery to allow maximum energy conservation, is being developed by researchers at the North Carolina Agricultural Experiment Station. Preliminary results indicate that above 25 ft^3 of methane can be produced per day when this 500-gal reactor is loaded on a continuous basis with the waste of ten 100-lb hogs. If we assume that the U.S. per capita use of natural gas is 60 ft^3/day presently this reactor could supply about 40% of the daily individual needs. Residues from this reactor, operated as a high rate digestor, must be returned to the land.

"Wastelage" derived from the ensiling of ground grass hay and manure has been successfully fed to brood cows, and for several years a whole corn–wastelage ration has been fed to finishing slaughter steers at Auburn University. Researchers with the Virginia and Michigan Agricultural Experiment Stations have been studying the suitability of poultry waste for refeeding. One of the nation's large beef cattle feeding companies recently began to include substantial portions of feed derived from cow manure in the normal diet of its herd. The U.S. Department of Agriculture estimated that the recovery of only one third of U.S. animal waste for use as feed would produce as much protein as is contained in this country's total annual soybean crop.


Animal waste management alternatives

Symbiotic activity of algae and bacteria in controlled reactors allows maximum conservation of waste components, because end products of bacterial metabolism are incorporated into algal cell mass by the photosynthetic energy trapping mechanism of green plants. In Taiwan, for example, the roofs of animal production units are used for algal propagation with manure-laden wastewater as the culture medium. Effluent water which trickles into the collection gutter is recycled as waterwash for this closed loop reactor.

Developmental work for the production of single-cell protein from animal manures and additional biological conversion schemes have been conducted for nutrient recycling, such as propagation of water hyacinths in secondary and tertiary lagoons and of fly larvae containing about 63% protein and 15% fat from inoculated manure. Currently more exotic processes, such as chemical extraction of nutrient-rich materials for subsequent refeeding, conversion to oil, gasification, and reforming to building materials, lure public attention. Sufficient data necessary to assess the feasibility of these complex systems have not been collected.



Methane digestor. *An animal waste-to-energy system*

Land application

All pretreatment alternatives have residues that must be terminally disposed. Ultimate land application of both solids and liquid is most practical for animal producers. Dry waste may be applied to land by many types of surface spreaders. Slurries can be land-spread or injected into the soil. Liquefied slurries and wastewater may be irrigated with equipment designed to handle variable volumes, with degrees of automation for large or small acreages.

Returning animal waste to the land has become more desirable because nitrogen fertilizer has recently increased from about 10¢ per pound to approximately 30¢ per pound and, at present, supplies are uncertain. The need to conserve the unused nutrients and energy in animal waste may have more profound long-range effects on the feedlot industry than compliance with proposed environmental quality criteria.

The most practical scheme may be to circumvent pretreatment alternatives by direct land disposal using either mechanical techniques or animals on pasture. A zero pretreatment scheme employing a large-scale deep plowing high-rate disposal procedure for feedlot waste has been investigated in Texas.

Land requirements are contingent on either the process or hydraulic limitations for the particular waste and plant-soil system. Nitrogen application per acre should not exceed the approximately 150–200 lb/yr for corn or 200–500 lb/yr for forage that the crops can assimilate, or excess nitrogen will be converted to nitrage which can be a pollutant and health hazard. Land spreading of waste should be conducted to apply waste uniformly; low erosion areas and sites away from streams or hillsides leading directly to streams should be selected, and grassed waterways or drainage paths should be avoided. A vegetated area between disposal areas and drainage systems should be provided. Waste should not be applied during storms, nor should it be applied to frozen ground. Irrigation of wastewater or slurries must be managed to prevent direct runoff during, or as a result of, any application event. However, surface runoff represents only one consideration, because extensive groundwater samplings by many workers have shown that nitrate concentrations were high in areas of heavy agricultural production.

Exemplary management systems

The total waste management scheme integrates materials handling, pretreatment, or utilization units or series of unit processes, and terminal receiver systems. The production facility and the degree of mechanization affect labor requirements for collection and transport. The value recovered, and thus the amount of land required for terminal disposal, is related to the pretreatment strategy.

Principles of spray runoff and BLWRS are incorporated into a commercial-sized undercage waterwash system employing recirculated water from an overland flow-series lagoon treatment which is being investigated by Overcash and Humenik. Waterwash is uniformly applied to a series of Reed Canary and Redtop grass terraces. The overland outflow is collected in a small lagoon which is kept anaerobic by direct manure inputs. Aerobic treatment by the overland flow reduces organics and converts nitrogen to nitrate. The objective is to obtain denitrification of the terrace effluent in the small anaerobic lagoon prior to overflow into the polishing-reservoir pond for recycled waterwash.

The Randleigh Dairy research unit at North Carolina State University has a typical waterwash facility. Wastewater is passed through a solids separator prior to discharge to a series lagoon system that collects all feedlot runoff. Solids can be recycled as bedding, forage supplements, fiberboard material, or a variety of other potential applications. This primary lagoon functions more like a contemporary stabilization pond because the cellulosic material that resists biodegradation and sedimentation is removed. Irrigation from either lagoon to forage or pasture lands is possible. Liquid from the final lagoon is recycled for flushing. This closed system for waste utilization and recycling satisfies the nonpoint source discharge requirement, because feedlot storm runoff is retained in the lagoon system, and terminal land irrigation all wastewater does not result in direct runoff.

The Botkins farm facility developed in cooperation with EPA and researchers from the Ohio Agricultural Experiment Station represents a high level of technology for treatment and effluent recycling as waterwash for the automated removal of waste from a 500-pig unit. Screened solids are aerobically digested pursuant to disposal on cropland. The liquid fraction is pumped back to siphon-activated washing tanks having chlorine disinfection equipment that has not yet been necessary for this odorless system.

Regulatory criteria

In fulfilling the requirements of the Federal Water Pollution Control Act amendments of 1972, EPA has published two sets of regulations affecting the animal production industry which establish a permit program and compliance criteria. The National Pollution Discharge Elimination System (NPDES) guidelines and permit form were published in the July 5, 1973, *Federal Register*, and the effluent limitation guidelines were published in the February 14, 1974, *Federal Register*. State regulations must be at least as restrictive as federal criteria to receive EPA approval.

These two documents specify that the producer who has 1000 slaughter or feeder cattle, 700 mature dairy cattle, 2500 swine weighing over 55 lb, 10,000 sheep, 55,000 turkeys, 30,000–100,000 chickens depending upon waste management procedures, or 5000 ducks, or any combination of livestock exceeding 1000 animal units must obtain an NPDES permit (an animal unit equals each preceding number divided into 1000—i.e., each swine represents 1000/2500 = 0.4 unit). However, not being required to apply for a permit does not exempt any animal production unit from the requirements of the Act, because no one is permitted to discharge pollutants into waterways. Additionally, a small operator must apply for a permit if the regional administrator of EPA or the state water control agency has identified his operation as a significant polluter.

Any animal production facility, where the density of livestock in any given area precludes the growth or production of crops or forage, is defined as a feedlot by the February 14 *Federal Register,* and is thus subject to both criteria. Two or more animal confinement facilities under common ownership are deemed to be a single production unit if they are adjacent to each other or if they utilize a common area or system for the disposal of waste. However, animal production units that incorporate management options to disperse or decentralize livestock to sustain vegetative cover for soil and crop assimilation of manure could reasonably be expected to obviate any significant units with fewer than the specified animal numbers and that employ management techniques to preserve ground cover would not be required to obtain permits.

The time frame for the regulations quoted from the February 14, 1974, *Federal Register* is: "This final regulation is promulgated as set forth below and shall be effective April 15, 1974." Although EPA has initiated the permit program, a deadline for application has not been set. Regional EPA offices which supply permit information, Short Form B for Agriculture, are developing an inventory of operations required to apply for an NPDES permit. The first level of compliance for existing units must be achieved by 1977 with adherence to final criteria by 1983. New units must be developed to meet final criteria.

The intent of EPA is apparently to develop effluent limitation guidelines for small feedlot operators once the current permit program becomes operational and additional technical and economic data are secured. This is spelled out by the following statement in the February 14, 1974, *Federal Register:* "Subsequent to the completion of this analysis, effluent limitations applicable to smaller operations will be proposed for public comment." EPA has recently released two documents concerning nonpoint sources of pollutants that make it apparent that sooner or later everyone will be affected to some degree.

Producers who have animals confined in any unit that does not support vegetative cover must not discharge any wastewater, or allow runoff of rainfall, which comes in contact with manure in housing or feedlot areas, to flow directly into a receiving water. The exception is runoff from 10-year-event storms in excess of a 24-hr duration for 1977 and a 25-year-event, 24-hr storm for 1983 regulations.

Retention ponds, constructed to contain the 24-hr, 24-year-event storm rainfall runoff that has come in contact with manure either in the housing area or land that is determined to represent a feedlot condition, must be operated as flood control devices by continuous emptying on terminal disposal plots maintaining vegetative cover. The following allowance has been made for extended periods of rainfall: "Waste pollutants in the overflow may be discharged to navigable waters whenever rainfall events, either chronic or catastrophic, cause an overflow of processed wastewater plus the runoff from a 24-hr, 25-year rainfall event (1983) for the location of the point source." However, no allowance is made for the point source discharge of waste pretreatment devices, such as lagoons, for less than the prescribed storm conditions.

These rules, which emphasize the desirability of terminal land disposal, are consistent with the efforts of research and extension personnel in agricultural waste management to recommend maximum utilization of fertilizer components with minimal environmental hazard; they further verify the difficulty of using contemporary municipal or small package treatment plants for agricultural waste. Municipal wastes are presently treated to allow discharge to receiving waters, whereas agricultural wastes are most logically applied to cropland for terminal disposal. Thus, the current thrusts of municipal and animal waste treatment technology are profoundly different. However, advantages of land-based systems being developed for animal waste may have important impacts on treatment strategies for domestic, agricultural processing, and industrial wastes.

Preliminary research indicated that the pollution potential of runoff from watersheds, where animal waste was land-spread according to recommended practices, is similar to the natural pollution load on streams draining agricultural lands devoid of farm animals. Thus, the no-discharge concept must not be extrapolated to include runoff from croplands or areas used for terminal deposition of manure, according to currently recommended practices.

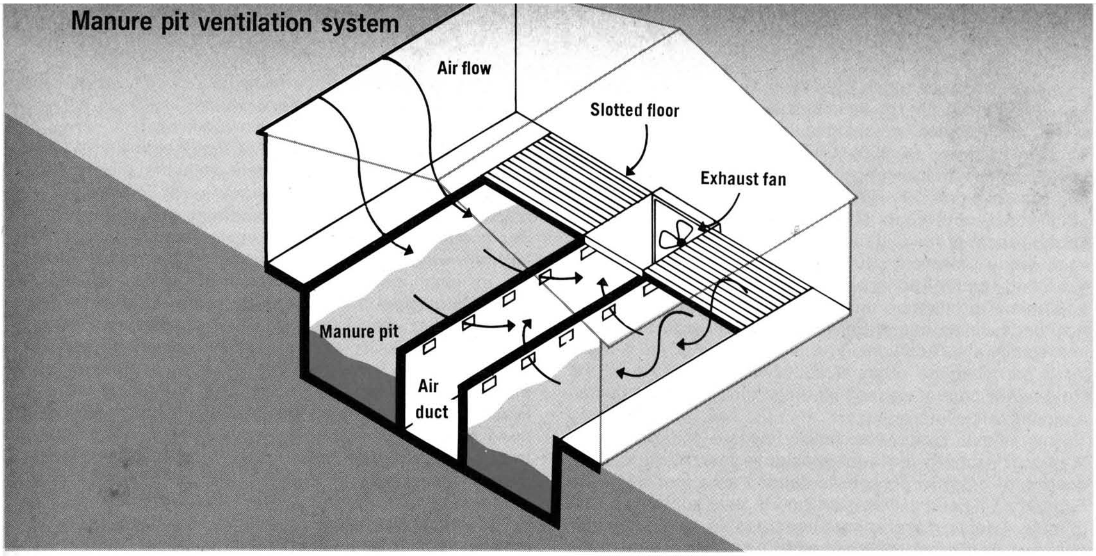
Terminal land application is the procedure most familiar to the agricultural community and is a valid approach to the goal of nonpoint source discharge (not zero discharge), if employed according to currently recommended best practicable technology. This practice also protects the basic agricultural philosophy that production residues should be recycled back to the land. However, any treatment or utilization scheme that results in an effluent that meets criteria for discharge of municipal or industrial wastewater should also qualify for direct discharge to preserve the integrity of the total EPA program.

Proposed effluent monitoring criteria

The criteria to be used in sensing point source discharge or achievement of effluent reduction consistent with best practical control technology have not been established. Paramount for the selection of parameters for effluent limitations and guidelines should be environmental protection, techical suitability, analytical requirements, and corresponding enforcement demands. Therefore, the minimum number of measurements that will completely assess the pollution potential of effluent from any feedlot source should serve as the monitoring basis. Naturally, no trivial, redundant, or misleading measurements should be included.

Research results indicate that any assessment made solely upon phosphorus is meaningless, and the measurement of both phosphorus and nitrogen gives overlapping or complementary information. Therefore, phosphorus is not suggested as an effluent parameter because its importance for determining pollution potential is subordinate to that of nitrogen and organics. However, it is recommended that all forms of nitrogen (ammonia, organic, and nitrate) be measured, so as to account for the total nitrogen load.

Selection of the parameter that provides the most technically sound and acceptable evaluation of the biodegradable organic waste load calls for consideration of a widely contested issue—the standard five-day biochemical oxygen demand (BOD_5) test. Actually, the only analytical technique currently available for directly measuring the organic content of wastewater is the total organic carbon (TOC) instrumental analysis. The disparity of BOD_5 data for uniform-weight animals reported in literature and research reviews vividly illustrates the difficulty



many researchers working with animal waste have had in obtaining reproducible BOD_5 data. Bush certainly summarizes the sentiments of many workers when he concludes, "BOD_5 is a source of confusion in process assessment and holds no theoretical or practical significance even if the test were accurate or convenient to perform."

Advantages of the chemical oxygen demand (COD) test are analytical ease, consistency of results, and the short time required when utilizing the 15-min digestion time for animal waste recommended by some researchers. The COD test provides a conservative measure of the ultimate demand which waste loads will have upon the oxygen resources of a receiving water, especially if a fraction settles to the streambed and therefore has a longer reaction time. Oxygen uptake rates can be determined by COD analyses with time.

The measurement of COD and all forms of nitrogen give insight to associate parameters such as phosphorus, TOC, BOD, total and volatile solids, bacterial densities, turbidity, color, and related parameters. Almost without exception, the level of these parameters will be controlled for animal waste if the COD-nitrogen criteria are met. Hence, it is proposed that COD and all forms of nitrogen are the most technically sound, convenient, and nonredundant measures to evaluate the pollution of effluent for discharge.

Economic ramifications

The Economic Analysis of Proposed Effluent Guidelines for the Feedlot Industry, referred to in the *Federal Register,* concludes that the effects of these criteria upon product price increases or employment would be quite small, while overall production is likely to increase. However, the cost-benefit aspects of any treatment system designed to produce a dischargeable effluent for animal waste, as is commonly done in conventional waste treatment systems, appear most unfavorable at present.

Costs for elimination of point source discharge of process wastewater and rainfall runoff have been generally estimated by EPA, USDA Economic Research Service, and many economic experts according to two basic assumptions:

- Livestock producers at present have the required equipment and land for the removal and disposal of solid manure; therefore, no additional costs for solid waste removal are required.
- Investment cost required for effluent control consists of lagoon and/or basin construction to curb runoff plus equipment for the removal and disposal of lagoon liquid.

Although many regional considerations such as climatic, geographic, land costs, and typical practices as well as initial investment vs. annual costs preclude a comprehensive evaluation, virtually all analyses conclude that the added costs for effluent control systems will be the heaviest on small producers. In the short run, the economic impact is expected to be greatest for swine and dairy producers, especially dairies in mountainous regions where rainfall and immediate runoff are high.

It is generally assumed that these pollution control guidelines will hasten the trend to fewer and larger farms. Supplies cost and, therefore, cost of dairy and pork products will be most affected over the near term, but adoptions of lower-cost technology and shifts to least-cost production regions are expected to dampen long-range economics.

Although economic projections support expansion of large operations where capacity can be added with nominal effects on production costs, the operational, pretreatment, and land requirements consistent with environmental regulations may also limit and severely change economics of large production units in many regions. Ultimately the most economical and environmentally sound production methods may be represented by medium-size producers who operate component segments as small units with sufficient land to assimilate and recycle production residues.

The most significant finding of the supporting technical analysis pursuant to publication of proposed effluent limitations in the September 7, 1973, *Federal Register* was:

"The best practicable control technology currently available for the feedlot industry is dependent upon the ability of available cropland to receive feedlot wastes and efficiently recycle them into usable crops. Both the amount of waste and their strength, as well as the type of crop produced, are direct functions of climatic conditions which vary exceedingly with location and time of year. In addition, the local variation in soil condition and topography will affect the application of the technology, as will traditional agricultural practices. Because of these highly variable circumstances, the application of the best practicable control technology currently available must be tailored on an individual basis to the local prevailing situation. This should be done in accordance with the advice of the knowledgeable technical experts available to the agricultural community."

Attendant to the implementation of these principles, waste management systems will be developed that are environmentally acceptable and economically feasible and most importantly will secure our vital needs—food and a quality environment.

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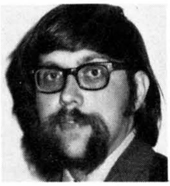

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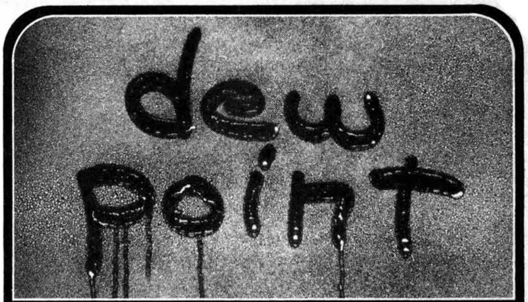

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FEATURE

That the environmental sciences encompass many disciplines is evident in the volumes of literature available. Present on-line computer systems aid in the storage and retrieval of pertinent information

Information systems enter space age

Virginia D. Caswell *University of California, Lawrence Livermore Laboratory, Livermore, Calif. 94550*

Subduing the mountain of information written about the environment is strenuous work. Like running up a down escalator, the effort is constant and in the right direction, but occasionally one wonders, breathlessly, if one can get to the top.

When Congress declared the 1970's the environmental decade, it projected the nation into a commitment not unlike that of the space program. Reflecting on the state of bibliographic control when Sputnik first launched the U.S. on a program to the moon, one can ask if methods of information storage and retrieval have advanced since then. Problems abound in a number of areas: in the nature of the literature, the methods available for control, and in the proposals made for a solution and their implementation.

Protecting the environment is an intricate activity. The environmental sciences bridge many disciplines, culminating in a multidisciplinary generation of information. Relevant developments in chemistry and biology; new techniques in the atmospheric sciences, civil engineering and air pollution control; advances in water resources engineering and the health sciences; improvements in electrical and mechanical engineering; new legislation; transportation; and energy management are the concerns of those who search the environmental literature. Not only are there problems that are characteristically technical, but there are those that encompass political, social, and economic aspects as well. These facets are also reflected in the literature.

As yet there is nothing equivalent to the extensive indexing and abstracting services that exist in the established branches of science and technology—*Biological Abstracts, Chemical Abstracts, Physics Abstracts,* and *Nuclear Science Abstracts.* These standard sources reflecting more and more the international interest in the environment cannot be neglected. Also of importance are those services specializing in environmental literature—*Air Pollution Abstracts, Pollution Abstracts, Water Pollution Abstracts, Environment Abstracts* (formerly *Environment Information ACCESS*)—and those with broad coverage such as *Engineering Index,* the *NASA Star,* and the *Government Research Abstracts.*

Not only is there a disconcerting number of secondary sources that are at times guilty of duplication and overlap, but there is a superabundance of primary publications as well—publications such as congressional hearings, documents, journal articles, theses, translations, monographs, and conference papers.

Fortunately, the trend to retrieve information with computers has developed rapidly. While this is no panacea, every little bit helps. There are now various compilations of machine-readable data, both federal and commercial, some of which are applicable to searching some aspects of the environmental literature. Not many organizations have available multiple data-base current-awareness systems. The lack of national standards for the transmission of this type of information has resulted in disparities in tape formats and variances in data elements, that, along with machine costs, present many problems for the potential user.

Professional societies intimately concerned with different aspects of the environment are just getting organized. Cumulative author and subject indexes, a welcome, if delinquent, adjunct to their publications are being published for the first time. Other associations are changing the emphasis of their programs; journals are being renamed to show that, in the modern vernacular, they are "with it"; new acronyms are appearing; and new organizations are being formed every day.

EIS prospects

During the past several years, the idea of a total environmental information system (EIS) has been explored by more than one group at national and international levels. The United Nations Conference on the Human Environment, held in Stockholm in June 1972, considered the need for information in the area of the environment so important that recommendations were made for an information referral service. As reported in the literature, this was proposed as a "modest and practical tool: to tell what information services exist, where they are, and how to gain access to them" ("Information," Pt.I, July-August, 1972). In May 1973, the U.S. House of Representatives passed a bill to provide for participation by the U.S. in the United Nations Environment Program (UNEP). A Senate bill on this subject, among other things, supports "fund allocations for the development and support of an international system for the exchange of information . . . the Information Referral Service being the principal element in this system" (*Congressional Record,* June 8, 1973). Signed on December 15, 1973, Public Law 92-188 provides for U.S. participation in UNEP.

In September 1972, William D. Ruckelshaus, then administrator of the EPA, speaking at an environmental information symposium sponsored by the U.S. Environmental Protection Agency (EPA) in Cincinnati, referred to our "uncoordinated or nonexistent retrieval systems" and admitted that environmental information is generated by some 75 different sources within the Federal Government alone. He agreed that "There is as great a need to organize and manage information as there is to make new discoveries." At the same conference, Dr. John W. Townsend, Jr., of the National Oceanographic and Atmospheric Administration (NOAA) suggested that a "national environmental and information system be established . . . eventually leading to a computer-to-computer query and reply capability." He said that it should not be a "monolithic center" but "an inter-related system of centers" which can provide users "with the types of environmental data they need, when they need it, in the forms and formats they require."

An Interagency Conference on the Environment, sponsored by the EPA and the Atomic Energy Commission (AEC), was held in Livermore (Calif.) in October 1972. One of the panel groups explored the desirability of establishing a comprehensive national environmental data system and the problems associated with such a system. They concluded that "data files should be widely available, compatible, and flexible enough to meet future demands," and agreed on the undesirability of a single all-inclusive information system. They envisioned, instead, a center that would act as a focal point for facilitating data bank access, interchange and interface; the obvious problems of the integration of current data banks, financial support, and responsibility were pointed out (CONF 721002).

Also in October 1972, Congress passed legislation to establish a national environmental data system and sent it to former President Nixon. Essentially the system was to serve as the central point "for the selection, storage, analysis, retrieval, and dissemination of environmental data made available to it by federal agencies, state and local governments, individuals and private institutions" (*Congressional Record*, Oct. 5, 1972).

This National Environmental Data System and Environmental Center Act of 1972 was subsequently vetoed by the President. In his memorandum to Congress he said "that while both of these titles sound desirable in theory, they would lead to the duplication of information or would produce results unrelated to real needs and wasteful of talent, resources, and the taxpayer's money." He went on to say that "I believe the centralized collection of environmental data should be related to specific policies and programs . . . the EPA and other agencies have consistently worked to strengthen the acquisition and exchange of such data and this effort will continue."

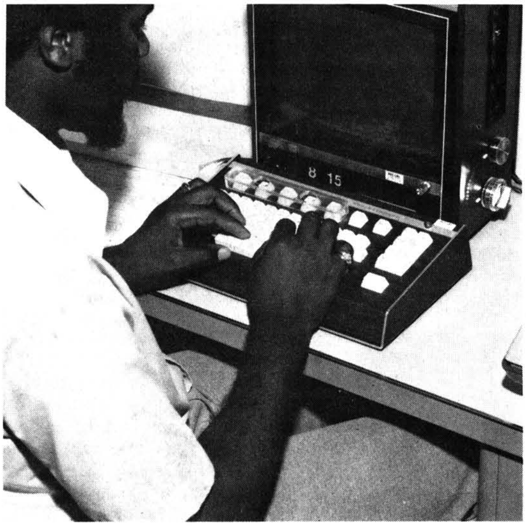
This pocket veto did not kill congressional desire for this legislation. A bill (H.R. 4732) was reintroduced into the House of Representatives in February 1973 for legislation to provide for the National Environmental Data System and Environmental Centers Act of 1973. While it restates, for the most part, the words used in the vetoed legislation, it also includes the following: "There is hereby established a National Environmental Data System. The Data System shall include an appropriate network of new and existing information processing or computer facilities both private and public in various areas of the United States, which, through a system of interconnections, are in communication with a central facility for input, access, and general management. It shall also include all of the ancillary software and support services usually required for effective information system operation."

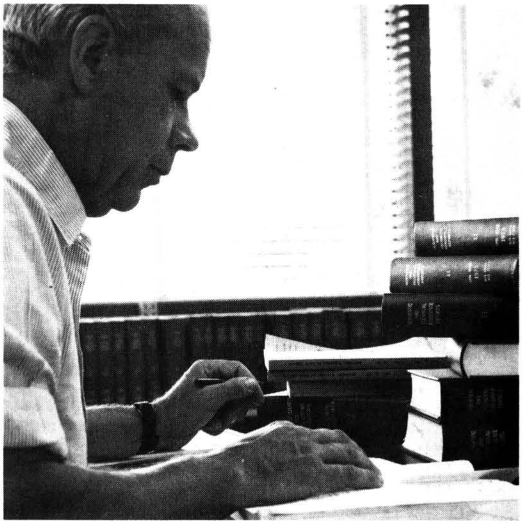
Meanwhile, in May 1973, a Senate bill was introduced to "authorize the establishment of centers for environmental research, education, data collection, and data analysis within the States and regions of the Nation" (*Congressional Record*, May 22, 1973). It is essentially the same as S. 681, passed by the Senate in the 92d Congress and similar to Title II of H.R. 56 passed by the House and Senate last year and later vetoed.

Present status

While the legislative process grinds on and conference rhetoric continues, what is being done at the working level? The answer seems to be that everyone is doing his "own thing." Many federal agencies have already developed data systems which handle environmental information along with the information in other subject areas. Notable systems are currently active in the Departments of Commerce, Agriculture, Health, Education and Welfare, Defense, and the National Aeronautics and Space Administration. And, as might be expected, the EPA is in the forefront with its own efforts.

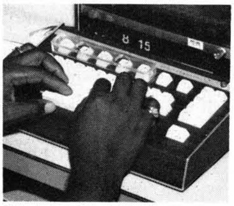
The EPA's Air Pollution Information Center (APTIC) at Research Triangle Park (N.C.) prepares *Air Pollution Abstracts*, a monthly publication available from the Superintendent of Documents on a subscription basis. APTIC also provides retrospective, machine-based literature searches on an individual basis. The National Environmental Research Center/Cincinnati operates within the EPA to provide scientific and technical information to staff members through the development of an EPA information network. And in the areas of environmental monitoring and control, the EPA has developed the following

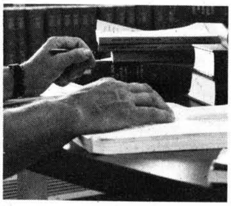




information systems to serve specific interests: NEDS (National Emissions Data System), SAROAD (Storage and Retrieval of Aerometric Data), STORET (National Water Quality Information System), SWIRS (Solid Waste Information Retrieval System), ENVIRON (Environmental Retrieval On-Line), and NOISE (Noise Information System). Access to these systems through remote terminals at EPA regional offices has been implemented or is being planned.

An Environmental Information System is being developed at AEC's Oak Ridge National Laboratory. Partially funded by the National Science Foundation, it is becoming a front-runner in providing a wide variety of environmental information on a nation-wide basis. The Environmental Information Systems Office (EISO) coordinates the activities of a number of information centers and their associated data bases, some of which are now available for on-line searching on the AEC/RECON system. RECON, based on Lockheed's DIALOG system and developed by the AEC Headquarter's Technical Information Center and Union Carbide for use with *Nuclear Science Abstracts*, is an interactive, computerized information retrieval system. Adopted by EISO for small data bases, RECON uses a natural language dialog for easy access to citations appearing in the Energy, Toxic Materials, Water Resources, Mercury, Heated Effluent, and Nuclear Science data bases.





NOAA is developing its own Environmental Data Service. It is advertised as a "comprehensive single-source service for data and information applicable to environmental problems" (*Environmental Data Service*, August 1971). In the development of ENDEX (Environmental Data Index), NOAA hopes to be able to provide a "rapid referral service to existing national and global environmental science data files."

Three useful services, not machine-readable but produced by government agencies, are: the *Environmental Awareness Reading List*, compiled by the Natural Resources Library of the Department of the Interior as a semimonthly listing; *Selected Water Resources Abstracts*, accumulated by the Office of Water Resources Research of the Department of the Interior, published bimonthly; and *Environmental Pollution and Control*, a weekly bulletin of report abstracts. All of these can be obtained by subscriptions placed with the National Technical Information Service (Springfield, Va.).

Outside the Government there is a corresponding amount of activity. A machine-readable data base, the *Environmental Science Citation Index*, produced monthly by the Environment Information Center, Inc., New York, gives interdisciplinary coverage of the literature in six broad categories. This same organization produces the *Environment Abstracts*, a monthly abstracting service in a conventional format. *Pollution Abstracts*, a bimonthly publication produced by Oceanic Library and Information Center (La Jolla, Calif.), abstracts technical and nontechnical literature over the entire environmental spectrum. *Environmental Periodicals Bibliography*, a publication of the Environmental Studies Institute, International Academy (Santa Barbara, Calif.), duplicates the tables of contents of journals in six subject categories on environmental matters. And, in the United Kingdom, the Scientific Documentation Centre Ltd. offers both current awareness services and retrospective literature searches on most environmental subjects.

William T. Knox, Director of the National Technical Information Service, appropriately summarizes all these efforts: "The technological area of greatest public concern today appears to be environmental pollution and conservation. At high policy levels, the new areas of concern also include energy and the faster application of more technology to U.S. manufacturing, construction, transportation, and service sectors . . . (and) in none of these areas is there a technological information system that has the traits of the existing federal systems. Instead, there are fragmentary operations of limited scope being carried out by numerous public and private organizations" (*Science*, August 3, 1973).

Projection

Exciting possibilities exist for the future owing to rapid developments in telecommunications, cable television, and the uses of communication satellites. Futurists speak of scientists having direct access, via desk-top terminals, to a network of national and international technical information banks; a national computerized research library, and home telephone access to computer files containing all books, magazines, and newspapers and other useful information. These are fascinating possibilities.

However, for those who must deal with requests for environmental information on a daily basis, the computer information network is probably the innovation closest at hand. It is no longer in the realm of science fiction to picture oneself sitting at a single computer terminal and accessing, in a matter of seconds, information available in the data bases on the AEC/RECON system, MEDLINE, (National Library of Medicine) and the National Technical Information system. The trend is dramatically in this direction.

That problems exist in coping with the sheer volume and diversity of environmental literature cannot be denied. Although possibilities for a total environmental information system seem remote and perhaps undesirable, today's information sources are workable, if somewhat a challenge. There is enough enduring interest in the state of environmental literature that given enough time, money, strong motivation, and the help of new technology, one will arrive at the top of the down escalator.

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CURRENT RESEARCH

Modified Cellulose Adsorbent for Removal of Mercury from Aqueous Solutions

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■ Scavenging inorganic mercury from aqueous solutions has been accomplished by a modified cellulose adsorbent containing vicinal thiol groups. The process is highly selective for mercury, is independent of pH over the range from pH 1 to pH 9, and is effective in acidic brine. A solution containing 1 ppm mercuric ion was passed through a column (10 mm i.d. × 23 mm) prepared from 0.5 gram of the cellulose derivative. Mercury concentration in the effluent was dependent upon the flow rate of the solution; however, at 50 ml/hr the effluent mercury concentration remained below 5 ppb for 60 bed volumes.

With increasing awareness of the health hazard that mercury constitutes in the biosphere has come a corresponding growth of interest in methods for preventing mercury pollution. Procedures currently in use for removing mercury from solution include precipitation as the sulfide or oxide, reduction-precipitation using an active metal such as zinc, reduction with sodium borohydride, ion exchange, and solvent extraction. Most of these methods suffer from the disadvantage that they "trade" one dissolved pollutant for another. In addition, reduction or precipitation techniques usually require the use of some reagent in excess of the quantity of mercury present to ensure complete removal of the mercury. The net effect is an increase in the abundance of dissolved substances. Ion exchange and solvent extraction procedures offer promise, but require substantial capital investment. An "ideal" method for mercury removal from process effluent would be one which is cheap, thorough, and effective under a wide range of operating conditions, and which does not introduce any new pollutant in the process. A sorption technique seemed potentially capable of satisfying these criteria.

The thiol (mercapto) group exhibits a high affinity for mercury. This is the basis for the use of thiol compounds [e.g., 2,3-dimercaptopropanol (BAL) and dimercaptosuccinic acid] in the treatment of mercury poisoning. It was decided to attempt to exploit this affinity by incorporating the thiol group into an insoluble matrix. Cellulose was chosen as the matrix because of its modest cost and ready availability.

Materials and Equipment

Powdered cellulose used in most experiments was Cellex N-1, a product of Bio-Rad Laboratories, Richmond, Calif.

^{203}Hg tracer, as the nitrate, was obtained from ICN Corp., Irvine, Calif.

Hydrogen sulfide gas was technical grade, obtained from J. T. Baker Chemical Co., Phillipsburg, N.J.

All other materials were of the highest purity available, and were readily obtainable from a number of domestic suppliers.

^{203}Hg determinations were performed using an NaI (Tl) ($1\frac{3}{4} \times 2$ in.) well-type scintillation counter. Determinations of other metals in solution were performed on a Perkin-Elmer model 403 atomic absorption spectrophotometer.

Procedures

Alkaline cellulose, prepared as described by Peterson and Sober (*1*), was maintained at 0–5°C during dropwise addition of allyl bromide (1–1.3 ml/g of cellulose). Continuous mixing was provided during this addition by use of a heavy glass rod. The doughy mixture was then transferred to a water bath and maintained at 60–65°C for 1–2 hr, with frequent remixing. The product was then suspended in a large volume of water and allowed to settle. After decanting the supernatant, the process of suspending and settling was repeated until the supernatant was nearly neutral. The material was collected on a suction funnel, washed with ethanol and ether, and air-dried. The etherified cellulose was brominated in a CCl_4 slurry, typically using 0.5 gram of bromine and 15–20 ml of CCl_4 per gram of solid and stirring overnight. The brominated derivative was added to a methanolic solution of NaSH prepared by dissolving solid sodium hydroxide in methanol and saturating the resulting solution with hydrogen sulfide. After stirring in this medium overnight, the final product was collected on a suction funnel and washed with 5% HCl and then with water until the wash was neutral. After washing with ethanol followed by ether, the material was air-dried. For brevity, the product, a white, nearly odorless, free-flowing powder, has been designated VDT cellulose, "VDT" denoting vicinal dithiol.

Two methods were employed for the measurement of mercury uptake by the VDT cellulose. Batchwise determinations were performed by adding a measured volume of ^{203}Hg-labeled mercury solution to a known quantity of VDT cellulose. The mixture was stirred at room temperature for periods of 20 min to 2 hr, and then filtered. The difference between the quantity of mercury in the filtrate and that in the original solution was assumed to be the amount adsorbed by the product. In continuous-flow experiments, a solution of ^{203}Hg-labeled mercury was passed through a column of packed VDT cellulose, typically 10 mm i.d. × 20 mm long. ^{203}Hg determinations were made on fractions of effluent.

Corrections for background radiation were applied to all determinations in these experiments.

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Results and Discussion

Initial studies were directed at determining the effects on mercury collection of the following parameters: pH changes; other metal ions in the solution; and the presence of high concentrations of salts. Table I presents data obtained from a series of batchwise experiments of varying pH. The pH of solutions used in these determinations was adjusted to the appropriate value by adding HCl or NaOH as necessary. Sodium chloride was added as required (to solutions with a pH greater than 1) to provide a uniform chloride concentration of 0.1*M* for all solutions. For each solution, the level of radioactivity remaining after treatment with the VDT cellulose was at least twice the background level, permitting calculation of the residual mercury concentration. The loading of the sorbent varied only slightly over the range of pH studied, and it appears that the sorption of dissolved mercury under these conditions is virtually independent of pH.

The capability of the product for removal of mercury from solutions containing other ions was investigated using batchwise measurements of metal uptake from solutions of mixed metal ions. A solution containing mercuric, ferric, cadmium, magnesium, and silver ions was prepared from the nitrate salts of the respective metals. Only mercuric ion (Table II) was removed to a significant extent from the solution. Similar results were obtained when the experiment was repeated using ferric, cupric, calcium, and lead ions together with mercury. In additional screening tests, no uptake of any of the following metals was observed: cobalt, nickel, chromium(III), antimony (as antimonyl tartrate), or arsenic (as arsenate). The observation that a small quantity of silver was removed prompted further experiments which revealed that in the absence of mercury, silver is sorbed by VDT cellulose to approximately the same extent (based on molar uptake per gram of sorbent) as mercury.

The high selectivity for mercury exhibited by VDT cellulose in these experiments indicates that its capacity for mercury uptake is not significantly diminished by the presence of other commonly occurring metal ions in the solution. This property could be important in removing mercury from a solution containing other, less hazardous dissolved species.

To test whether the cellulose derivative could effect removal of mercury to the level required for potability, a solution of ^{203}Hg-labeled mercury at a concentration of 1 ppm was passed through a column (10 i.d. × 23 mm) containing 0.5 gram of VDT cellulose at an initial flow rate of 50 ml/hr. Figure 1 depicts the mercury concentration in the effluent as a function of effluent volume. For approximately 60 column-volumes, the mercury level remained below the standard of 5 ppb (parts per billion) presently recommended by the U.S. Public Health Service for drinking water. Because this level was increasing, the flow rate was reduced to 30 ml/hr. This resulted in an apparent plateau at a level below 8 ppb for the duration of the experiment. Additional runs at varying flow rates indicated that the mercury level in the effluent reaches an equilibrium value that is dependent upon flow rate. At 60 ml/hr, for example, this level was approximately 20 ppb for a column identical to the one used in the experiment represented in Figure 1. Because the extent to which mercury is removed from a given solution is a function of flow rate (residence time), the selection of operating conditions necessary to achieve a predetermined effluent mercury level would require additional trials.

It has been estimated (*2*) that as of 1970, 47% of the mercury "lost" in the United States was in brines and sludge originating in chlor-alkali plants. The potential of VDT cellulose for removing dissolved mercury from such systems was determined by using a simulated chlor-alkali brine (50 ppm of mercury, 4*M* sodium chloride, pH 2.5) that was passed through a column of packed VDT cellulose (10 i.d. × 12 mm) at a flow rate of 30 ml/hr. The results of mercury determinations in the effluent (Figure 2) indicate that thorough scavenging of mercury from such solutions is possible. More than 99.6% of the influent mercury was removed uniformly until saturation of the adsorbent was approached, at which point the mercury concentration in the effluent rose rapidly. The loading of mercury by the cellulose amounted to ~30 mg/g at the point of breakthrough. This is somewhat lower than the 40 mg/g adsorbed from solutions containing only mercuric chloride

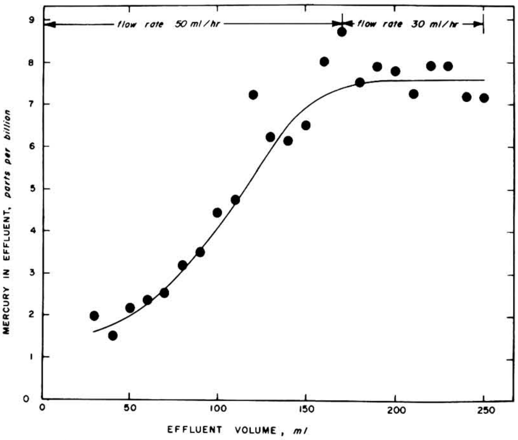


Figure 1. Effluent mercury concentration as function of effluent volume

Table I. Mercury Collection as Function of pH[a]

Solution, pH	Mercury adsorbed, mg Hg/g VDT	Mercury remaining in soln, ppm	Mercury removed, %
1	9.6	0.60	97.0
2	9.6	0.42	97.9
3	9.8	0.38	98.1
4	9.6	0.38	98.1
5	9.8	0.26	98.7
6	9.8	0.32	98.4
7	9.6	0.32	98.4
8	9.8	0.14	99.3
9[b]	9.6	0.32	98.4

[a] All solutions were initially 20 ppm in Hg^{2+}. VDT cellulose (50 mg) was added to 25 ml of mercuric chloride at the indicated pH. Contact time was 140 min.

[b] At pH 10, turbidity (presumably mercuric oxide) was observed in the solution.

Table II. Mercury Uptake in Presence of Other Metal Ions[a]

Ion	Concentration before VDT treatment, ppm	Concentration after VDT treatment, ppm	Metal adsorbed, mg/g VDT
Hg^{2+}	3100	150	70
Fe^{3+}	1200	1200	0
Cd^{2+}	500	500	0
Mg^{2+}	380	380	0
Ag^{+}	2000	1900	2.5

[a] VDT cellulose (1 gram) was stirred with 25 ml of a solution containing the indicated concentrations of metal ions. Contact time was 45 min. All metals were determined by atomic adsorption spectrophotometry.

or nitrate at similar concentrations (Figure 3). The reason for this is not known; however, the efficiency of collection of mercury was not diminished even in the nearly saturated chloride solution. The performance of three commercial ion exchange resins in removing mercury from the simulated brine was compared with that of VDT cellulose under identical experimental conditions (Figure 2). Only the anion exchange resin (Dowex-1) was capable of removing a significant amount of the influent mercury; however, the extent of mercury removal by this resin decreased steadily to approximately 97.5% by the end of the experiment.

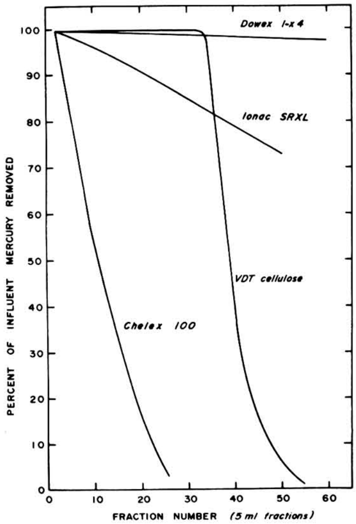


Figure 2. Mercury removal from a simulated chlor-alkali brine

For each sorbent, 300 mg (dry weight, based on prior determinations) was used in preparation of the column. Bed heights for the various sorbents were VDT cellulose, 11 mm; Chelex-100, 21 mm initially, diminishing to 14 mm on introduction of the brine solution; Dowex-1, 10 mm; SRXL, 7 mm. SRXL resin, a polystyrene-divinylbenzene copolymer containing amidine groups, is no longer marketed by the Ionac Chemical Co. A resin believed to be identical is available as Srafion NMRR from the Ayalon Water Conditioning Co., Ltd., Haifa, Israel. The older "SRXL" resin was on hand in this laboratory and was used in this test simply for comparison in the chlor-alkali brine system

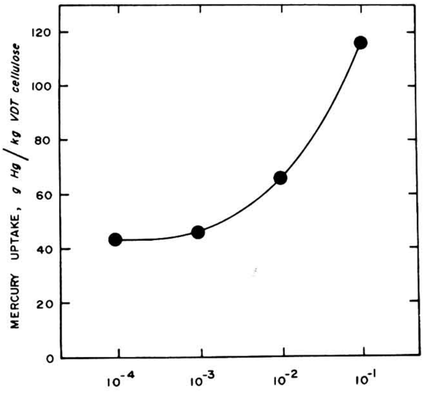


Figure 3. Mercury uptake as function of mercury concentration

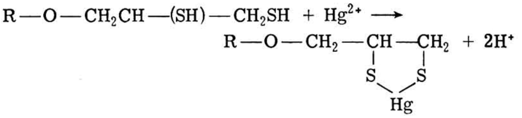
The process by which mercury is removed from solution by VDT cellulose has been referred to as "adsorption" for ease of reference. The actual mechanism is believed to involve covalent sulfur–mercury bond formation. The preparative sequence used was designed to introduce vicinal thiol groups into the cellulose backbone by the following route (where R denotes cellulose):

$$\underset{\text{alkaline cellulose}}{R{-}O^-Na^+} + CH_2{:}CHCH_2Br \longrightarrow \underset{\text{I}}{R{-}O{-}CH_2CH{:}CH_2} + Na^+ + Br^-$$

$$\text{I} + Br_2 \longrightarrow \underset{\text{II}}{R{-}O{-}CH_2CHBrCH_2Br}$$

$$\text{II} + 2HS^- \longrightarrow \underset{\text{VDT cellulose}}{R{-}O{-}CH_2CH(SH)CH_2SH} + 2Br^-$$

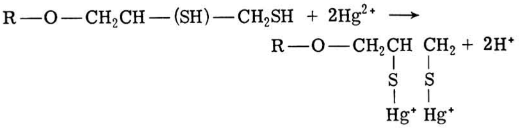
The interaction of VDT cellulose with mercuric ions could then be represented as



$$R{-}O{-}CH_2CH{-}(SH){-}CH_2SH + Hg^{2+} \longrightarrow R{-}O{-}CH_2{-}\underset{S}{CH}{-}\underset{S}{CH_2} + 2H^+ \quad (S\text{–}Hg\text{–}S)$$

This postulate is corroborated by the observation that the pH of a solution containing mercuric ion decreases rapidly with the addition of VDT cellulose. In the absence of dissolved mercury, the pH of an aqueous suspension of VDT cellulose remains constant and nearly neutral.

The sulfur content of VDT cellulose (1.6%, Galbraith Laboratories, Inc., Knoxville, Tenn.) corresponds to 0.5 mmol of S per gram of VDT cellulose. If all sulfur is present as vicinal thiol groups, this would permit a maximum Hg uptake of 0.25 mmols (50 mg) per gram of VDT cellulose by the proposed mechanism; however, in solutions containing high concentrations of mercuric ion, the capacity of VDT cellulose for mercury uptake increases (Figure 3). It is clear that at mercury concentrations greater than $\sim 10^{-3}M$, this mechanism cannot account for the extent of mercury uptake. It is tempting to speculate that the stoichiometry of thiol–mercuric ion interactions changes at high mercury concentration to



$$R{-}O{-}CH_2CH{-}(SH){-}CH_2SH + 2Hg^{2+} \longrightarrow R{-}O{-}CH_2\underset{\underset{Hg^+}{|}}{\underset{S}{\underset{|}{CH}}}\ \underset{\underset{Hg^+}{|}}{\underset{S}{\underset{|}{CH_2}}} + 2H^+$$

explaining the apparent high capacity of VDT cellulose for mercury removal from concentrated solutions. The existence of thiol groups was demonstrated using Ellman's reagent, 5,5′-dithiobis(2-nitrobenzoic acid) (*3*). VDT cellulose, when treated with a solution of this reagent buffered at pH 9, yields the yellow color characteristic of the reaction of the reagent with thiol groups; however, the thiol content calculated from the reported extinction coefficient (molar absorptivity) for the reagent is much lower than the analytical sulfur content indicates. It is possible that a large fraction of the thiol groups is sterically inaccessible to the bulky Ellman reagent. Alternatively, air oxidation may have rendered some of the thiol groups unreactive to the reagent, which would explain the discrepancy.

Experiments utilizing the allylic either precursor to the VDT modification have shown that this derivative also binds mercury under some conditions; however, no mercury is taken up by this derivative from solutions containing mercury plus $0.1M$ chloride. In a control experiment, powdered commercial cellulose was treated exactly as in the preparation of VDT cellulose, but with the omission of the organic etherifying agent, allyl bromide. This material exhibited no affinity for mercury. This observation is reinforced by a report by Friedman and Waiss (*4*) who observed no uptake of mercury by native cellulose (cotton). Thus, although some mercury adsorption probably occurs through mechanisms other than thiol-mercury interactions, it is believed that the thiol moiety is responsible for the high selectivity of the product as well as the thoroughness of its action.

The emphasis in these studies has been on the scavenging of inorganic mercury; however, VDT cellulose was also tested for uptake of methyl mercuric ion. A solution of $CH_3{}^{203}HgCl$ ($5 \times 10^{-4}M$; 100 ppm of Hg) was passed through a column packed with 300 mg of VDT cellulose. Mercury determinations on fractions of effluent indicated that, as in the case of inorganic mercury, thorough removal of methyl mercuric ion is achieved up to the saturation point. The loading of the sorbent at the point of breakthrough was 63 mg of CH_3Hg^+ per gram of cellulose. Batchwise experiments confirmed that the molar capacity for methyl mercury parallels that for inorganic mercury under the conditions studied.

Repeated attempts to find a stripping agent that would remove mercury from loaded adsorbent failed. Among the agents investigated were aqueous solution of HCl, disodium EDTA, ethylenediamine, thiourea, alkaline sodium cyanide, and sodium sulfide. None of these methods succeeded in stripping more than $\sim$30% of the bound mercury.

The experiments described above were performed using VDT cellulose prepared from a commercial purified cellulose powder; however, material having essentially identical properties, including capacity for mercury uptake, was prepared from a pulp made in our laboratory from unbleached waste newspapers. The prospect of using waste cellulosic materials for the preparation of the VDT modification should be significant, in that it may permit economical one-cycle use of the material. If recovery of the mercury was necessary or desirable, this could be accomplished by ignition of the loaded adsorbent followed by condensation of the mercury vapor. In lieu of this, the loaded adsorbent might simply be compressed, encapsulated, and buried.

The compressibility of VDT cellulose probably renders it unsuitable for large-scale applications requiring high volumes, or for treatment of solutions containing large quantities of suspended particulates; however, the high efficiency of this product in removing even trace quantities of dissolved mercury suggests its potential utility as a final polishing agent for mercury-containing solutions. The innocuous nature of the product makes it a candidate for treatment of ingested mercury without concomitant depletion of other necessary metal ions.

No study was made to determine the rate of loss of activity of VDT cellulose; however, no reduction in the capability of the product to function as described was observed even after storage in a closed container for periods up to several months.

Acknowledgment

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Selective Absorption Tubes and Emission Technique for Determination of Ambient Forms of Mercury in Air

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■ Detection and determination of particulate mercury, methylmercury(II) chloride-type compounds, mercuric chloride-type compounds, elemental mercury, and dimethylmercury have been achieved using sequential, selective absorption tubes for separation and a dc discharge spectral emission type detector—a highly selective and sensitive device. By observation of the 253.65 nm Hg emission line intensity, a lower limit of detection of 0.01 ng Hg was obtained. Consequently, analyses at concentrations as low as 0.1–0.5 ng/m^3 for air samples of 0.1 m^3 or less could be obtained. The method has been applied to analysis of air in buildings. The preponderance of volatile mercury forms is elemental mercury, but substantial concentrations of mercuric chloride- and methylmercury(II)-type compounds were also detected.

Mercury is known to be involved in biological systems. It is methylated by methanogenic bacteria and is also apparently biochemically methylated in higher animals and in humans (*1*). The methylmercury(II) halide compounds are comparatively volatile as is elemental mercury, dimethylmercury, and mercuric chloride. Consequently, these compounds are suspected to be involved in a global cycle for the element, the evidence for which is increasing, but concerning which few data are available because of the lack of adequate analytical techniques. A better understanding of the environmental chemistry of mercury clearly requires the analysis of samples for the several types of mercury compounds present.

Elemental mercury is known to be a major environmental form, especially near geothermal areas and mercury ore deposits. It is likely the major form of mercury from coal burning and volcanoes (*2*). Elemental mercury in air may be determined directly by atomic absorption detection devices at concentrations as low as 15 ng/m^3 (*3*) and probably lower with modification to provide for collection of large samples. Atomic absorption, although widely used, does not detect the methylmercury(II)-type compounds or mercuric chloride–type compounds in air unless these forms are converted to elemental mercury prior to analysis. No techniques have been developed to date for the determination of methylmercury(II)-type compounds, mercuric chloride, or dimethylmercury at very low concentrations in air. Particulate mercury in air can be determined by analysis of filter pads (*4*).

A primary objective of this work has been to develop techniques for detection of suspected ambient levels (1–100 ng/m^3) of methylmercury(II)-type compounds, dimethylmercury, mercuric chloride–type compounds, elemental mercury and particulate mercury in air. Field applications have also been carried out to verify the suspected presence of the various volatile forms of mercury in air and to demonstrate the applicability of the technique. In addition to the applications reported here, an environmental analysis study has been conducted (*5*).

Since some prior information was available, the selection of the five forms of mercury to be analyzed was not entirely arbitrary. Elemental mercury and particulate mercury were known environmental forms of mercury. Dimethylmercury and methylmercury(II)-type compounds were selected as analytes because both can be biologically generated and are volatile forms of mercury. Mercuric chloride was selected as a model compound to represent any volatile inorganic mercury compounds. Methylmercury(II) chloride was selected as a model compound to represent all volatile methylmercury(II)-type compounds. The separation problem was solved using elemental mercury, dimethylmercury, and the model compounds, methylmercury(II) chloride and mercuric chloride. The separation scheme developed converts air-sampled mercuric compounds to mercuric chloride and methylmercury(II) compounds to methylmercury(II) chloride.

A dc discharge emission detection system described previously (*6–8*) was selected for use as the mercury detector because of its known high sensitivity and selectivity. In preliminary work this system had a lower limit of detection of 0.01 ng Hg. This gives a concentration limit of detection of 0.1 ng Hg/m^3 when 100-liter air samples are collected.

The use of sequential specific absorption tubes for the various mercury compounds sought was considered the best approach to detection because the same air sample could be analyzed for the several chemical forms of mercury sought. Developmental work was eventually successful in providing the specific absorption tubes needed and the technique necessary to their employment.

Sequential Specific Absorption Tube System

Specific detection of the volatile mercury forms was achieved based upon selective amalgamation or absorption and chemical reactions. The amalgamation of elemental mercury with gold, silver, and copper was first studied.

Silver wool was first tested as an absorber, but proved to be unsatisfactory. Mercury, no matter what the compound used, was incompletely and slowly removed from silver wool by heating. This was attributed to the diffusion of mercury into the silver wire mesh during and after sampling. The silver wire mesh packed into absorption tubes hardened after several uses resulting in sample chaneling—an undesirable characteristic. Silvered glass beads, 60–80 mesh, were found to be the best silver metal-type absorbers. The thin silver layer on the beads released absorbed mercury rapidly and quantitatively upon heating.

After the success with silvered glass beads it was decided to use gold-coated beads to obtain the same type of mercury absorption and to minimize the amount of gold used. Gold coating the 60–80 mesh glass beads was done by reducing auric chloride-coated beads with hydrogen gas at an elevated temperature. Mercury was readily absorbed by and released from (upon heating) gold-coated beads.

Absorption of mercury metal by the coated beads is apparently a rapid process. Sampling rates of 1.5 liters of air per minute produces a face velocity of 50 cm/sec in the 10-mm o.d. (8-mm i.d.) tubes. Since the sampling face velocity is approximately 100 cm/sec in the packed bead bed, sample residence time is 10-msec/cm length of bead bed. All elemental mercury was absorbed in the top 0.5–1.0 cm of the silver- or gold-coated glass beads. Dimethylmercury was absorbed in the top 1–2 cm of the gold-coated beads.

Dimethylmercury was not absorbed by copper or silver metal but was absorbed quantitatively by gold. Methylmercury(II) chloride is absorbed by silver metal but slowly volatilizes off from a silver metal surface when air is passed through it at 20–30°C for more than 5–10 min.

Dimethylmercury and methylmercury(II) chloride are demethylated to elemental mercury upon removal from metallic gold by heating. Methylmercury(II) chloride is demethylated when removed from silver by heating. This was found in experiments using atomic absorption mercury detector at the outlet end of heated metal absorption tubes containing the alkyl mercury compounds of interest.

It was apparent after this initial work that although a silver–gold two-stage system with a filter would separate dimethylmercury from the other forms, methylmercury(II) chloride leakage off from silver would lead to erroneous results, and no other value for mercuric chloride, elemental mercury, or methylmercury(II) chloride individually could be obtained. The separation of methylmercury(II) compounds from mercuric chloride–type compounds and retention onto a specific absorption tube for each was necessary. This separation proved to be the most difficult problem to solve because mercuric chloride and methylmercury(II) chloride exhibited similar volatilities in the absorption tube systems studied. It was eventually found that a column 3% SE-30 on 45–60 mesh Chromosorb-W HCl, vapor treated, retains mercuric chloride (possibly as a hexachloromercurate complex) while passing methylmercury(II) chloride, elemental mercury, and dimethylmercury. Methylmercury(II) bromide or iodide or acetate or other volatile forms are probably converted to methylmercury(II) chloride on the HCl-treated Chromosorb-W tube. Mercuric chloride, bromide, nitrate, and acetate were retained in approximately the top 4 cm of the Chromosorb-W (HCl) columns. Columns 7 cm long were used.

A nonsiliconized Chromosorb-W column initially treated with NaOH to 0.15 meq/g of column packing quantitatively absorbed methylmercury(II) chloride while quantitatively passing elemental mercury and dimethylmercury. Methylmercury(II) chloride is probably converted to the less volatile hydroxide by the alkaline column. Methylmercury(II) chloride was retained in approximately the top 3 cm of the Chromosorb-W (NaOH) column. Columns 6 cm long were used.

A Gelman Co. glass fiber filter, Type A, was used as a particulate filter to complete the stack of absorption tubes. Type A filters have a minimum 99.7% retention test for particles as measured by a dioctyl phthalate penetration test. By assembling the absorption tubes in the appropriate order and pumping air through them, mercury in air was separated into five forms. Table I summarizes the composition of the specific absorption tubes and their function in accomplishing this. Analyses for the five forms of mercury may be achieved by analysis of the individual sections of the absorption tube stack.

Experimental

Instrumentation. The mercury analysis apparatus consisted of a quartz discharge chamber of the design shown in Figure 1 attached to a conventional recording spectrometer system described previously (7). Helium carrier gas was passed through a silvered glass bead trap to remove mercury and then through the sampling tube being analyzed, or a sample transfer tube, prior to the discharge chamber. Mercury on the sampling tubes was driven off (deamalgamated) by heating with a Nichrome wire heater coil. Volatilized mercury was detected in the dc discharge by observing the 253.65-nm Hg emission line. The magnitude of the signal observed for a given amount of mercury is dependent upon slit width settings, photomultiplier voltage, amplifier gain, and the voltage range of the strip chart recorder. To a lesser extent the dc discharge power level influences the recorded signal. All of these instrument parameters were set to provide for a noise level of 1–2% full scale on the recorder for the highest sensitivity and a factor of 10 less sensitivity for larger samples. Adjustments in sensitivity can be made during calibration with standard samples of mercury vapor on gold sample transfer tubes. The scanning capability of the detection system permits verification of detected materials as mercury by scanning during the appearance of signal peaks.

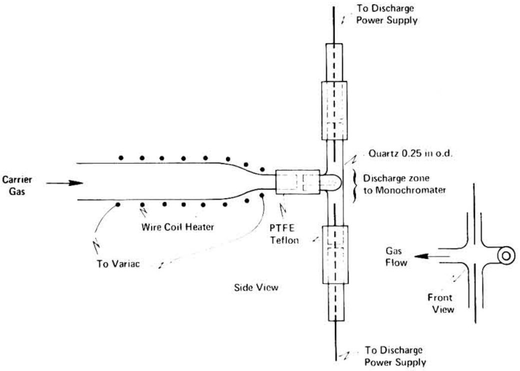

Figure 1. Detector design

Table I. Specific Absorption Tubes for Mercury in Air

Tube order no.	Composition	Function
1	Glass wool filter, preheated to blank	Removes some particulate, passes other mercury forms
2	Chromosorb-W, 45–60 mesh, 3% SE-30	Removes $HgCl_2$, particulate which passes the filter; passes CH_3HgCl, $(CH_3)_2Hg$, and elemental Hg
3	Chromosorb-W, 45–60 mesh treated with 0.05M NaOH	Removes CH_3HgCl; passes elemental Hg and $(CH_3)_2Hg$
4a	Silvered glass beads	Removes elemental Hg; passes $(CH_3)_2Hg$
4b	Gold-coated glass beads	Removes $(CH_3)_2Hg$

Preparation of Absorption Tubes and Filter Holder. Design of the absorption tube stack sections and sample transfer tube is shown in Figure 2. All tubes except the filter holder and filter analysis tube were constructed of quartz.

Filter holders were constructed of borosilicate glass. Filter circles were cut to the 10-mm o.d. size, from larger filter circles, fired in the filter heater to remove any mercury by heating to 500–550°C and then placed in the filter holder. Less than 0.5 ng of Hg was found on each of the glass wool circles in the heat treatment. Filter circle blanks were zero after heating.

Absorption tubes, Figure 2, were constructed of 10 and 6 mm o.d. quartz tubing. The large section was 13 cm long and the small end 3 cm long. Quartz was used to permit rapid cooling of tubes after heating by immersing them in water while still passing carrier gas through them. Glass wool was used to retain Chromosorb-W or coated glass beads. Chromosorb-W was preheated to 450–500°C for 30 min after packing into the quartz absorption tubes but prior to siliconizing or treatment with NaOH. This removed considerable mercury and minimized mercury background in later use.

Chromosorb-W (HCl) tubes were packed to a 7-cm length. Chromosorb-W was siliconized by adding a piece of SE-30 weighing approximately 60–70 mg to the top of the packed tube and then, while passing helium carrier gas, slowly heating the tube with a wire coil heater until the SE-30 melted and vaporized onto the Chromosorb-W. Excess silicone was allowed to vaporize off the column by heating for 10–20 min at approximately 300°C. Excess silicone was removed from the tip of the tube. Siliconized Chromosorb-W was treated with 10 cc of HCl vapors from a concentrated hydrochloric acid reagent bottle. Chromosorb-W (HCl) columns thus prepared were retreated with HCl vapor after 8–10 uses.

Chromosorb-W (NaOH) tubes were packed to a 6-cm length. Sodium hydroxide treatment consisted of adding sufficient 0.05 NaOH to completely wet the Chromosorb-W packing and then drying by heating while passing helium carrier gas through the column. These tubes could not be retreated with NaOH after several uses because it led to excessive leakage of methylmercury(II) chloride. Chromosorb-W (NaOH) tubes were discarded after failure in performance tests with methylmercury(II) chloride.

Silvered glass beads were prepared by the conventional silver nitrate, ammonia, and formaldehyde silvering technique. The 45–60 mesh glass beads were 90–100% silver coated as determined by microscopic inspection. The silver coating was 13.8% silver by weight on the beads.

Gold-coated glass beads were prepared from gold metal. Gold metal was dissolved in aqua regia and treated with concentrated HCl to remove nitrates and convert all dissolved gold to auric chloride. Hydrochloric acid–washed glass beads were then added. The auric chloride–glass bead mixture was slowly evaporated to near dryness while stirring. The semisolid mass of auric chloride and glass beads was packed into a glass tube and heated in a small tube furnace while passing helium or nitrogen carrier gas through the tube. Hydrogen gas was added through a "T" into the carrier gas and a small amount of auric chloride was evolved during the process. The resulting glass beads were approximately 50–70% surface coated with gold. The beads were approximately 20% gold by weight; 12 grams of gold metal were used to coat 50 grams of glass beads. Sample transfer tubes, gold bead tubes, and combination silver bead–gold bead tubes were prepared by simply packing the quartz tubes with 1.5–2.0 cm of silvered or 2–3 cm of gold-coated beads and then carrying them through a blanking treatment. These tubes should be

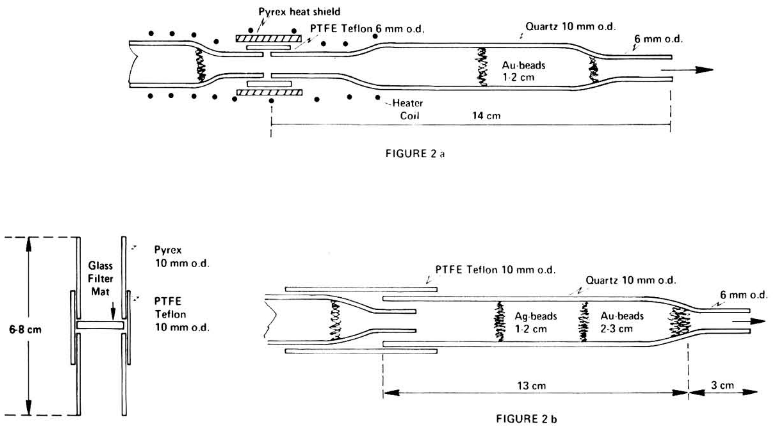

FIGURE 2 a

FIGURE 2 b

FIGURE 2 c

Figure 2. Absorption and sample transfer tube designs

(*a*) Sample transfer tube (attached to Chromosorb-W with heater coil). (*b*) Silver–gold absorption tube (shows attachment to stack). (*c*) Filter holder

heated to 550–650°C while passing air through them occasionally to remove carbon deposited from decomposition of silicones or other organic matter. The performance of the transfer tubes should be periodically compared to that of a freshly prepared silver-coated bead tube to detect the need for the heating in air treatment.

Blanking the Absorption Tubes. All tubes must be blanked prior to use. Gold-coated and silvered beads were heated to approximately 500°C for 3–6 min while passing helium carrier gas through the tube. Several heating treatments were required to blank newly prepared tubes. Once properly blanked, no residual mercury, less than the limit of detection, was left on either the gold or silver tubes after normal use and analysis. Any of the tubes treated with more than 50–100 ng of mercury compounds usually required two or more heatings and "reverse firing" to obtain a satisfactory blank condition. Reverse firing consisted of heating the large end of a sampling tube while passing helium in a direction reverse of that of sampling.

Both Chromosorb-W tubes slowly build up blanks of 0.01–0.04 ng of Hg per day after prior blanking. Consequently, it is necessary to blank these tubes prior to use, with storage over two days not recommended. Blanking was accomplished by twice carrying out the analysis procedures for the Chromosorb-W tubes. The first heating was simply to air, and the second was into a sample transfer tube to check on the blank level of the absorption tube.

Air Sampling Procedure. Samples were drawn through the assembled sample stacks by small pumps at flow rates from 0.75–2 l./min. Flow rates were monitored by rotameters calibrated by use of a wet test meter. Sample volumes of 20–200 liters were collected depending upon the expected mercury-in-air concentrations. Stacks must be calibrated for flow rate for best accuracy in sample volume.

Parafilm, American Can Co., was used to close the ends of sampled stacks when storing prior to analysis. Samples were stored no longer than 18 hr prior to analysis, although there has been no indication of sample deterioration on standing over as long as four days. Silver- and gold-coated bead tubes did not build up any background mercury or lose a mercury sample when stored for at least one week. Parafilm gave satisfactory performance in preventing dust from entering the prepared tubes. No diffusion of mercury through the Parafilm was noted over at least two days in our tube use and storage area which analyzed 100 ng of Hg/m^3.

Tube Analysis Procedure. After air sampling, stacks were disassembled and treated in the following manner. The particulate filter was dropped without handling directly into an empty, blanked Pyrex tube of the same size as the silver–gold sampling tubes. This tube was assembled with a heating coil around it directly attached to the dc discharge detector. After air was removed by passage of carrier gas, the discharge was turned on and the tube heated at a rapid rate by passing the ac current through the heating coils by means of an autotransformer. Mercury compounds on the particulate filter were detected as a single peak during thermal treatment. The glass filters were heated to approximately 550°C during analysis.

Chromosorb-W (HCl) absorption tubes and the Chromosorb-W (NaOH) tubes were analyzed in a similar manner. These tubes were attached to a blanked, double-small-ended gold absorption as shown in Figure 2. Chromosorb-W (HCl) tubes were heated for 12 min, to approximately 250°C, by an autotransformer-controlled ac voltage. Mercuric chloride was driven off onto the gold tube during this heating. Care must be exercised to avoid heating to the point at which all SE-30 is also driven off the absorption tube.

Chromosorb-W (NaOH) tubes were heated to approximately 300°C for 6 min. The double-ended gold sample transfer tubes were subsequently analyzed by heating them to 470°C with helium carrier gas while attached to the detector at the downstream end. Mercury compounds thus pass through the entire length of the double-ended tube prior to detection in the dc discharge detector and facilitates separation of mercury from water or other volatile organic materials, if present. Figure 3a is a typical response pattern for a gold sample transfer tube.

The silver–gold absorption tubes were analyzed in two steps. Connected to the detector at the gold end, the gold section was heated first, driving off any absorbed dimethylmercury. The electrical contact was then moved so that

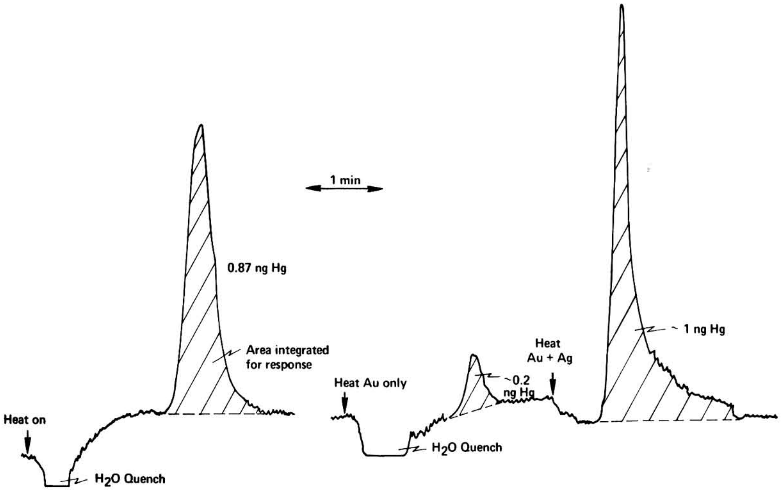

FIGURE 3 a

FIGURE 3 b

Figure 3. Typical response recordings

(*a*) Sample transfer tube. (*b*) Silver–gold absorption tube

both the silver and gold tubes were heated simultaneously. This removed all absorbed mercury metal on the silver column. Figure 3b gives a typical response pattern.

Results of all five analyses were then used, with appropriate calibration curves and sample size data, to calculate the amount of mercury present of each of the detected types.

Calibration. All mercury forms analyzed except possibly the particulate are eventually detected as elemental mercury by heating analyses trapped on gold-coated or silvered beads. The rate of desorption had no influence on the detection response, but low heating rates spread out mercury response peaks. Calibration may most easily be obtained by use of saturated mercury metal vapor in air. A gas-tight 0–0.5-ml syringe was used to sample mercury vapor above a metal pool in a test tube fitted with a rubber septum. The test tube was kept in a water bath at room temperature with the temperature measured to ±1°C. Vapor pressure data were used to calculate the amount of mercury in air delivered from the syringe onto silver or gold tubes used in instrument response calibration.

Methylmercury(II) chloride solutions in 95% ethanol, dimethylmercury in chloroform, and mercuric chloride in HCl acidified (2 ml/l.) aqueous solution were also used as standards. Methylmercury(II) chloride, mercuric chloride, and dimethylmercury vapor samples were unsuitable for calibration by syringe injection. Reproducibility of vapor injection was extremely poor. Methylmercury(II) chloride vapors contained a small amount of dimethylmercury. No difference was observed in the retention of vapor samples as compared to solution samples of mercuric chloride, dimethylmercury, or methylmercury(II) chloride. Laboratory grade helium from Air Reduction Co. was satisfactory for use as a carrier gas without cryogenic purification.

Reagents and Solutions. Dimethylmercury obtained from Eastman Kodak Co. was used without purification. Methylmercury(II) chloride obtained from Research Organic/Inorganic Chemicals Corp. was recrystallized once from absolute alcohol. Mercuric chloride obtained from J. T. Baker Co. was used directly. Chromosorb-W and silicone SE-30 were obtained from Varian Aerograph Corp., Walnut Creek, Calif. Dimethylmercury solutions at 1000 ppm prepared in chloroform solvent were stable for several weeks. Methylmercury(II) chloride solutions at 250 ppm in chloroform were stable for at least three months. Solid methylmercury(II) chloride stored in an Erlenmeyer flask as a vapor sample source did decompose to an extent, giving dimethylmercury and mercury metal vapors. Mercuric chloride solutions at 100 ppm made up in acidified distilled water were also stable for at least eight weeks. Small amounts of mercury metal, approximately 1–2% of the total present, were found in mercuric chloride solutions upon standing several weeks.

Results and Discussion

Response and Limits of Detection. All mercury compounds give equivalent responses in the analysis system when based upon mercury content. A typical response curve prepared using both methylmercury(II) chloride (three standards) and elemental mercury (seven standards) has the following regression line over the range 0.1–5 ng of Hg; all error is assumed in the response area.

$$\text{Area (cm}^2) = 2.367\ (\pm 0.066\ \text{std dev})(\text{ng Hg}) + 0.0234\ (\pm\ 0.178\ \text{std dev})$$

Response of the instrumentation changes slowly over its period of use, owing, in part, to a slow buildup of material on the detector walls. Small amounts of silicone from the Chromosorb-W (HCl) tubes are probably responsible. Daily calibration is recommended. Response linearity has been noted over the range 0.02–20 ng.

Limits of detection for the instrumentation, calculated from response area and noise area data, were 0.01–0.02 ng of Hg per sample. Limits of detection for particulate mercury, elemental mercury, and dimethylmercury are the same on a per-sample basis. Nevertheless, because of low blank values, 0.03–0.05 ng of Hg per sample, found for some of the Chromosorb-W tubes, the concentration limit of detection is somewhat poorer for mercuric chloride- or methylmercury(II)-type compounds in air. These limits should be near 0.3–0.5 ng/m^3 if 100-liter air samples are taken.

Performance of Separation Tubes. The detection of small amounts of mercury on the specific absorption tubes requires that sample tube blanks be as small as possible, preferably below the limit of detection. Numerous tests of the silver and gold tubes indicated they had blank values less than the limit of detection, 0.01 ng, even on storage up to seven days. Chromosorb-W (NaOH) and Chromosorb-W (HCl) tubes did exhibit blank values which slowly increased with time of storage between use. Typical blank values for the 11 tubes prepared for survey work were: Chromosorb-W (NaOH), average, 0.012 ng ± 0.012 std dev (31 values); and Chromosorb-W (HCl), average, 0.024 ng ± 0.024 std dev (32 values) per day of storage.

An accurate speciation of mercury depends upon accuracy in retention and removal of each form of mercury on its specific absorption column. Mercuric chloride, methylmercury(II) chloride, elemental mercury, and dimethylmercury were used in numerous tests of the stacks both during and after their development. Each stack was tested for mercuric chloride and methylmercury(II) chloride separation after initial preparation. Quality control is maintained by a 20–30% random check on a group of stacks just prior and after each environmental analysis study. Quantitative retention of methylmercury(II) chloride was used in these quality control tests because leakage (poorer than 80% retention) of the Chromosorb-W (NaOH) tubes was the most frequently encountered malfunction. Failure to quantitatively retain methylmercury(II) chloride was observed in approximately 10% of the tubes after two to three uses. An average life of approximately five uses was experienced before failure of methylmercury(II) chloride retention tests.

Table II. Recovery of Mercuric Chloride and Methylmercury(II) Chloride from Chromosorb-W Tubes

Sample, μg	1st heating,[a] %	2nd heating, %	3rd heating, %
Methylmercury(II) Chloride from Chromosorb-W (NaOH)			
3.03	93.6	5.2	1.2
3.03	95.9	2.8	1.4
Mercuric Chloride from Chromosorb-W (HCl)			
2.00	100	—	—
2.00	96.8	3.2	—
4.00	100	0	—
1.00	98.9	1.1	—
1.00	100	0	—

[a] See procedure.

Quantitative removal of mercuric chloride and methylmercury(II) chloride from Chromosorb-W (HCl) and Chromosorb-W (NaOH) during heating is occasionally determined by repeated heating periods. Table II gives some typical results. This type of study is necessary when first using a Nichrome wire heater to determine if tubes are being sufficiently heated.

Since ambient air was to be analyzed it was recognized that performance over a range of temperature and humidity values needed to be investigated. Table III gives performance data for the separation of the mercury forms at some of the temperature extremes available at our location. Attempts to use a cold room were unsuccessful because of very high elemental mercury levels present, a common laboratory problem in the development of sensitive methods for mercury.

Dimethylmercury and elemental mercury are not absorbed by the Chromosorb-W columns even at the lower

Table III. Performance Tests of Absorption Tubes

		Percent of Hg found on each tube				
Test conditions	Sample compn	Chromosorb-W, HCl	Chromosorb-W, NaOH	Ag beads	Au beads	% total Hg recovered
33°C 85% rh 30 min pump	MC, 2 ng MMC, 2 ng	48	48	2		100
31°C 30 min pump	MMC, 2 ng	6	88	6	0	111
31°C 30 min pump	MMC, 2 ng	0	97.6	2.4	0	101
31°C 60 min pump	MMC, 2 ng	9	8	4	0	
30°C 30 min pump	MMC, 2 ng	2.4	95.2	2.4	0	103
33°C 68% rh 120 min pump	MMC, 2 ng	1.5	97	1.52	0	100
29°C 86% rh 120 min pump	None (blank) Au—bead filtered Air	<0.01 ng	<0.01 ng	<0.01 ng	<0.01 ng	—
33°C 120 min pump	MC, 2.86 ng	94	6	0	0	
26–30°C 10 hr	MC, 2.86 ng	47	9	—	44[a,b]	100
34.5°C 58% rh 120 min pump	MC, 2.86 ng	90	—	—	10[a]	100
		94	—	—	6[a]	100
		94	—	—	6[a]	100
12.2°C 93% rh 5 min pump	Hg° vapor, 2.6 ng	0	0	100	0	100
		0	0	100	0	100
10.1°C 5 min pump	DMM, 2.1 ng	0	0	0	100	100
		0	0	0	100	100
2°C 2 min pump	DMM, 2.1 ng	0	0	0	100	100
2°C 2 min pump	Hg° vapor, 3 ng	0	0	100	0	100
3–4°C 37 min pump	MMC, 2.02 ng	20	80	0	0	100
		15	85	0	0	100

[a] Sum of silver and gold columns. [b] Slow reduction of $HgCl_2$ over long pumping times produces elemental Hg.
— Indicates column not used; rh, relative humidity.

Table IV. Results of Air Analyses in Buildings

			Ng/m³					
Date	Sample	Cubic meters of air sampled	$Hg_{(p)}$	Hg(II)	MMC	Hg°	DMM	Σ
9/24/73	USF chem lecture hall, before class	0.0175	0	8.5	36	400	0	445
	Gold–Co column	0.036						460
10/2/73	USF chem lecture hall, before class	0.0175	2.9	42	12	310	0	367
	Gold–Co column	0.036						351
10/2/73	Same room after class	0.0175	0	12	25	500	12	549
	Gold–Co column	0.036						557
10/4/73	USF chem lecture hall, before class	0.0175	0	31	14	390	0	435
	Gold–Co column	0.036						600
10/4/73	Same room after class	0.0175	0	18	15	120	0	153
	Gold–Co column	0.036						155
10/8/73	House no. 1 bathroom	0.015	—	43	4.4	200	0	247
	House no. 1 bedroom	0.015	—	0	10	37	0	47
	House no. 1 living room	0.015	—	2.7	23	110	0	136
	House no. 1 kitchen	0.015	—	12	0	888	0	100

temperature and short sampling time. These rapidly pass through the Chromosorb-W columns. Tests with both dimethylmercury and elemental mercury at 22°C indicate that both are completely absorbed in the upper 1 cm of the metal-coated glass bead columns. Many field tests at temperatures up to 33°C and over sampling times up to 2 hr have shown no leakage of absorbed elemental mercury off of silver onto the gold-coated bead column section.

Mercuric chloride is over 90% retained on the Chromosorb-W (HCl) column. A similar retention of methylmercury(II) chloride on the Chromosorb-W (NaOH) column was obtained. The most severe test of the Chromosorb-W columns are indicated by the 27–33°C and high humidity data with a 2-hr sampling period. Mercuric chloride and methylmercury(II) chloride do not leak off onto other columns even at these temperatures. Also important, methylmercury(II) chloride readily passes through the Chromosorb-W (HCl) at 3–4°C. In this test some retention of methylmercury(II) chloride on the Chromosorb-W (HCl) was noted so lower temperatures could further restrict its separation from mercuric chloride.

Reliability of analysis of real samples was studied by comparing a total mercury value from the absorption tube stack with a total mercury absorbing column (a gold bead column). The single tube and the stack were sampled at the same place and over the same period of time to avoid time and location fluctuations in mercury concentration. This is best done by mounting the intake end of the single tube and stack so that they are no more than 1 cm apart (or touching tip-to-tip). Gold bead tubes are the only type capable of giving total mercury in air because dimethylmercury is not absorbed by silver and methylmercury(II) chloride is not quantitatively absorbed. Data in Table IV give analysis results for mercury in air in buildings. A comparison of total mercury absorbed by a single gold tube and total mercury on an absorption tube stack is available.

Repeatability of the stacks was demonstrated by simultaneous analyses of two or three stacks. Differences in results are due, in part, to sample flow rate differences and, in part, to uncertainties in tube blank values.

Limitations and Interferences. No current method exists for the detection of specific mercury compounds at the 1-20 ng/m³ range we encountered. Consequently, it was not possible to directly compare results of this with another known method. Our verification of identity of the known mercury forms depends largely upon performance of the model mercury compounds in the analysis system. Compounds obtained from the absorption tubes after environmental sampling did contain mercury as determined from spectral scans of peaks obtained during analysis. Performance in the analysis of environmental samples also supports the qualitative aspects of the method. Methylmercury(II)-type compounds were found at suspect locations. For example, bell jars were used to trap vapors from a lake exhibiting methylation of heavy metals (*9*). Methylmercury(II) compounds and dimethylmercury were in the air trapped above the water. Analysis of water from this lake by the membrane probe method (*7, 8*) indicated 20–30% of the mercury present in water was in the form of methylmercury(II)-type compounds. Methylmercury(II) compounds and dimethylmercury were noted in trapped air over the ground deliberately treated with mercuric chloride (*5*).

Identification of mercury compounds is an operational definition in the case of mercuric chloride-*type* compounds and methylmercury(II)-*type* compounds. Although not tested, the more volatile organomercury halides such as ethylmercury(II) chloride should be found on the Chromosorb-W (NaOH) tube. Phenylmercury(II) chloride, a much lower volatility compound, remained quantitatively on the Chromosorb-W (HCl) column where it was placed in retention tests.

Hydrogen sulfide and sulfur dioxide (20-ml samples) injected by syringe into the sampling stacks did not constitute an interference in the analysis of any of the mercury forms. Silver on the glass beads is slowly converted to the sulfide after long use but still removes elemental mercury from air samples efficiently. Silver beads in the silver-gold columns were generally replaced after 3–6 months of intermittent use.

Water vapor is not a serious interference. Silver–gold absorption tubes and wet absorption tubes were dried before heating to analysis by first heating at a low temperature.

A possible limitation is reaction between some of the mercury compounds during sampling. For example, mercuric chloride and dimethylmercury are known to react:

$$HgCl_2 + (CH_3)_2Hg \longrightarrow 2CH_3HgCl$$

The possibility of this reaction being an interference was tested. Samples of 1 and 2 ng of mercuric chloride were placed on the Chromosorb-W (HCl) column at 22°C. Samples of 2 ng of dimethylmercury vapor were then passed through the stacks with a clean air flow of 1.5 l./

min for 4 min. All of the dimethylmercury was recovered on the gold section. No methylmercury(II) chloride was produced. Dimethylmercury is rapidly drawn through all of the absorption tube sections thus allowing little time for reaction.

A similar experiment was conducted with 1 ng of mercuric chloride and 3-ng samples of elemental mercury. No loss of mercury metal was noted indicating no reaction between it and mercuric chloride.

No indication of reaction has been noted between dimethylmercury and elemental mercury or between mercuric chloride and methylmercury(II) chloride.

A limitation of the method is the necessity of considerable care in handling of the absorption tubes prior and during analysis so as to avoid mercury contamination. The authors found it necessary to do the analytical work in an office area (100 ng of Hg/m^3 in air) to avoid contamination in their usual laboratory area (300–800 ng of Hg/m^3). Handling of mercury compounds and spilling the more concentrated stock solutions also should be avoided.

Finally, for the most accurate work, occasional performance tests of the Chromosorb-W columns and blank determinations must be made.

Applications. This method has been used to study the distribution of forms of mercury out of doors (*5*) and in houses and buildings. Data on the distribution of mercury in a large lecture hall and in the home of one of the authors (RSB) are given in Table IV. Elemental mercury is the major form found but methylmercury(II)-type compounds are also found. Total mercury in buildings and homes is much higher than outside ambient mercury in air (3–6 ng/m^3), also noted by Foote (*10*) but without speciation data. Although elemental mercury is the predominant mercury form found, significant amounts of the methylated mercury compounds are also found.

With reasonable care, this method is suitable for the analysis of ambient forms of mercury in air down to the 0.5-ng/m^3 concentration. Analyses require approximately 0.5 hr per stack of absorption tubes and sampling times up to 2 hr for the lower ambient concentrations of mercury. It is not a continuous analysis method. Nevertheless, information on the distribution of volatile forms of mercury in air can be obtained in a study area, something heretofore unavailable. Further work on the use of the technique in environmental chemistry studies is under way.

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Distribution of Atmospheric Mercury Species Near Ground

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■ A recently developed technique makes possible the routine analysis of atmospheric samples for "particulate" and "volatile" mercury. The "volatile" fraction can be analyzed for several chemical species. This work presents the results of some Tampa Bay area analyses and diurnal studies of atmospheric mercury speciation. The mercury in air in the area investigated was primarily "volatile" (>90%) and was composed of significant proportions of mercury(II)-type compounds, methylmercury(II)-type compounds, and elemental mercury. Dimethylmercury was rarely observed. Results were quite variable suggesting a variety of sources and irregular wind transport processes. The data indicate that background mercury concentrations and the percentage distribution of mercury species in air in a local area may be established by mercury emanations from the ground or from adjacent bodies of water.

Mercury is a prominent environmental pollutant with a variety of natural and man-made sources (*1–6*). Because of the high volatility of elemental mercury and some of its compounds, it is widely dispersed in the earth's atmosphere. Nevertheless, few data are available describing its distribution between volatile and particulate fractions and no data exist relating to the chemical forms of mercury in air. The large number of volatile and stable organic and inorganic mercury compounds, as well as the apparent extensive involvement of mercury, in biological systems makes it imperative that we obtain speciation data in order to acquire an adequate understanding of the geochemical cycling of mercury, the extent to which man is altering that cycle, and the degree to which toxic mercury compounds pose an environmental threat.

While the concentration of total mercury in terrestrial air free of obvious pollution is generally in the range of 1–10 ng Hg/m^3 (*7–9*), the total range of atmospheric mercury values reported in the literature is almost 10^7! Williston observed a moderate variation, two- to fivefold, in atmospheric mercury at a single location during the course of a windy day in the San Francisco Bay area. This probably reflects wind transport from various local sources. The burning of fossil fuels, smelting operations, and general industrial activity all contribute mercury to the air, and Williston noted that elevated mercury concentrations coincided with high smog levels. A number of natural sources also release mercury. Measurements in air over the Hg-mineralized area near Ord mine in Arizona showed up to 600 ng Hg/m^3 (9). Neville (*10*) reported levels of over 10^6 ng Hg/m^3 in a mercury mine. In Hawaii and Iceland, studies indicate that volcanic activity increases local mercury in air by as much as 100,000-fold over the ambient levels mentioned above.

Mercury metal, mercuric oxide, and mercury halides are all potential chemical forms of mercury emanations from both natural and man-made sources. A wide range of inorganic mercury compounds can be methylated by biological systems, and methylation is known to occur in soil, sediments, and aquatic organisms (*11–13* and others). This may lead to the release of dimethylmercury and methylmercury(II) compounds to the atmosphere. Evidently biodemethylation reactions are also widespread (*14* and others). Further, dimethylmercury reacts with mercuric chloride (disproportionates) to produce methylmercury(II) chloride.

An extremely sensitive analytical technique for the several chemical forms of mercury at ambient levels in the atmosphere has been developed. Details of the analytical methods are given elsewhere (*15*). We present here the results of some limited Tampa Bay area survey studies and diurnal studies. The occurrence and distribution of particulate mercury [$Hg_{(p)}$], defined as that portion of the total retained by a Gelman Instrument Co. Type A glass fiber filter, mercury(II)-type compounds [Hg(II)], methylmercury(II)-type compounds (MMC), mercury metal (Hg°), and dimethylmercury (DMM) are reported.

Experimental

Samples of air were drawn through a connected series of 10-mm quartz tubes containing selective absorbers for the various chemical species of atmospheric mercury. The first component is a Gelman Instrument Co. Type A glass fiber filter to retain "particulate" mercury. The "volatile" mercury species, which pass this filter, enter a tube containing 45–60 mesh Chromosorb-W which has been siliconized (5% by weight SE-30 methyl silicone) and then treated with HCl vapors. This acid-washed column retains Hg(II)-type compounds and passes other volatile mercury forms. Beneath this is a second Chromosorb-W column treated with sodium hydroxide to retain methylmercury(II)-type compounds while passing Hg° and DMM. Mercury metal is collected by forming an amalgam with silver on silvered, 60–80 mesh glass beads. Dimethylmercury passes through the silver and is retained by a column of glass beads coated with gold. In the development of the series of selective absorption tubes (speciation stacks), mercuric chloride and methylmercury(II) chloride were used as the "model" compounds for, respectively, mercury(II)-type and methylmercury(II)-type compounds. [In validating the analysis technique, mercury compounds other than the "model" types were also tested (*15*).] The reader is reminded that the determination of mercury speciation in this study is based on an operational definition. Consequently, any mercury from environmental samples on the Chromosorb-W (NaOH) tube is *called* methylmercury(II) type. Mercury found on the Chromosorb-W (SE-30, HCl) tube is *called* mercury(II) type. A 2-cm gold-coated glass bead column is used when measurements of total mercury only are required since gold will amalgamate with all of the above-mentioned mercury compounds.

The components of this stack are connected together with 1.0 cm of PTFE Teflon sections and taped to ensure a leakproof fit. For sampling, the speciation stack was fitted into a pump trap—a short column containing silvered glass beads to protect against back diffusion from the pump—and air was drawn through the stack by means of a small diaphragm pump which created a vacuum of about 25 in. of Hg. Air flow through the stack was about 1.5 l./min and was monitored by means of a rotameter inserted between the pump trap and the pump. Calibrations of flow rate through the speciation stacks were made with a Precision Scientific Co. wet test meter. Corrections for temperature and water saturation were made in accordance with ASTM test #D 3195-73.

The mercury collected by the various components of the speciation stack was analyzed by dc discharge emission spectroscopy (*16, 17*). Sections of the speciation column were placed in line with the helium carrier gas and heated to desorb or deamalgamate the mercury they contain. Mercury was swept into the discharge tube, excited by a helium plasma, and the Hg emission line at 253.65 nm was observed in a conventional spectrometer, photomultiplier, amplifier, and recording system. Standardization was achieved by the use of 100–500 μl samples of air saturated with Hg° vapor at a known temperature. The noise-limited limit of detection of this system is approximately 5×10^{-12} gram of Hg.

Blanks for the various sections of the speciation stack vary. The glass fiber filters for particulate collection were prefired before use and thereafter exhibited blank values of less than 5×10^{-12} gram of Hg. The gold tubes had similar values. Blanks for the silvered glass bead columns, base-treated Chromosorb-W, and acid-washed Chromosorb-W tubes averaged <0.01 ng, 0.012 ± 0.012 ng (1 σ), and 0.024 ± 0.024 (1 σ) ng of mercury, respectively.

The analytical uncertainty in a given analysis is ±0.01 ng of Hg. However, the calculations of concentration in environmental samples also include uncertainties in the flow rate of air through the speciation stacks. This uncertainty is ±6% (1 σ), estimated from flow rate measurements (at a single temperature) on six separate speciation stacks. Thus, the analytical precision at one standard deviation was about ±6% for $Hg_{(p)}$, Hg°, and DMM. For the Hg(II) type and the MMC type, there were 0.13-ng/m^3 and 0.07-ng/m^3 uncertainties (1 σ), respectively, for a 2-hr sampling owing to blank variations, in addition to the 6% uncertainty in the volume of air sampled.

Environmental Sampling and Results

The chemical speciation of atmospheric mercury was studied as a function of local geographic variation as well as diurnal variation at a single location. Figure 1 shows the location of sampling stations on a grid that we established for periodic surveys of the Tampa metropolitan area. It includes stations near industrialized sites (6, 8, 9, 11), several locations adjacent to upper Tampa Bay (7, 8, 9, 10), an urban residential area sampled 35 meters from the center of an interstate highway (3), several suburban sites (1, 2, 4, 5), and a rural station (11). Surveys of this grid were not entirely synoptic, owing to problems of logistics and varying pumping times, but were generally completed within a 6-hr period, after which the speciation stacks were returned to the laboratory for analysis.

When an air sample was collected, tip of the speciation stack was about 1 meter above ground level. At station 6 the ground surface was concrete pavement, at stations 9 and 11 it was gravel, the samples at station 7 were collected over water, and at the other locations the ground cover was grass. At all stations, the field apparatus was located 10 meters or more away from any buildings. At several locations it was possible to plug the pumps directly into 110-V ac outlets via extension cords, but at others a 12-V marine battery and inverter provided power. While tests showed no significant mercury emanations from the diaphragm pumps, they were placed about 2 meters downwind of the sampling stack as a precautionary measure. Additionally, both ends of the speciation columns were kept sealed with Parafilm before and after sampling to prevent diffusion of mercury from the atmosphere into the sampling tubes, and to keep out dust.

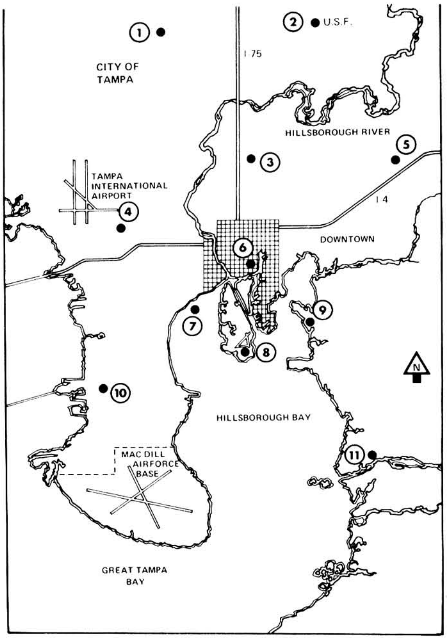

Figure 1. Location of air sampling stations in Tampa metropolitan area

Table I shows the results of two surveys of the Tampa area made on August 3 and November 3, 1973. The distribution of total mercury over the sampling grid is highly variable, ranging from 9–300 ng/m^3 (mean = 66) for the August 3 sampling, and from 2–15 ng/m^3 (mean = 6.5) on November 3. In both of the surveys reported here, as well as previous partial surveys, the highest mercury levels were found at the southern stations. This is particularly true for station 8 (Davis Island), adjacent to a heavily industrialized area, immediately to the east, and surrounded on three sides by Hillsborough Bay—one of the most polluted areas of Great Tampa Bay. The distribution of the individual mercury species was also quite variable except for DMM which did not appear to form a significant portion of the atmospheric mercury in the area surveyed. At times, each of the species $Hg_{(p)}$, Hg(II) type, MMC type, and Hg° made up over 60% of the total mercury.

When we consider concentration of the various mercury forms, certain consistencies in the survey results are also evident. On a given day "particulate" mercury and mercury metal were considerably more uniformly distributed than were either mercury(II)-type or methylmercury-type compounds. Nevertheless, while mean values of Hg° in the Tampa area were not significantly different on August 3 and November 3, the "particulate" fraction averaged about 4 ng/m^3 on the former date but only 0.1 ng/m^3 on the latter. This difference in "particulate" mercury corresponds to a difference of a factor of two in the concentration of atmospheric condensation nuclei as measured by television station WTVT (Tampa-St. Petersburg, Fla.) at the time of our samplings on August 3 and November 3. Data (12 samples) on "particulate" mercury in Tampa air and the number of condensation nuclei per unit volume were obtained over the period 30 April to 3 November, 1973. Results indicate that there is a definite positive correlation between these two parameters.

At station 1, a study of the diurnal variation of mercury species was made. The sampling covered a period of more

Table I. Regional Variations in Speciation of Atmospheric Mercury in Tampa, Fla.

			ng/m^3 of						
Station	**Date**	**Time**	**Hg_p[a]**	**Hg(II)[b]**	**MMC[b]**	**Hg°[a]**	**DMM[a]**	**Σ**	**Remarks**
1	3 Aug. 73	07h45–08h15	2	24	15	4	0	45	Wind, calm; 25°C
	3 Nov. 73	07h05–09h13	0	0.8	1.0	0	0	1.8	Wind, calm; 19.5°C
2	3 Aug. 73	08h14–08h44	1	7	19	3	0	30	29°C
	3 Nov. 73	11h25–13h31	0	1	0.2	2.7	0	3.9	25.5°C
3	3 Aug. 73	12h21–12h51	2	0	0	7	0	9	Wind, SE 5 Kt; 31°C; >5000 vehicles/hr on I-75
	3 Nov. 73	13h12–15h12	0	Trace	Trace	2	0	2	Wind, NE 2–8 Kt, 23.5°C
4	3 Aug. 73	11h20–11h50	7	0	8	3	0	18	33°C
	3 Nov. 73	07h27–09h35	0	5.8	0.5	3.7	0	10.0	Wind, E 1–2 Kt; 20.5°C
5	3 Aug. 73	13h15–13h45	4	19	0.5	2	0	25.5	34°C
	3 Nov. 73	10h35–12h41	0.2	7	0.4	4.4	0	12	Wind, NE 2–5 Kt; 25°C
6	3 Aug. 73	12h08–12h38	13	0	3	4	1	21	Wind, SE 5–10 Kt; 34°C
	3 Nov. 73	10h12–12h20	0	Trace	0	2.4	0	2.4	Wind, NE 5–7 Kt; 24°C
7	3 Aug. 73	08h50–09h05	3	11	59	7	3	83	Wind, S 10 Kt; 28°C
	3 Nov. 73	07h42–09h32	0	0.4	0	4	0.3	4.7	Wind, E 1–10 Kt; 22°C
8	3 Aug. 73	09h34–10h09	7	220	22	49	0	298	Wind, SE 5 Kt; 29°C
	3 Nov. 73	07h25–09h47	0.5	0.8	Trace	14	0	15.3	Wind, E 4–10 Kt; 21°C
9	3 Aug. 73	10h27–10h57	1	16	11	5	0	33	Wind, SE 10 Kt; 30°C
	3 Nov. 73	10h16–12h23	0.5	1.5	0.3	5.6	0	7.9	Wind, E 4–8 Kt; 24°C
10	3 Aug. 73	07h53–08h23	7.5	0	119	0	1	127.5	Wind, SSE 5–10 Kt; 26°C
	3 Nov. 73	07h50–09h54	0	0	2.8	5	0.2	8	Wind, ENE 1–3 Kt; 20.5°C
11	3 Aug. 73	11h12–11h42	0	13	22	5	0	40	Wind, SW 5 Kt; 30°C
	3 Nov. 73	10h32–12h22	0.1	0.3	0	3.3	0	3.7	Wind, NNE 5–10 Kt; 25°C

[a] Precision of data is ±6% (1 σ). [b] 3 August—1-hr pumpings; 3 November—2-hr pumpings. For precision, see text.

than 2.5 days during which 33 consecutive 2-hr samples were taken using the speciation stacks at a height of 1 meter above the ground surface.

Periodically air was sampled for total mercury at the same time as the speciation stack but 1–2 meters away. A 2-cm gold tube was used. This comparison was made on 10 samples. The mean value for the speciation stacks was 6.8 ng Hg/m^3 and that for the 10 gold tubes was 7.4 ng Hg/m^3. These two means are not significantly different at the 99% level; however, some of the individual comparisons showed differences in excess of a factor of two.

Figure 2 shows the results of the diurnal study. In the lower portion of the figure is plotted total mercury as a bar graph indicating that each sample was integrated over a 2-hr period. The error bars indicate an uncertainty of 1 std dev. The smooth curve is a running average of three consecutive 2-hr samplings and is intended to help illustrate the general trend in total mercury with time.

Values for Hg(II) type, MMC type, and Hg° are plotted in the upper portion of Figure 2. Uncertainties in these determinations, while not indicated graphically, are ±6% for mercury metal, ±18% for mercury(II)-type, and ±13% for methylmercury(II)-type compounds at 1 σ. Dimethylmercury was observed in only nine of the 33 samples with an average value of 0.4 ng/m^3 for the nine samples in which it was found. "Particulate" mercury was observed more frequently, averaging 0.4 ng/m^3 (0.0–1.4), but showed no obvious trends with time of day.

As in the geographic study, the data in Figure 2 show considerable variability. In view of what we believe to be reasonable estimates of the analytical uncertainty, a significant portion of this variability would appear to be real. We consider only two of the 33 samples to be questionable—the sample from 16h00–18h00 on September 25 which was 80% MMC type, and the 00h00–02h00 sample on September 26 which showed 42 ng/m^3 of Hg(II) type, and 23 ng/m^3 of Hg°.

Such variability of the results makes the elucidation of possible trends with time somewhat difficult. In this study, however, total mercury was consistently higher at night than in the daytime. This also appeared to be true for mercury metal, and mercury(II)-type and methylmercury(II)-type compounds. Table II shows the mean values for daytime and nighttime concentrations of Hg(II) type, MMC type, and Hg°, as well as the other species measured. The differences in these mean values for all but DMM and "particulate" mercury are statistically significant at the 95% confidence level. In contrast to the concentrations, the percentage distribution of the mercury species in the day vs. night groupings do not show significant differences.

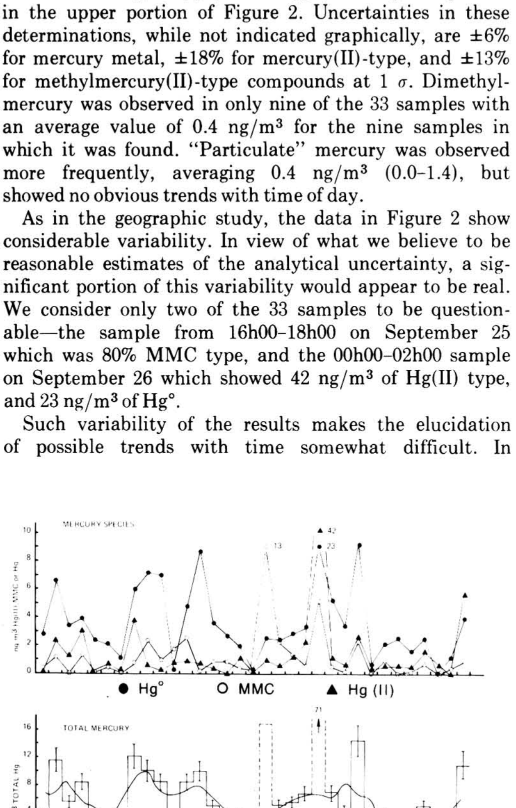

Figure 2. Diurnal variation of total mercury and mercury species at station 1

Figure 3 shows the short-term variability of total mercury which was investigated at station 2. Two gold tubes were alternately pumped and analyzed on a 10-min time scale. The field apparatus was located about 10 meters from the entrance of the laboratory building and 20 meters from the edge of a parking lot, with the tip of the sampling tubes approximately 0.5 meter above the grass. Between 11h50 and 13h00 on October 5, a third 2-cm gold sampling tube was pumped tip-to-tip with the two which were switched every 10 min. During this period, the single tube pumped for 70 min indicated an average mercury content of 6.3 ng/m^3, while the seven 10-min samples gave an average of 5.7 ng/m^3 which includes the one value which reached 24.4 ng/m^3. If this extreme value were excluded from the 70-min average, a concentration of 4.4 ng/m^3 would be computed. Between the hours of 20h00 and 21h00 on October 8, a thunderstorm occurred. The rain appears not to have affected the total mercury content of the air. During all three segments of this study a noticeable wind was blowing except between 05h30 and 07h00 on October 9. The nine samplings in this calm period exhibited a maximum deviation of ±11% from the mean value, as compared with the ±10% uncertainty at the 2-σ level for this study.

To assess the possible effects of near-ground micrometeorological conditions on our sampling procedures, the diurnal variation of total mercury in a 10-meter vertical profile was observed at station 2. Here sampling was conducted utilizing a 35-ft tower of 1.25-in. diam antenna masting hinged at ground level so that it could be raised and lowered to change the gold sampling tubes. Samplers were connected to pumps on the ground by means of tubing and when the tower was in the raised position air was drawn directly into the gold tubes from heights of 0.1, 1.0, 5.0, and 10.0 meters above the ground. To obtain nearly continuous sampling, two sets of four gold tubes each were employed, and the flow rate through each tube in a given position on the tower was measured.

Table III gives the results of 32 profiles taken over a 28-hr period. For samples 1–6, results were 10–20 times higher than total mercury over the profile for the rest of the study—perhaps representing contamination from a local source, or the ending of a high pollution inversion condition in the Tampa area. They are not considered further here. Samples 7 through 32 averaged 3.2 ng Hg/m^3 as determined by integrating the area under each profile. Over half of these samples showed a pronounced gradient

Table II. Mean Values of Day and Night Mercury Species Concentration[a] and Percentages of Total Mercury at Station 1 for Period September 24–26, 1973

Time	$Hg_{(p)}$	Hg(II) type	MMC type	Hg°	DMM	Σ Hg	No. of values
Day	0.27 (6%)	0.86 (19%)	0.63 (14%)	2.67 (60%)	0.05 (1%)	4.48	19
Night	0.17 (2%)	1.58[b] (19%)	1.56 (19%)	5.03[b] (60%)	0.06 (<1%)	8.40	13

[a] ng/m^3. [b] Excluding the values for the sample 0000–0200 hr September 26.

with atmospheric mercury decreasing as a function height above ground. The average profile was: 0.1 meter, 4.9 ± 0.8; 1.0 meter, 3.6 ± 0.4; 5.0 meters, 3.2 ± 0.6; 10.0 meters, 2.7 ± 0.9 ng Hg/m^3. The uncertainty is 1 std dev about the mean value for each height.

To smooth out some of the variability of these results, a running average of three consecutive samples for each height was computed and the data were fitted (by eye) with a curve as shown in Figure 4. Wind velocity (at 1–2 meters), and dry bulb air temperature (at 0.25 meter), recorded at the beginning of each sampling period, are also plotted. A gradient was established at about the time the wind velocity approached zero (22h00–01h00). Thereafter the vertical profile became increasingly more uniform with height, attaining maximum uniformity at the time of the temperature minimum (06h00). In the morning hours, as the temperature rose rapidly, the gradient was re-established and maintained for several hours even though the wind velocity had also increased.

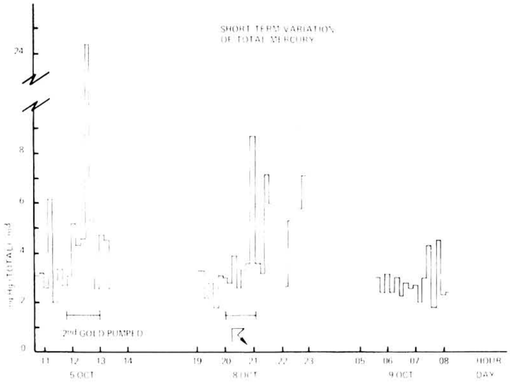

Figure 3. Short-term variation of total mercury in air—10-min sampling intervals

Table III. Diurnal Variation of Total Mercury in 10-Meter Vertical Profile

Sample	Time	ng Hg/m^3 at[a] 0.1 meter	1.0 meter	5.0 meter	10.0 meter	Integrated Σ
1	13h30–13h52	9.5	13	110	14	
2	13h59–14h23	28	20	100	74	
3	14h33–15h03	12	20	40	21	
4	15h07–15h37	13	9	38	32	
5	15h42–16h12	7	21	116	8	
6	16h18–16h48	9.1	6.2	17	19	
7	17h42–18h12	3.5	1.5	0.5	1.1	1.0
8	18h16–18h46	0.9	2.3	2.1	0.9	1.9
9	19h00–19h30	3.3	1.9	0.3	1.4	1.1
10	19h44–20h14	1.0	1.3	2.3	0.6	1.6
11	20h32–21h01	3.1	2.7	1.4	1.3	1.8
12	21h16–21h46	0.1	3.6	3.1	0.5	2.4
13	22h09–22h39	—	3.3	0.9	2.1	2.1
14	22h55–23h25	2.7	3.2	2.9	0.6	2.3
15	23h34–00h04	7.0	4.7	2.7	3.9	3.6
16	00h25–00h55	5.2	5.2	5.1	2.5	4.4
17	01h26–01h56	5.1	4.4	7.1	—	
18	02h15–12h45	3.4	3.4	2.9	1.7	2.8
19	03h02–03h32	5.8	3.8	4.0	5.3	4.4
20	03h57–04h27	2.5	2.4	3.0	2.2	2.7
21	04h55–05h40	5.2	5.2	6.5	9.0	6.7
22	05h50–06h35	5.4	4.7	4.7	2.0	4.1
23	07h05–07h42	7.8	5.2	4.9	8.9	6.1
24	08h01–08h41	5.5	5.6	6.9	2.8	5.2
25	08h58–09h43	8.7	4.3	2.5	4.5	3.8
26	09h52–10h32	8.4	4.6	4.5	11	6.3
27	10h38–11h18	8.6	5.2	3.0	2.3	3.8
28	11h32–12h12	4.7	3.3	4.6	0.9	3.3
29	12h31–13h01	7.6	4.0	1.1	1.2	2.2
30	13h20–14h00	5.0	2.9	2.9	0.5	2.4
31	14h10–14h50	6.1	2.2	0.7	1.3	1.5
32	14h57–15h37	5.7	2.5	1.8	—	

[a] Precision of data in ±10% (2 σ).

The speciation of mercury in air over soils enriched with inorganic mercury was also investigated. Five 5-gal glass water jugs, with the bottoms removed, were used to cover enriched and control patches of lawn. One liter of 100 ppb Hg(II) solution was poured on the ground and the experimental bottle placed over it. The mercuric chloride solution contained about 0.5% Hg° and less than 0.0005% DMM. After four days, the original test patch was again enriched, as before, and a second test area was spiked with $HgCl_2$ by injecting the solution, 10 ml at a time, into the ground to a depth of 6–10 cm. The control jug was located on the same lawn 14 meters distant from the experimental jugs. The area covered by each jug was 0.05 m^3 and the volume of air enclosed was about 15 liters. Samples of 15 liters of air were periodically taken by pumping from the top of the bottles. Replacement air moved in around the bottom edge. The bottles were sealed at the top between samplings.

Figure 5 shows the mercury speciation in the air over the experimental and control patches. Where the $HgCl_2$ solution was poured onto the ground there was an immediate release of Hg°, and subsequently a release of methylmercury(II)-type compounds after the first enrichment and dimethylmercury after the second. Two days after the first enrichment experiment began, total mercury had reached an average level of 38 ng/m^3 (October 17–19) which was about six times the average level of 6.5 ng/m^3 in the control jug over the same time period. The distribution of mercury species as a percentage of the total, however, was not significantly different between the experimental and control bottles, nor was it significantly different in a second control jug placed on a lawn in a different location (7 km away). Where the $HgCl_2$ was injected, there was no dramatic release of Hg° and no DMM was observed. Methylmercury type reached a peak after one day, as in the first enrichment by pouring.

Discussion

A most significant feature of these results is the occurrence of at least four chemical species of atmospheric mercury. For the most part, the mercury is in a "volatile" form. The "particulate" fraction averaged only 4% of the total mercury in the 54 speciation measurements which we report here. The other 96% was divided as follows: Hg(II) type, 25%; MMC type, 21%; Hg°, 49%; DMM, 1%. As can be seen, however, the species distribution is highly variable and this breakdown may or may not be representative of the general atmospheric mercury distribution.

The wide range of values for all the mercury species (except DMM) shown in Table I, suggests that a number of sources for these species exists in the area we are studying. To identify specific point sources within the sampling grid is not possible from the few data we have so far obtained. Furthermore, the wind transport of mercury away from sources is irregular as shown by the short-term and diurnal variations of total mercury (Figures 2 and 3). Nevertheless, on a geographic basis it is clear that the southern stations (6–11) show higher mercury values than the northern stations (1–5). On August 3 the winds were generally from the southeast during the time of sampling.

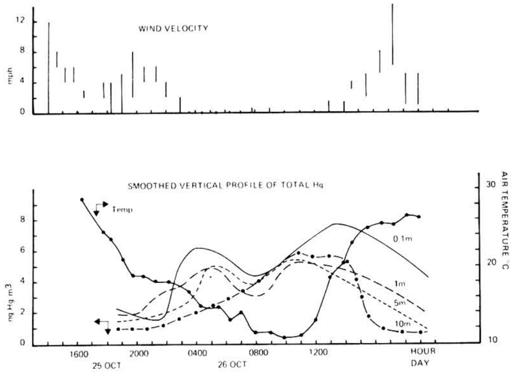

Figure 4. Diurnal variation of: total atmospheric mercury at 0.1, 1.0, 5.0, and 10.0 meters above ground level; wind velocity at 1–2 meters; and air temperature at 0.25 meter. Mercury data smoothed—see text

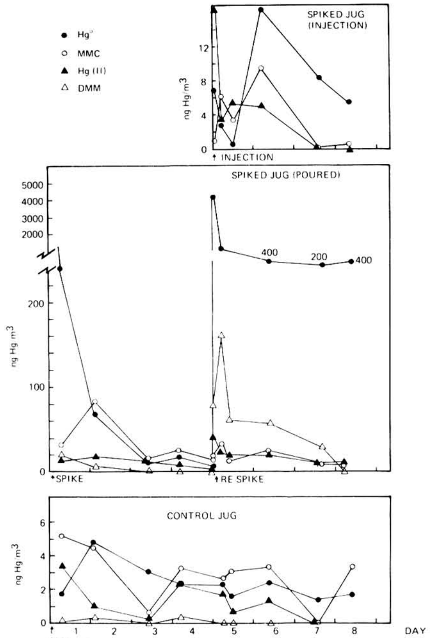

Figure 5. Speciation of mercury in air over soil enriched with mercuric chloride.

Stations 6, 9, and 11, where the wind blew primarily over the land, had total mercury values which were, on the average, five times lower than those observed at stations 7, 8, and 10 where the wind had blown over the water of Hillsborough Bay. On November 3 the winds were northeasterly and the total mercury was much lower and more uniformly distributed over the grid than on the August 3 survey. But again, southwestern stations (7, 8, and 10) showed higher total mercury on the average than the southeastern stations (6, 9, and 11) or the northern stations (1–5).

Foreback (*18*) found mercury in the surface sediments where the Hillsborough River empties into the bay to be in excess of 0.5 ppm Hg (wet weight basis). On the average, the sediment mercury values decrease from about 0.4 to 0.04 ppm from the mouth of the river 10 miles south to Great Tampa Bay (0.01–0.02 ppm), similar to the distribution observed by Klein and Goldberg (*19*) near a sewer outfall. Mercury analyses of the water (*18*) averaged 0.5 ppb (0.08–2.0) for upper Hillsborough Bay—considerably higher than the seawater values reported recently by several investigators (*20, 21*). Gardner and Riley (*22*) found mercury values in excess of 0.2 ppb near an area in the Irish Sea used for the dumping of sewage sludge. On two occasions, after the known dumping of raw sewage into Hillsborough Bay, Foreback found that mercury in surface waters was about 50% "organic," being present as methyl- or phenylmercury. Recently Fitzgerald and Lyons (*23*) reported that about 50% of the total mercury in New England nearshore waters was "organic."

We have noted in several experiments that total mercury in the air under jugs (previously described) placed in the water for several days at the edge of a small lake averaged about 30 times higher than total mercury in the air outside the bottles. From this observation, it appears likely that Hillsborough Bay is one general source for the atmospheric mercury in the Tampa area. In both surveys, stations 7 and 10 showed the highest levels of methyl-type and dimethylmercury in the atmospheric samples—quite possibly the result of biomethylation of mercury in the Hillsborough Bay sediments and water (*13, 24*). Demethylation of mercury compounds in sediments with the concomitant release of Hg° is also known to occur (*14*) and may be one source of the high mercury metal values observed at station 8. The existence of a dynamic equilibrium between methylation and demethylation of mercury compounds in sediments and water may be reflected in the distribution of atmospheric mercury species over the water. We plan more experiments to investigate this in detail.

The results of the two diurnal studies suggest that emanation from the ground is another general source for a number of atmospheric mercury species. In both cases we observed a tendency for total mercury to increase at night and decrease in the daytime in direct opposition to the air temperature fluctuation, whereas McCarthy et al. (*9*) recorded a direct correlation between air temperature and the content of mercury in air over a Hg mineralized area. A reasonable explanation for our observation would appear to be micrometeorological effects. During the calm hours of the night with stable temperature stratification, mercury emanations from the ground can establish a pronounced gradient of mercury in the lower 10 meters of the atmosphere. During the daytime, winds erode or homogenize the gradient so that the average mercury measured at 1 meter is less in the day than at night. Figure 4 shows that, in general, the mercury in air at 0.1 meter is significantly higher than at 10 meters above ground. The radium content of air shows a similar diurnal variation—higher at night, with the establishment of a gradient, and lower during the day (*25*). That mercury is diffusing out of the ground is further suggested by the observation of Sergeev (*26*) that the mercury content of air in bore holes is higher than that in the atmosphere above them. In areas of high Hg mineralization, mercury emanations from the ground may be so strong as to override the micrometeorological effects we observed, and show a positive relationship to temperature as in the study of McCarthy et al. (*9*).

As noted, the percentage distribution of the mercury species, plotted in Figure 2, shows much less regular variation between night and day than does total mercury. This suggests that ambient atmospheric mercury speciation in a given area may be controlled by processes occurring in the ground. Soil microorganisms are known to methylate inorganic mercury (*11*), and both Hg° and Hg(II) are probably present in the soil and on the ground surface, the result of atmospheric particulate matter deposition. Our soil enrichment studies support the laboratory studies of microbial methylation of mercury. The immediate release of mercury metal when $HgCl_2$ was poured on the ground may reflect the Hg° initially present in the enrichment solution. The first step in Hg methylation, however, is the reduction to Hg°, and this may also have occurred in our experiments. In any event, the subsequent release of either DMM or MMC suggests that biomethylation had taken place.

The background levels of mercury and the distribution of mercury species in the air over a local area would be a function of the mercury content of the soil, the structure of the biological community and the type of ground cover. Deviations from the ambient levels and species distribution would be expected to occur by horizontal advection of air from other areas. We believe the very large "peak" of inorganic Hg which occurred between 00h00 and 02h00 on 26 September (Figure 3) represents a dramatic example of this. The wind shifted from northeast to southerly during the night of September 25–26, possibly bringing into the area of station 1 the result of an industrial "stack clearing." Williston (*8*) observed similar such "peaks" in his study in the San Francisco Bay area.

Seasonal variations are likely to have an effect on the rates and types of mercury emanations from the ground, producing the results noted by Williston; a positive long-term correlation with temperature. The lower mean Hg content observed in the November 3 survey compared with the August 3 survey may in part be due to a 7°C decrease in the average temperature at the time of sampling on the two days. The results of studies in progress will establish the seasonal variation patterns of atmospheric mercury speciation in the Tampa metropolitan area.

Conclusions

"Particulate" mercury, in general, represents a small fraction (<10%) of the total mercury in air near the ground.

The "volatile" mercury is composed of mercury(II)-type compounds, methylmercury(II)-type compounds, mercury metal, and to a much lesser extent, dimethylmercury.

The atmospheric distribution of mercury species near the ground is variable reflecting a large number of sources and irregular rates of transport by wind.

Both inorganic mercury and methylated mercury appear to emanate from aquatic systems and from the ground surface. The mercury content and biological makeup of these systems may be responsible for the ambient level and speciation of atmospheric mercury in a local area.

The toxicity of methylmercury(II) compounds and their apparent widespread occurrence in air samples suggest it is of considerable importance to undertake further studies to elucidate the manner and rate at which they are injected into the atmosphere.

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Acute Effects of Outboard Motor Effluent on Two Marine Shellfish

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■ Mussels (*Mytilus edulis*) and oysters (*Ostrea lurida*) exposed to a diluted effluent from a two-cycle outboard motor in a running seawater system displayed physiological stress, degeneration of gill tissue, and uptake of paraffin hydrocarbons from the effluent. Mussels showed an immediate response to the pollutant as well as a significant delayed mortality after removal from the pollutant. The oysters were less affected by the pollutant.

Outboard motor effluent may be a significant source of petroleum pollution in the aquatic environment. A conservative estimate of the portion of fuel discharged to the environment would be of the order of 10% of all two-cycle outboard fuel used (*1*). While the effects of major oil pollution from tanker spills, bulk fuel transfers, pipelines, and offshore drilling have been studied, the effects of continuous low-level water pollution by outboard motors has generally been overlooked (2). However, there is increasing evidence that motor exhaust contributes to taste and odor in fish flesh and that adverse biological effects are observable (3).

A preliminary qualitative study using oysters (*Ostrea lurida*) and mussels (*Mytilus edulis*) was conducted using diluted outboard motor effluent at the Fish Commission of Oregon Research Laboratory in Newport, Ore. Histopathological examinations were conducted at the Oxford, Md., facility of the Middle Atlantic Coastal Fisheries Center of the National Marine Fisheries Service (NMFS), and paraffin hydrocarbon uptake determinations were made at the Seattle facility of the Northwest Fisheries Center, NMFS.

Experimental Methods

Effluent Exposure. An 18-hp outboard motor was run in a clean barrel containing 260 liters of unfiltered seawater (Yaquina Bay, Ore.) until a measured amount of fuel, 100 ml of outboard lubricating oil plus 4800 ml of regular gasoline, passed through the motor (running at a speed of 1200–1500 rpm's) in about 100 min. Approximately 250 liters of the effluent was drawn off from under the unburned fuel layer on the surface of the water. This procedure was repeated six times over a 10-day interval. No estimate of the ratio of unburned fuel to original fuel input was made.

The effluent solution containing both dissolved and emulsified petroleum products and by-products was stored in a 300-liter reservoir tank. A floating siphon device in the reservoir provided a constant flow of the effluent at 0.1 l./min into unfiltered running raw seawater flowing at 0.9 l./min forming a 10% effluent solution immediately prior to its application to the test specimens. One hundred native oysters (37-mm average length) and 150 bay mussels (47-mm average length) collected in upper Yaquina Bay remote from marinas or areas of known pollution and conditioned in the laboratory tanks for two weeks were placed in the test tank. The raw seawater provided the necessary food supply to the organisms being tested. A control tank supplied with raw seawater at 1 l./min contained the same number of organisms as the test tank. Tank temperatures ranged from 10–12°C for the duration of the exposure.

The number of each species exposed and sampled was limited by the size of the test tank, availability of organisms, chemical analysis requirements, and the observed mortalities. Test and control specimens were collected after periods of one day (10 each mussels and oysters for histopathology; 15 mussels and 20 oysters for hydrocarbon analysis), five days (10 oysters for histopathology and 25 oysters for hydrocarbon analysis), and 10 days (eight oysters for histopathology and 25 oysters for hydrocarbon analysis). Due to the preliminary nature of these experiments, duplicate runs were not made.

Histopathology. Individual organisms were fixed immediately after removal from the tanks and later embedded, sectioned, and stained. The histopathological condition of the thin sections was determined by microscopic examination.

Hydrocarbon Uptake Determinations. The paraffin hydrocarbon analysis (4) of the organisms began with methanol–benzene Soxhlet extraction followed by percolation of the solvent-free extract through silica gel/alumina. The final separations and quantification were by hydrogen-flame gas chromatography. The results were expressed in ppb—dry extracted weight (10^{-9} gram paraffin hydrocarbon/gram dry extract weight) for samples over the *n*-paraffin hydrocarbon range n-$C_{14}H_{30}$ to n-$C_{37}H_{76}$. Hydrocarbons detected down to n-$C_{10}H_{22}$ are also plotted although they may not always be quantitatively reproducible.

The petroleum hydrocarbons in the effluent were extracted by shaking a 1-liter sample in a separatory funnel

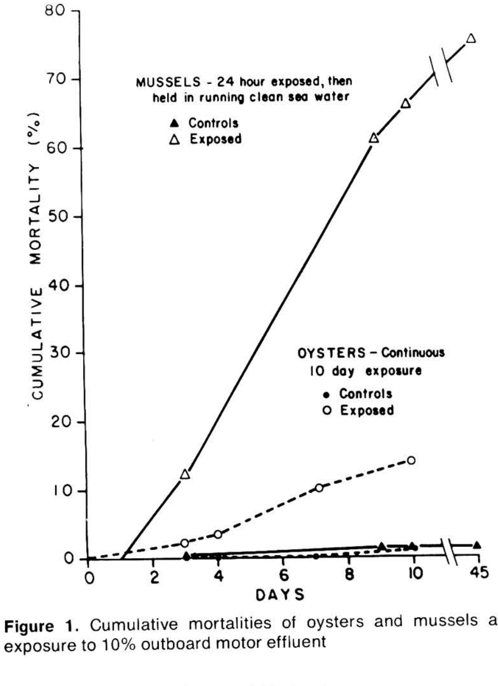

Figure 1. Cumulative mortalities of oysters and mussels after exposure to 10% outboard motor effluent

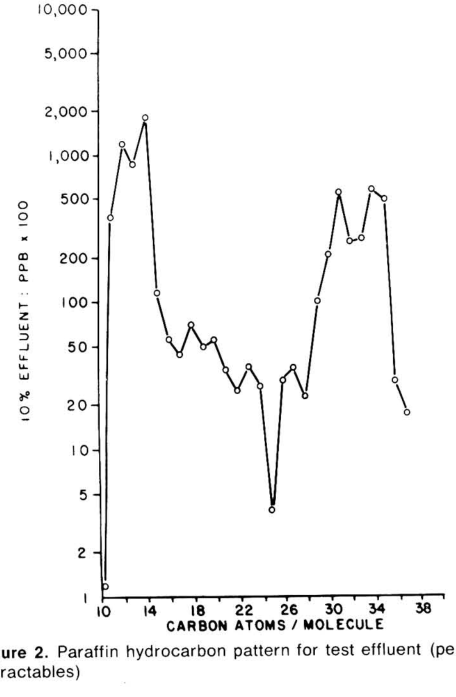

Figure 2. Paraffin hydrocarbon pattern for test effluent (pentane extractables)

with 100 ml of triple-distilled pentane. This extraction was repeated twice with equal volumes of fresh pentane. The organic solvent fractions were combined, dried over extracted anhydrous sodium sulfate, carefully evaporated by rotary vacuum evaporation at reduced temperature, and the final concentrate was weighed. This extract, as well as a solvent blank using cold tap water, was chromatographed on silica gel–alumina (3:2 v/v, using triple-distilled pentane) and analyzed by gas chromatography in the same manner as the biological samples.

Results

Exposure Studies. After the end of the first 24 hr of exposure to the diluted effluent, almost all of the mussels showed stress (gaping). The oysters reacted by closing their shells and apparently not pumping water. Due to the extreme degree of stress, the mussels were removed and placed in fresh running seawater, while the oysters continued in the running diluted effluent. At the end of 10 days, the oyster mortality totaled 14% (Figure 1). The experiment with the oysters was terminated after 10 days of exposure when all of the organisms had either been sampled or had died. The delayed mussel mortality totaled 66% at the end of 10 days (one-day exposure and nine days in fresh running seawater) and increased to 75% after 45 days (Figure 1). The control mussels and oysters showed a cumulative mortality of 1% during the 10 days of the experiment.

These mortality data provide a comparison between the two species and between the test and control groups but were not further utilized to compute median tolerance limits, which were beyond the scope and objective of this preliminary qualitative study.

Histopathological Investigations. There were no significant histological differences between the test oysters exposed to effluent for one day and the controls. The oysters exposed five and 10 days showed degeneration of the gill tissue in comparison with controls. In several of the 10-day effluent-exposed oysters, the gill tissue had completely degenerated, and "normal" postmortem changes were beginning to take place (*5*).

Only the one-day exposed mussels were examined, and they showed histological evidence of gill tissue degeneration accompanied by some dilation of the tubules of the digestive diverticulum. These changes were not as noticeable in the one-day control mussels, and what little pathology was present in the control samples could probably be attributed to inadequate fixing of the original samples.

Hydrocarbon Uptake Analysis. The paraffin hydrocarbon pattern of the material extracted into the pentane from the effluent shows a bimodal distribution of normal paraffin hydrocarbons (Figure 2, C_{12-14} and C_{30-35} regions) plotted on a logarithmic scale. The total n-paraffin hydrocarbon content (n-C_{14-37}) of the 10% diluted test effluent obtained by summing the concentrations of the individual n-paraffin hydrocarbons was 50.1 ppb from a total pentane-soluble extract of 4.575 ppm. By use of the same analytical extraction procedure, surface seawater samples collected in Puget Sound, Wash., gave n-paraffin hydrocarbon contents from 2.33 ppb at locations remote from known sources of petroleum pollution to 7.32 ppb in industrial-commercial harbors.

The exposed mussel sample (one-day) hydrocarbon pattern (Figure 3A) appears to have a basic similarity with the control mussel pattern in the range n-C_{17-29} in that the peaks at carbon numbers 17, 20, 23, and 25 and troughs at 19, 21–22, 24, and 28 agree. The concentrations are in the same orders of magnitude except for n-C_{21} which is less than 1 ppb for the controls compared to 36 ppb for the exposed. Below C_{17} and above C_{29}, however, the two mussel patterns are significantly different in both shape and content. The exposed sample has a pattern which appears to be similar to the effluent pattern (Figure 2). If the hydrocarbon pattern of the control mussels rep-

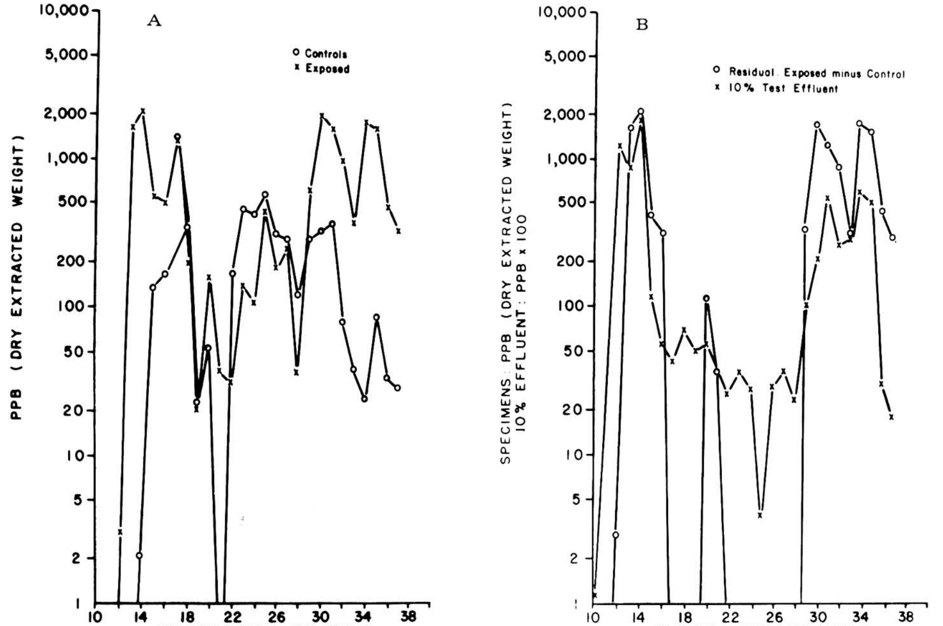

Figure 3. Paraffin hydrocarbon patterns for mussels

A. Exposed specimens compared with control specimens after one day of exposure. B. The "residual" hydrocarbon pattern (exposed minus control specimens) compared with effluent pattern resents the biogenic hydrocarbons naturally occurring in the mussels, then the exposed sample pattern represents the sum of the biogenic plus the pollutant taken up by these organisms. By subtracting the paraffin hydrocarbons of the controls from the exposed organisms, the resulting "residual" hydrocarbon pattern should give an approximation of the pollutant patterns (Figure 3B). The "residual" pattern of the exposed mussels agrees with the effluent hydrocarbon patterns with peaks at 14, 30–31, an 34, and troughs at 17–28, 32–33, and 37.

The oysters after one day had similar patterns for bot the test and controls (Figure 4) at both the low and hig ends, below C_{18} and above C_{26}, while the middle rang paraffin content of the test organisms was less than th controls (C_{20}, 10 vs. 300 ppb).

The five-day exposed oysters compared with the one

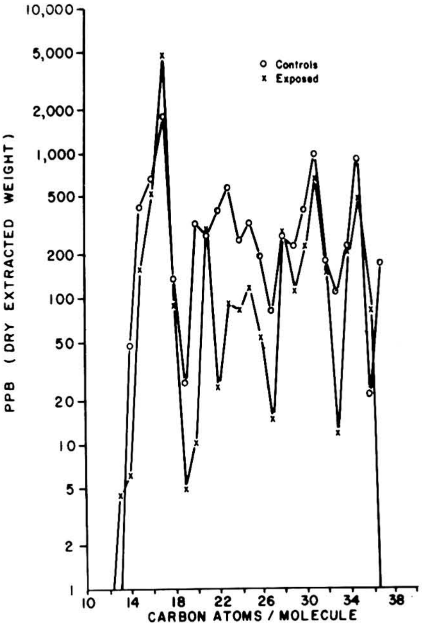

Figure 4. Paraffin hydrocarbon patterns for oysters after one day of exposure

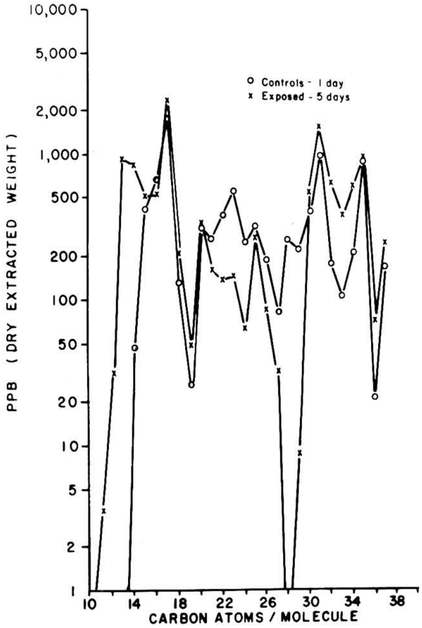

Figure 5. Paraffin hydrocarbon patterns for oysters after five days of exposure

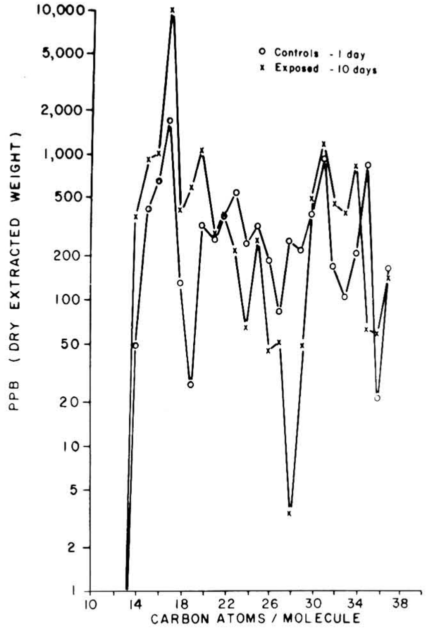

Figure 6. Paraffin hydrocarbon patterns for oysters after 10 day of exposure

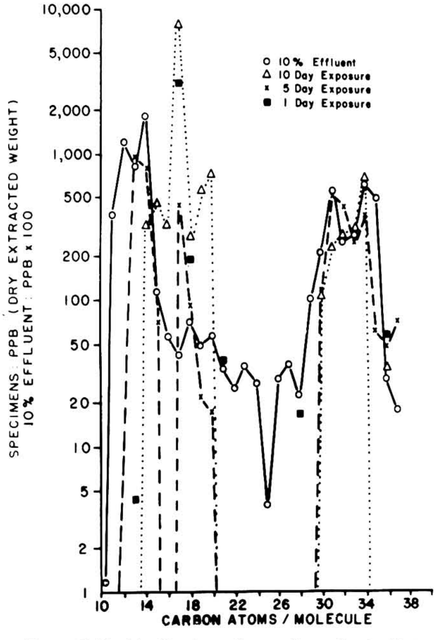

Figure 7. Residual hydrocarbon patterns for oysters

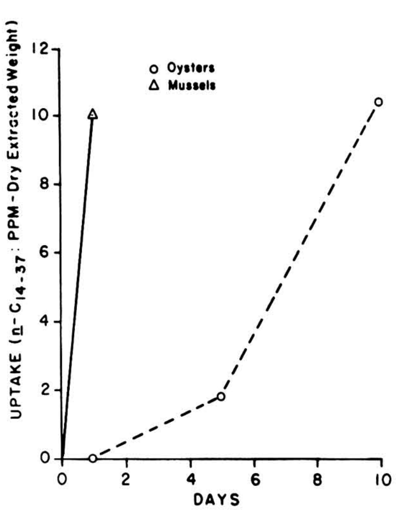

Figure 8. Uptake of paraffin hydrocarbons by oysters and mussels from 10% outboard motor effluent

day controls (no five- or 10-day oyster controls collected) show slight increases in hydrocarbon content below C_{16} and in the C_{32-34} region, which could be the result of uptake from the effluent (Figure 5). Also there is a marked decrease in the paraffin hydrocarbons at C_{23-24} compared to both the one-day exposed and one-day controls.

The 10-day exposed oyster patterns display the same increase seen in the previous exposed oyster patterns at C_{32-34} (Figure 6). There is a definite similarity with the five-day exposed pattern, and although not all individual hydrocarbons match identically, the agreement is generally better than 75% in spite of unavoidable analytical and biological variability. Below C_{15} there is no indication of effluent uptake; this absence could be due to evaporative losses during the processing of the sample. Oyster "residual" patterns were calculated and plotted (Figure 7). The five-day and 10-day exposed samples display an enrichment of *n*-paraffin hydrocarbons in the C_{30-34} region similar to that of the effluent while the five-day exposed sample also shows the effluent pattern below C_{15}. The enrichment in the C_{16-20} range in both residual patterns does not appear to be due to the incorporation of petroleum hydrocarbons from the effluent.

The uptake of paraffin hydrocarbons summed over the range *n*-C_{14-37} correlates closely (Figure 8) with the cumulative mortality results. The mussels had a rapid uptake of 10.0 ppm in one day, while the oysters took 9–10 days to accumulate the same level. The various parameters which can be calculated from the paraffin hydrocarbon data (*4*) for the mussels and oysters are summarized in Table I.

Summary and Conclusions

From observations it was evident that stress to mussels from the exposure to diluted outboard motor effluent occurred much more rapidly than to oysters, and the cumulative mortality in mussels after 10 days was 66% compared with 14% for oysters. The histological examination confirmed that gill tissue damage occurred within the first 24 hr of exposure for mussels but not for oysters.

Oysters have the capability of closing their shells for long periods of time which would exclude pollutants. Mussels, on the other hand, may not be able to prevent external pollutants from entering through the byssal opening (*6*). If oysters remain closed for extended periods of time, the hydrocarbon patterns could be expected to change as body lipids are metabolized.

The physical properties of the pollutant may also be of considerable importance to the impact of the pollutant to the mussel. Field studies and laboratory bioassay studies (*7*) have shown that the lighter refined petroleum products (such as heating oils and diesel oil) are taken up by mussels quickly and retained up to five weeks after removal of the pollutant under controlled conditions. On the other hand, heavy more viscous refined products and some crude oils may not pass through the small byssal thread opening and are not taken up by the organisms as readily. Field studies have shown that mussels can withstand considerable exposure to heavy products such as bunker oil (*8*), and aged Navy Special Fuel Oil (*9*); laboratory bioassay studies (*10*) tend to support these findings (mineral oil and No. 5 fuel oil).

The high sensitivity of the mussels to the diluted effluent suggests that small amounts of petroleum, including outboard motor wastes, may adversely affect these organisms. Oysters may be able to exclude a pollutant for short periods, but chronic exposure could be deleterious. terious.

Acknowledgments

We wish to recognize the histopathological examination provided by Fred G. Kern and Robert A. Murchelano in Pathology Investigation of the Middle Atlantic Coastal Fisheries Center at Oxford, Md.

Table I. Paraffin Hydrocarbon Uptake Data Analysis of Mussels and Oysters

Species and type of sample	Day after start	Solvent extractables, ppm	Total paraffin hydrocarbons, ppm	Total *n*-paraffins C_{14-37}, ppm	*n*-C_{17}/pristane	Major paraffin hydrocarbon		*n*-C_{16} ratio	Carbon preference index, CPI_{20-36}	Carbon preference index, CPI_{14-20}	Unresolved peak envelope, C_{17}/background	Unresolved peak envelope, C_{17}/C_{28}
Mussels (Mytilus edulis)												
Controls	1	139,900	5.8	5.6	6.01	C_{17}	23.4%	36.6	1.4	3.0	1.3	2.3
10% effluent	1	147,800	17.4	15.6	5.19	C_{14}	12.0%	33.3	0.9	1.3	1.2	0.6
Oysters (Ostrea lurida)												
Controls	1	159,100	9.1	9.0	14.7	C_{17}	19.7%	13.4	1.7	2.3	2.9	0.9
10% effluent	1	216,000	8.8	8.5	15.5	C_{17}	54.7%	16.2	1.7	8.0	3.0	0.7
10% effluent	5	171,100	11.9	10.8	14.8	C_{17}	20.4%	20.4	1.6	2.4	2.3	0.5
10% effluent	10	155,800	19.7	19.4	38.4	C_{17}	51.1%	19.5	0.9	5.6	2.6	0.5
Effluent												
10% test	0	4.575	0.0744	0.0501	0.77	C_{14}	24.4%	89.4	1.3	0.6	2.0	0.04

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Treatment of Aqueous Effluents from $UF_6(g) \rightarrow (NH_4)_4[UO_2(CO_3)_3](s) \rightarrow UO_2(s)$ Conversion

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■ Increasing use of the $UF_6(g) \rightarrow (NH_4)_4[UO_2(CO_3)_3](s) \rightarrow UO_2(s)$ conversion process for manufacturing UO_2 fuels has led to the development of different processes to treat the aqueous effluents generated during several stages of the UO_2 conversion. The mixture of these effluents contains large amounts of $NH_4{}^+$, $CO_3{}^{2-}$, F^-, and a relatively small amount of U. This article describes a novel treatment process comprising four main stages. These aim at the recovery of CO_2 by acidification through a unique gas liberation circuit, the precipitation of U as $UO_4 \cdot 2NH_3 \cdot 2HF$ (a novel compound), the removal of F^- by precipitation, and the recovery of NH_3 and part of the H_2O by distillation and rectification of the two latter components, respectively. The CO_2, NH_3, H_2O, and U so recovered can be returned to the conversion process, while the treated effluents and the $CaF_2/Ca(OH)_2$ solid, which meet currently accepted or anticipated environmental standards, can be safely discarded.

One of the industrial processes to manufacture UO_2 fuels for light water moderated nuclear reactors is the $UF_6(g) \rightarrow (NH_4)_4[UO_2(CO_3)_3](s) \rightarrow UO_2(s)$ conversion (*1*). In this process, the intermediate solid, tetraammonium tricarbonatouranate (or AUC, as commonly called in industry), is precipitated by introducing $NH_3(g)$, $CO_2(g)$, and $UF_6(g)$ into H_2O. The precipitate is filtered, calcined to UO_3, and reduced to UO_2 powder.

At different stages of the conversion process certain aqueous effluents are generated. The mixture of these effluents contains large amounts of $NH_4{}^+$ (80 to 120 g/l.), various carbonate species (up to 65 g/l., expressed as $CO_3{}^{2-}$), F^- (50 to 80 g/l.), and a small amount of U (up to 300 mg/l.). Furthermore, it has a titratable basicity of 2.0-2.5 eq/l. and a pH of 8.5-9.5. Obviously, the concentrations of the radioactive and toxic components must be reduced to levels below the safe limits currently accepted or anticipated in the USA before the effluents can be released to the environment. This article describes a process of treating the effluents generated during the $UF_6 \rightarrow AUC \rightarrow UO_2$ conversion. The treatment process, tested in a pilot plant, is semicontinuous and comprises four stages (Figure 5):

A continuous $CO_2(g)$ liberation circuit.

A batch precipitation stage to precipitate U with H_2O_2 as $UO_4 \cdot 2NH_3 \cdot 2HF$.

A batch system to precipitate F^- with an excess amount of CaO and to distill off NH_3 and H_2O.

Rectification of NH_3 solution.

The treated effluents contain <100 mg $NH_4{}^+$/l., <10 mg F^-/l., and <1 mg U/l. The NH_3, CO_2, U, and H_2O can be recovered economically and returned to the conversion process.

Fundamentals of the Process

First Stage. Before describing this stage, it would be appropriate to describe the bench scale experiments carried out to investigate the thermal decomposition of the effluent mixture. In a series of batch experiments, known volumes (a few liters) of the effluent mixture were heated under atmospheric pressure. The temperature, pH, titratable basicity or acidity (as determined by ordinary acid-base titration), residual volume, and residual $NH_4{}^+$, $CO_3{}^{2-}$, and F^- concentrations of the solution were measured at certain intervals throughout heating. It was observed that $NH_3(g)$, $CO_2(g)$, and H_2O are liberated during the initial stages of heating, as described by the following chemical equations:

$$NH_4{}^+(aq) + OH^-(aq) \xrightarrow{\Delta} NH_3(g) + H_2O \qquad (1)$$

$$2NH_4{}^+(aq) + CO_3{}^{2-}(aq) \xrightarrow{\Delta} 2NH_3(g) + CO_2(g) + H_2O \qquad (2)$$

$$NH_4{}^+(aq) + HCO_3{}^-(aq) \xrightarrow{\Delta} NH_3(g) + CO_2(g) + H_2O \qquad (3)$$

Figure 1 shows a plot of the solution temperature as a function of V_R/V_I where V_R and V_I are the residual and initial liquid volumes, respectively. The residual concen-

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trations of NH_4^+, CO_3^{2-} (total carbonates), and F^- are plotted as functions of V_R/V_I in Figure 2. As heating proceeds, the titratable basicity of the solution decreases and eventually the solution turns acidic by continuous loss of $NH_3(g)$ (Figure 3). Further heating simply results in liberation of more $NH_3(g)$ and H_2O and an increase in titratable acidity, described by the following chemical equations:

$$NH_4^+(aq) + F^-(aq) \xrightarrow{\Delta} NH_3(g) + HF(aq) \quad (4)$$

$$HF(aq) + F^-(aq) \xrightarrow{\Delta} HF_2^-(aq) \quad (5)$$

It should be pointed out that because of the strong $NH_3(aq)/NH_4F$ buffer system, the pH varies extremely slowly throughout heating (Figure 4). Consequently, the titratable acidity, rather than pH, is used as a control parameter in the process.

It is obvious from the foregoing discussion that a clean separation of $NH_3(g)$ and $CO_2(g)$ could not be achieved simply by heating the solution because the vapor phase thus obtained would contain both of these gases until all of the carbonates are removed from the solution. An additional process step would then be required to carry out the desired separation. Instead, a unique method for selective removal of $CO_2(g)$ was developed.

In essence, the $CO_2(g)$ liberation circuit comprises a $CO_2(g)$ expeller and an evaporator and is operated continuously (Figure 5). The effluents are fed into the expeller where the $CO_2(g)$ is liberated selectively by acidifying the effluents, as shown by the following chemical equations:

$$CO_3^{2-}(aq) + 2H_3O^+(aq) \longrightarrow CO_2(g) + 3H_2O \quad (6)$$

$$HCO_3^-(aq) + H_3O^+(aq) \longrightarrow CO_2(g) + 2H_2O \quad (7)$$

The necessary acid is produced by boiling the solution withdrawn from expeller in the evaporator at 118–120°C and under atmospheric pressure. This set of conditions guarantees an acidity of 3–3.5*N* in the evaporator outflow, the composition of the NH_3-HF-H_2O system being univariant above 117°C (*2*). Under steady state conditions, if the expeller contents are maintained at a titratable acidity of 1–2*N*, the stream leaving the expeller is essentially free of carbonates. A certain portion of this stream, so chosen that the total fluoride content of the circuit re-

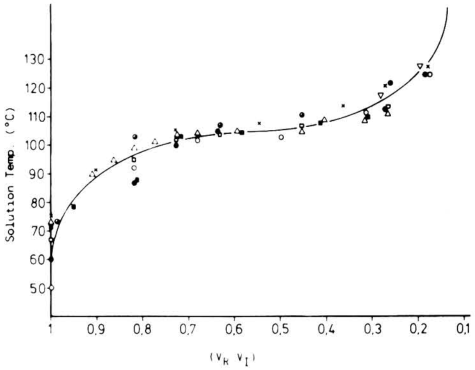

Figure 1. Heating curve for AUC effluents (V_R = residual volume; V_I = initial volume)
Results from 8 different grab samples

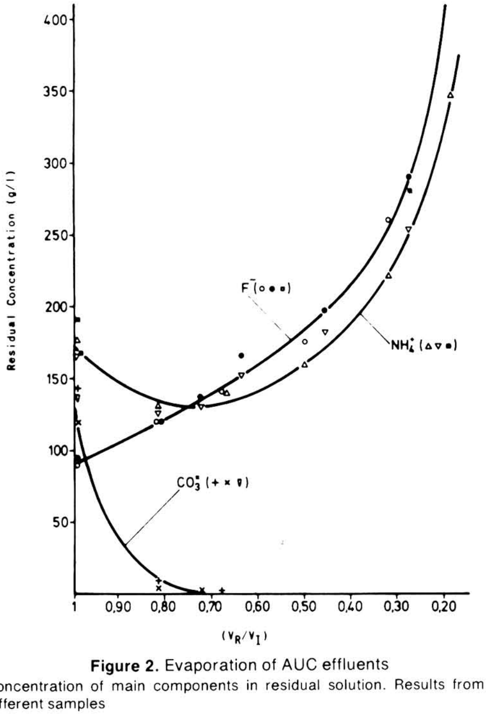

Figure 2. Evaporation of AUC effluents
Concentration of main components in residual solution. Results from 3 different samples

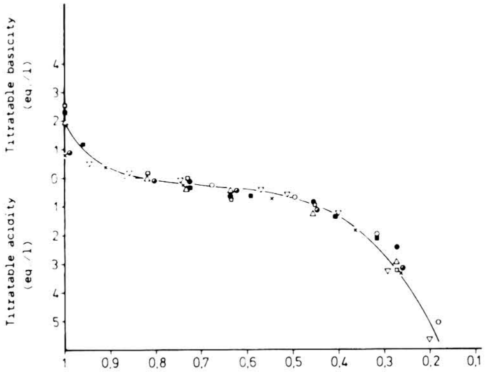

Figure 3. Evaporation of AUC effluents
Titer of residual solution. Results from 8 different samples

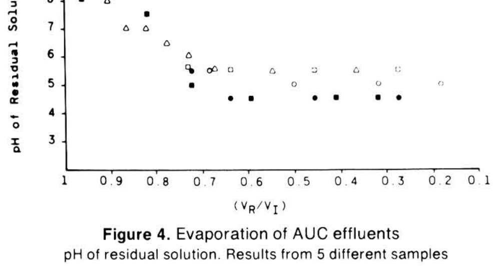

Figure 4. Evaporation of AUC effluents
pH of residual solution. Results from 5 different samples

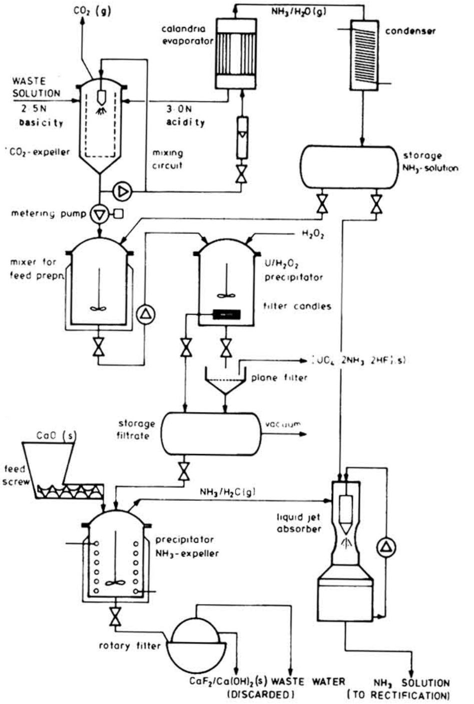

Figure 5. Process flowsheet for AUC effluent treatment

mains fixed, is withdrawn into the second stage. The temperature of the expeller solution is kept below 80°C to minimize the liberation of $NH_3(g)$. The vapors, NH_3-H_2O mixture, from the evaporator are condensed through a heat exchanger.

It should be pointed out that during the initial phase of the operation (before the desired steady state conditions are reached), the liquid stream going into the evaporator from the expeller is not free of carbonates. Consequently, the condensed liquid, contaminated with carbonates (Equations 1–3), must be collected separately until the steady state conditions are achieved and recirculated through the circuit. During the pilot plant tests, the steady state conditions were achieved within a few hours, and the circuit then was operated continuously, as long as desired, without carbonate contamination.

Second Stage. The recovery of small quantities of uranium from waste solutions by precipitation with H_2O_2 is a well-known technique in uranium technology [e.g., Gens (*3*)]. While the preparative precipitation with H_2O_2, which yields, depending on the temperature, either $UO_4{\cdot}4H_2O$ or $UO_4{\cdot}2H_2O$ (*4*), is usually carried out in a strongly acidic medium, in our process a new principle is employed to precipitate the uranium with H_2O_2: Completeness of the precipitation of small amounts of U with H_2O_2 depended on the $NH_4^+(aq.)/F^-(aq)$ ratio's being nearly unity which occurs at pH 9. Therefore, the pH of the carbonate-free solution withdrawn from the expeller is adjusted to the empirical value of nine by adding a portion of the NH_3 solution obtained in the first stage. The solution is heated to 50°C while being stirred, and an appropriate amount of H_2O_2 solution, corresponding to an approximately 20-fold excess relative to UO_2^{2+}, is added at once. The resulting yellow precipitate is a novel compound which has been identified as $UO_4{\cdot}2NH_3{\cdot}2HF$ (*5*). The precipitation may be represented by the following equation:

$$UO_2^{2+}(aq) + H_2O_2(ex) + 2NH_4^+(aq) + 2F^-(aq) \longrightarrow [UO_4 \cdot 2NH_3 \cdot 2HF](s) + 2H^+(aq) \qquad (8)$$

After 1 hr of aging, filtration is carried out using immersed filter candles and a plane suction filter, as shown in Figure 5. The supernatant is drawn through the immersed filter candles to retain a portion of the U compound in the precipitator as seeding material for the next batch. The seeding material is essential to recover more than 99.9% of the U as an easily filterable solid in a short time. The filtrate, which contains less than 1 mg U/l. and large amounts of NH_4^+ and F^-, is transferred into the CaF_2 precipitator of the third stage. The U solid can be introduced back into the UO_2 conversion process.

Third Stage. The filtrate transferred from the second stage is heated to 80°C prior to the addition of CaO. Then, an approximately 20% excess amount of CaO, relative to the F^- present, is added slowly through a feed screw while the reaction mixture is stirred vigorously and held at 90°C. The expulsion of $NH_3(g)$, which begins during the precipitation of CaF_2 at 80–90°C, is completed after the precipitation by boiling the slurry at about 104°C. The NH_3 and the H_2O distilled off are led into a liquid jet absorber where they are combined with the $NH_3(aq)$ solution from the first stage. The reactions that take place in the third stage can be represented by the following equations:

$$CaO(s) + H_2O \longrightarrow Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq) \qquad (9)$$

$$Ca^{2+}(aq) + 2F^-(aq) \longrightarrow CaF_2(s) \qquad (10)$$

$$NH_4^+(aq) + OH^-(aq) \xrightarrow{\Delta} NH_3(g) + H_2O \qquad (11)$$

The concentrated $NH_3(aq)$ solution leaving the jet absorber is transferred to a rectification unit in the fourth stage, not shown in Figure 5. A rotary drum filter is employed to filter the CaF_2 slurry. Because of the 20% excess of CaO used, the cake is a mixture of CaF_2 and $Ca(OH)_2$. The filtrate contains <1 mg U/l., <10 mg F^-/l., and <100 mg NH_4^+/l. Owing to dissolved $Ca(OH)_2$, the pH is approximately 12.

Fourth Stage. Separation of NH_3 and H_2O through rectification under pressure is a straightforward technique in chemical industry. The $NH_3(g)$ and H_2O, which are recovered, can be recycled into the UO_2 conversion process.

Equipment

The $CO_2(g)$ expeller is a cylindrical vessel with a water-cooling jacket. Its interior is lined with rubber to resist the highly corrosive acidic fluoride solution. The contents of the expeller are circulated externally and are introduced back into the expeller through a nozzle which brings about an effective mixing and improves the $CO_2(g)$ effervescence. There is a polypropylene disengager placed in the expeller to improve the separation of gas bubbles from the liquid. The liberated $CO_2(g)$ goes through a disentrainer and a demister where the $H_2O(1)$ is retained. The liquid level in the expeller is kept constant by means of two electromagnetic-type plastic floater switches which control the effluent feed rate into the expeller.

The calandria evaporator is made of impregnated graphite blocks placed in a steel heating jacket. The graphite material has an excellent resistance to acidic fluoride solutions. The temperature of the evaporator solution [a direct measure of its acidity (Figures 1 and 3)] is controlled by regulating the steam supply to the evaporator through a diaphragm-type steam reducing valve. The liquid level in the evaporator is kept constant by regulating the flow from expeller into the evaporator through a diaphragm-type regulating valve made of PTFE, responding to the hydrostatic head. The liberated gases go through a PTFE demister and a tube and shell-type heat exchanger and are collected in a polyethylene storage vessel.

The feed preparation vessel of the second stage is made of stainless steel and is equipped with a steam jacket and a stirrer.

The U/H_2O_2 precipitator is made of polyethylene and is equipped with a stirrer and built-in filter candles. Both the filter candles and the filter plate are made of Pall Grade H stainless steel with a porosity of 0.4 μ (98% nominal holdback). The CaF_2 precipitator (s/s) is equipped with a stirrer, a steam jacket, and a cooling coil. An underpressure of approximately 20 cm H_2O, provided by the liquid jet absorber, is maintained to speed up the expulsion of $NH_3(g)$ and $H_2O(g)$.

The CaO feed screw, the rotary drum filter, the liquid jet absorber, and the NH_3/H_2O rectification unit are commercially available items.

Conclusions

The treatment process described above has two major novel aspects which could have applications beyond the scope of this work: First, the CO_2 liberation circuit provides a unique method to separate CO_2 selectively from solutions containing other volatile components—e.g., NH_4^+, where the selective removal of CO_2 cannot be accomplished by heating the solution. The CO_2 liberation is brought about through acidification, but without adding any adjuvants. Instead, the necessary acid is produced internally in a controlled manner. A possible use of the circuit would be to separate CO_2 and NH_3 continuously from aqueous solutions of NH_4HCO_3 or $(NH_4)_2CO_3$. In this case, a fixed amount of F^- (as HF, or NH_4F, or NH_4HF_2) would be added into the CO_2 expeller to produce the necessary acid, and no expeller solution would be withdrawn from the circuit. Consequently, all of the F^- added would remain in the circuit and be used repetitively to provide the acid solution needed to liberate CO_2. The $NH_3(aq)$ obtained from the condenser would be rectified.

Second, the technique for precipitating U with H_2O_2, developed during the course of this work, provides a new method to recover U as an easily filterable solid with a yield greater than 99.9%. In addition, the solid thus obtained, $UO_4 \cdot 2NH_3 \cdot 2HF$, is a novel compound that could be utilized for other purposes in science and technology.

The process was successfully tested in the pilot plant for approximately 1.5 years. During this extensive test program, the process was studied and evaluated in detail, the process control parameters were optimized, and properties of the materials of construction were evaluated. Based on the pilot plant data, a commercial-size effluent plant was designed. Furthermore, the pilot plant tests demonstrated that the process can be controlled to perform its intended uses in an economical and reliable fashion.

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Characterization of Organics in Secondary Effluents

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■ The composition of soluble organics in secondary effluents from various treatment plants has been investigated. On the whole, the results obtained were repeatable within a relatively low degree of deviation. Gel permeation chromatography reveals that the majority of the humic compounds isolated from the secondary effluents are within a molecular weight range of 1000–5000. The acidic functional groups of those compounds are mostly carboxylic with a small percentage of phenylhydroxyls. A number of specific compounds have been identified within the fraction of ether extractables, by using mass spectrometer coupled with gas chromatograph.

In the earlier publication the authors (*1*) reported on the investigation concerning the composition of soluble organics in secondary effluents. About 40–50% of the organics constitute the so-called humic substances, the other groupings being anionic detergents, carbohydrates, proteins, tannins and lignins, and ether extractables.

This work has now been extended: In addition to the secondary effluents obtained from high-rate trickling filters, the effluents from stabilization pond and from an extended aeration activated sludge plant have been examined for the composition of their soluble organics. Moreover, a more detailed investigation of the humic compounds, as well as the ether extractables isolated from the effluents, has been carried out.

The humic content of secondary effluents is of special interest, as it represents a considerable part of the whole soluble organic matter (*1*). The physicochemical treatment processes are greatly influenced by the anionic character of the humic compounds, as well as by their relatively high molecular weight. The ether extractables, on the other hand, are supposed to contain the main objectionable organics which may cause problems in reclaimed water because of their possible detrimental health effects.

Experimental

The samples of secondary effluents were collected from three plants: Greater Haifa Municipal Treatment Plant employing trickling filters (T.F.), Experimental Stabilization Pond connected to the Municipal Plant (S.P.), and Extended Aeration Activated Sludge Plant receiving wastewater from a strictly residential area (A.S.). The samples of secondary effluents to be examined were collected and subjected to a fractionation procedure described in the previous paper (*1*). The determination of the COD of each fraction and subsequent material balance computations of the organics were made according to procedures described in the same paper.

The humic compounds and the ether extractables isolated during the fractionation of the T.F. effluent were further examined.

Humic Substances. The investigation of humic substances included examination of their ir spectrum, determination of the functional acidic groups carboxylic and phenolhydroxylic, and estimation of their molecular weight distribution. The humic substances isolated from secondary effluents were further divided into humic, hymathomelanic, and fulvic acids. The humic and hymathomelanic fractions were then dissolved in 0.5*M* NaOH, reprecipitated with 0.5*N* HCL; washed thoroughly with distilled water, and dried in a vacuum desiccator. Each of the isolated fractions (including fulvic acid) was weighed and an aliquot was dissolved in ethylene diamine for carboxyl and phenolic hydroxyl determination. Another aliquot dissolved in 0.25*M* NaOH was assigned for molecular sieving.

The acidic functional groups were determined by potentiometric titration in nonaqueous medium, using platinum-saturated calomel electrode combination (*2*). The 0.1*M* solution of sodium aminoethoxide in ethylene diamine, calibrated against benzoic acid, was applied as titrant. To avoid interferences of CO_2 from the air, the titrations were carried out in a current of nitrogen.

The molecular weight distribution was examined by fractionation on Sephadex gels G-25, G-50, and G-75 having exclusion limits 100–5000, 500–10,000, and 1000–50,000 (by dextrans), respectively (*3*). The gel chromatographic procedure utilized a glass column of 5-mm i.d. filled with about 45 ml of swollen Sephadex. The sample volume used did not exceed 2 ml. The 0.01*M* solution of NaCl adjusted to pH 8 was applied as eluant. At a flow rate of 12 ml/hr approximately, the effluent was collected in fractions of 2 ml each. The received fractions were evaluated photometrically at 350 nm. The Sephadex columns were calibrated with Blue Dextran having molecular weight 2×10^6 excluded from all the gels. The samples of humic acids being examined were first passed through the gel column G-25. The portions of eluate excluded from this gel were collected and reduced in volume in a rotating evaporator. The next fractionation was made on G-50 and on G-75, respectively. For evaluating the molecular weight distribution, the elution patterns from the three gels were considered. The areas corresponding to the respective ranges of molecular weight were measured and expressed as percent of the total area included under the elution pattern from G-25.

Ether Extractables. The study on identification of the ether extractables was made by using the combination gas chromatography–mass spectrometry. In this technique minute quantities of the extracts are separated into their components by gas chromatography, and the separated fractions are directly transferred to the ion source of a mass spectrometer where they are immediately analyzed. Identification of the contaminants was accomplished by the analysis of their fragmentation patterns upon electron impact, and the structures assigned were confirmed by comparison with published mass spectra. In some cases, mass spectra of authentic compounds were measured for comparison under similar conditions. Attempts to match spectra [by hand, using the Index of Mass Spectral Data (*4*)] were also made. In the case of those compounds which are not indexed, the spectra matching could eliminate some other possible structures.

Before injecting the ether extractables fraction into the GC–MS combination, some pretreatment appeared necessary. The fatty acids and their esters present in the ether extractables were separated by basic hydrolysis in 8% methanolic solution of KOH. The methanol was evaporated off and the residue taken up in distilled water and washed with ether. The water phase was acidified (pH 1), and the fatty acids were extracted with ether and methylated by using BF_3–CH_3OH solution. The chromatographic separation of the methyl esters was done in a column of DEGS 15% on Chromasorb W. The remaining ether extractables were prefractionated on neutral alumina column, using eluants with increasing degree of polarity (from hexane to acetic acid). The particular fractions obtained in this manner were subsequently injected into the GC–MS system.

Results and Discussion

Distribution of Organic Groupings. Results of examining samples of secondary effluents from different treatment plants are gathered in Table I. On the whole, the results obtained during examining the above effluents are repeatable within relatively low degree of deviation.

The average distribution of the organic groupings and fractions is shown in Table II. The results, in general, correspond to the findings reported in the earlier publication

Table I. Composition of Soluble Organics in Secondary Effluents as Percent of Total COD

	Constituent, %								
Sample[a] of sec. effl. and its COD as mg O^0/l.	Proteins	Carbohydrates	Anionic detergents	Tannins and lignins	Ether extractables	Fulvic acid	Humic acid	Hymathomelanic acid	Total
TF COD = 160	18.9	7.1	19.6	1.1	13.4	20.8	13.5	7.1	101.5
TF COD = 180.5	21.4	5.4	14.1	1.6	15.6	30.2	9.7	6.8	104.8
TF COD = 148.3	21.6	6.7	13.3	1.4	10.8	27.5	12.9	7.8	99.9
TF COD = 158.1	24.3	6.0	15.6	1.2	15.6	23.5	10.9	6.4	102.9
TF COD = 172.1	21.7	4.2	20.5	1.4	11.7	25.2	15.7	10.3	107.3
SP COD = 120.4	21.4	8.0	11.2	2.4	10.3	27.9	14.3	6.2	101.7
SP COD = 153.2	20.8	7.5	13.1	1.8	13.2	25.3	15.1	7.2	107.0
AS COD = 105.5	21.0	5.1	15.6	1.3	16.5	16.8	9.6	4.8	90.7
AS COD = 135.7	23.4	5.1	15.3	0.8	16.7	29.6	4.3	5.8	101.0
AS COD = 112.7	24.8	4.6	15.9	1.0	19.9	24.0	7.0	6.6	103.8
AS COD = 167.4	23.0	3.6	17.2	0.9	12.2	25.6	3.6	1.9	98.0

[a] TF, trickling filter; SP, stabilization pond; AS, extended aeration activated sludge.

Table II. Distribution of Organic Groupings in Secondary Effluents—Mean Values

Organic groupings and fractions	Percent of total COD: Municipal wastewater; high rate trickling filter	Municipal wastewater; stabilization pond	Domestic wastewater; extended aeration activated sludge
Proteins	21.6	21.1	23.1
Carbohydrates	5.9	7.8	4.6
Tannins and lignins	1.3	2.1	1.0
Anionic detergents	16.6	12.2	16.0
Ether extractables	13.4	11.9	16.3
Fulvic acid	25.4	26.6	24.0
Humic acid	12.5	14.7	6.1
Hymathomelanic acid	7.7	6.7	4.8

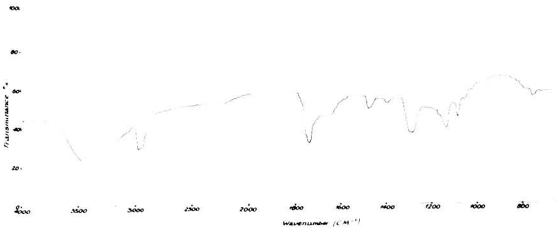

Figure 1. Ir spectrum of fulvic acid isolated from secondary effluent (T.F. plant)

(*1*). They show that the distribution of the main organic fractions is similar for the various biological treatment units studied. The percent of humic acid and the total humic substances is to some extent smaller in the effluents from the pure residential area than in effluents of municipal origin.

Characterization of Humic Substances. The ir spectra of humic and fulvic acids isolated from secondary effluents show a fairly great resemblance (hymathomelanic acid has not been examined). A typical ir spectrum of fulvic acid is presented in Figure 1. The main absorption bands are in the regions of: 3400—hydrogen-bonded OH; 2980, 2940, 2860, 1460—methylene and methyl stretching; 1730—C=O of carboxyl and ketonic carbonyl; 1630—amide carbonyl or aromatic C=C; 1270, 1130, 1080—carbon-oxygen C—O stretching. This is in accordance with the findings of some other investigators who concluded that the ir spectra of humic preparations usually indicate a highly unsaturated structure having hydroxyl and amide or/and carboxyl functional groups (*2, 5–7*).

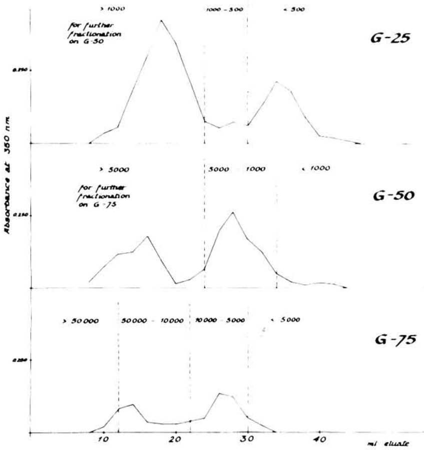

Figure 2. Elution pattern of fulvic acid from secondary effluent and its molecular weight distribution (by dextrans) using sephadex gels

Table III. Acidic Groups of Humic Compounds Present in Secondary Effluents

Humic compound	Acidity in meq/g: Total acidity	Carboxyl	Phenolic hydroxyl
Fulvic acid	12.3	9.2	3.1
Humic acid	8.3	8.3	—
Hymathomelanic acid	8.7	8.7	—

Table IV. Molecular Weight Distribution of Humic Substances from Secondary Effluents

Molecular weight range	Percent of humic compound present: Fulvic acid	Humic acid	Hymathomelanic acid
<500	27.5	17.9	4.5
500–1000	7.8	6.2	12.2
1000–5000	35.7	29.4	48.0
5000–10,000	15.3	7.8	28.0
10,000–50,000	9.4	36.7	7.5
>50,000	4.3	2.0	0

Analytical results showing the content of carboxyl and phenolic hydroxyl groups of humic compounds are presented in Table III.

The total acidity of the humic compounds arises mainly from the dissociable hydrogen in aliphatic and aromatic carboxyl groups and in phenolic hydroxyl groups (*8*). The presence of those acidic groups, especially carboxyls, increases the solubility of humic compounds and enhances their resistance to coagulation, thus increasing their lifetime in the water. This may explain the fact, that fulvic acid, having greater acidity than humic and hymathomelanic acids (Table III), is also more widespread in effluents (Tables I and II). The relatively low content of the phenolic hydroxyl group may be caused by deficiency of lignin residues in the effluent (*9*).

An example of fractionating sample of fulvic acid from secondary effluent by using Sephadex gels G-25, G-50, and G-75, respectively, has been given in Figure 2. The molecular weight distribution of humic substances isolated from secondary effluents (T.F. plant) is presented in Table IV. The majority of fulvic and hymathomelanic acids isolated from secondary effluents have molecular weights ranging

Table V. Molecular Weight Range of Major Part of Humic Substances in Various Waters and in Secondary Effluent

Source of humic compound and reference	Molecular weight range of major part of humic compound
Lake water (*10*)	Over 10,000
Natural waters (streams) (*11*)	700–10,000
Moorland water (*12*)	100,000–200,000 and <10,000
River water (*13*)	700–5000
Secondary effluents (our findings)	1000–5000

from 1000–5000, whereas most of the humic acid is present in the range 10,000–50,000. A relatively great amount of fulvic acid has been found in the range less than 500.

It may be interesting to compare the molecular weight distribution of humic compounds from various sources (natural waters). Table V gives a compilation of findings of several investigators.

Characterization of the Ether Extractables. In the study of the composition of the ether extractables by using GC-MS combinations, the following series of fatty acids has been identified:

Nonanoic acid, $CH_3(CH_2)_7CO_2H$
Decanoic acid, $CH_3(CH_2)_8CO_2H$
Undecanoic acid, $CH_3(CH_2)_9CO_2H$
Dodecanoic acid, $CH_3(CH_2)_{10}CO_2H$
Tetradecanoic acid, $CH_3(CH_2)_{12}CO_2H$
Pentadecanoic acid, $CH_3(CH_2)_{13}CO_2H$
Palmitic acid, $CH_3(CH_2)_{14}CO_2H$
Stearic acid, $CH_3(CH_2)_{16}CO_2H$

The occurrence of fatty acids with an uneven number of carbon atoms (C_9, C_{11}, C_{15}) can be explained by assuming that those acids are formed by biological oxidation of the unsaturated acids during the treatment processes of wastewaters. It is noteworthy that no unsaturated acids have been found among the ether extractables from secondary effluents.

The other identified compounds are as follows:

Hydrocarbons: *n*-alkanes $C_{17}H_{36}$–$C_{35}H_{72}$ (19 compounds)

Alkyl benzenes: isopropyl benzene and dodecyl benzene

Higher aromatics: naphthalene, methylnaphthalene, diphenyl, diphenylmethane, dioctylphthalate, phenol, and triethylphosphate

The study has shown that by using this technique it is possible to identify a large number of specific organic compounds. The investigation has been somewhat limited because the mass spectrometer used in this work is a low-resolution instrument (Atlas CH_4) that can provide only nominal masses, leaving a large number of contaminants that cannot be identified unequivocally. High-resolution mass spectrometer coupled with gas chromatography would make possible identification of additional specific compounds. Once identified, those compounds could then be monitored by simple techniques.

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Determination of Permeability Profile of Surface Terrain

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■ A simple method has been developed and tested for determining the profile of permeability to the flow of a liquid through typical surface cover in permafrost regions. Permeability data are required for the evaluation of the magnitude of oil spills on such terrain. The method involves simple in situ measurements of flow and levels and enables permeability to be calculated at various depths below the surface. Typical results for regions around Norman Wells, Northwest Territories, Canada, are presented. Permeability to oil is unaffected by the initial moisture content of the surface cover.

In the event of a spill from an oil pipeline traversing land, the spreading of oil from the site is determined by the slope of the terrain and the permeability and the absorptive capacity of its surface to oil. These factors have been considered with special reference to the proposed Mackenzie Valley pipeline by Mackay et al. (*1*). The present purpose is to describe a simple method of determining the permeability of the surface by simple field experiments.

During the summer of 1973 at Norman Wells, Northwest Territories, Canada, the surface presented by the ground consists of live mosses with some lichen, several centimeters in thickness, supporting some other plants and grasses. The roots of the moss reach into submerged growth of previous seasons accumulating and consolidating organic detritus which extends to a basement in gravel or clay. The depth from surface to basement is usually in the range of 200–500 mm (Figure 1).

Through the profile of the ground, the porosity of the structure decreases from very open in the moss to practically none in the basement which may in fact be frozen. It is evident that there is a great variation in permeability to flow and absorptive capacity with depth.

The study reported here was undertaken with the following objectives: to define a typical profile of flow permeability and to discover any effect of moisture condition of the surface layer on permeability to the flow of oil.

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Figure 1. Typical surface terrain profile, Norman Wells, Northwest Territories, Canada

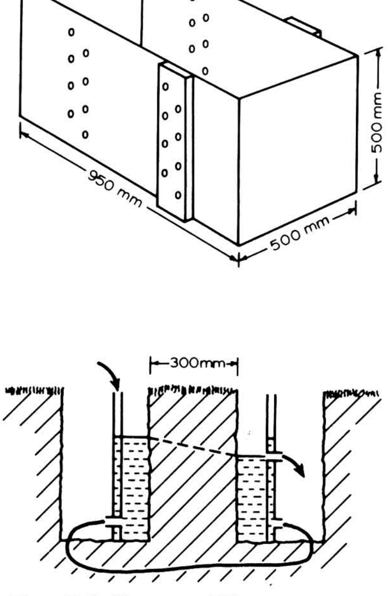

Figure 2. Cell for permeability measurements

Test Sites

The tests were conducted at Norman Wells, Northwest Territories, on August 1 and 2, 1973, under summer conditions. Norman Wells lies in the taiga ecotone climatic zone on the Mackenzie River, at 65°17′N 126°48′W. In July, the net mean daily solar radiation is between 100 and 110 W/m^2 and the mean daily temperatures are 26.7°C maximum and 8.9°C minimum. The mean July precipitation is 56 mm. The "summer" period (daily mean temperature above 0°C) can be considered to be from April 20 to September 17 (*2*). Norman Wells lies in the discontinuous permafrost region (*3*).

The vegetation at Norman Wells consists of riverine forest, mostly black spruce. Localities in the black spruce forest with typical moss growth and basement conditions were sought. Eventually two separate sites were chosen. The first test location had a moss and root layer about 80 mm thick and basement in clay at 250 mm. The ground was entirely moist but there was no free water down to the basement level. The second site chosen had a basement in gravelly clay at 500 mm and a moss and root layer down to about 150 mm and free water at the depth of 400 mm. The first site was on generally sloping ground but was itself almost level. The second was in the trough of a minor valley and would be in the course of surface water in times of drainage.

Test Procedure

Flow tests to measure permeability were conducted in a test cell placed in the ground on site. A sketch of the device is shown in Figure 2. The construction was of galvanized steel sheet and consisted basically of four walls; side walls to isolate the test sod from the surroundings and front and back walls to form inlet and outlet wells for the fluid. Compartments with closed bottoms were provided on the front and back walls for use as liquid inlets or level wells as desired. Ports in the walls of the cell and in the inner and outer faces of the compartments could be opened or closed with corks as needed, so providing flexibility in flow arrangements.

In placement of the test cell, the requirements were that the surface of the ground should be level, locally, and that a basement of relatively impermeable material could be reached. A saw blade was used to make cuts for the side walls, the front and rear faces of the sod were cut and excavated, and the cell was set in. Contact on the side walls was maintained by packing material against the outsides where necessary, while sealing at the bottom of the front and back walls was effected by consolidation of the earth and by packing with additional clay. In the second test cell, some attention had to be given to maintenance of bottom sealing under conditions of high liquid level inside the cell.

With the test cell set in, a flow of water was run to the inlet side and allowed to penetrate the sod, build a level in the outlet dam, and to overflow. Measurements of inlet and outlet flows were made by measuring cylinder and stopwatch. Inlet and outlet levels and the difference between them were determined, the difference measurement being facilitated by the arrangement to transmit liquid level from one end of the cell to the other.

Such measurements of flow and hydraulic gradient were made for various average levels of flow. At higher levels, where the permeability of the ground increased, larger flows were required to give readily measurable differences in liquid depth.

Tests were made with water at each site and with Norman Wells crude oil at the first site. Norman Wells crude has a sulfur content of 0.3 weight percent, a specific gravity of 0.833 (15.6°C), and a pour point of −51.1°C (*4*). The viscosity was taken to be about seven times that of water at the temperature of the experiment (*1*).

Permeability Results

In most tests, the steady inflow rate exceeded the steady overflow rate from the discharge dam. This was because of leakage from under both the inlet and outlet dams. Tests with flow discrepancies of more than 25% were rejected and repeated after attempts to stem the leakage. In acceptable cases, the inflow and outflow were averaged as the best estimate of flow through the sod.

The results are expressed in Tables I-III as (volume flow)/(width of cell) (hydraulic gradient). Values are given for several different levels above the cell basement. Hydraulic gradient is the difference in liquid levels between the front and back faces of the test sod divided by the length of the sod. It is the driving force for flow of the liquid. Flows obtained at differing gradients can be compared directly when normalized in this way.

These results are given graphically in Figures 3 and 4.

The profile of permeability, where permeability is defined as (flow)/(area) (hydraulic gradient), is derived from the slope of these graphs. Figure 5 gives the permeability for Cell No. 2 for which the more complete range of values can be found.

Shown also on this figure are some limits to permeability which have been estimated from the properties of a sample of moss material brought from Norman Wells in

Table I. Flow in Cell No. 1—Water

Level above basement, mm	Flow, 10^{-3} m^2/sec	Temp, °C
110	0.77	14
110	1.02	14
130	1.03	14
130	1.14	14
160	1.54	14
160	1.91	14
190	2.37	14
190	2.64	14

Table II. Flow in Cell No. 2—Water

Level above basement, mm	Flow, 10^{-3} m^2/sec	Temp, °C
220	0.14	15
220	0.12	15
260	0.57	15
260	0.56	15
310	2.21	15
310	1.85	15
310	1.34	15
350	3.8	15
355	3.7	12
355	3.9	12
410	16.1	12
410	21.5	12
410	17.0	12
410	15.6	12
415	30	12

Table III. Flow in Cell No. 1—Oil

Level above basement, mm	Flow, 10^{-3} m^2/sec	Temp, °C
160	0.21	21

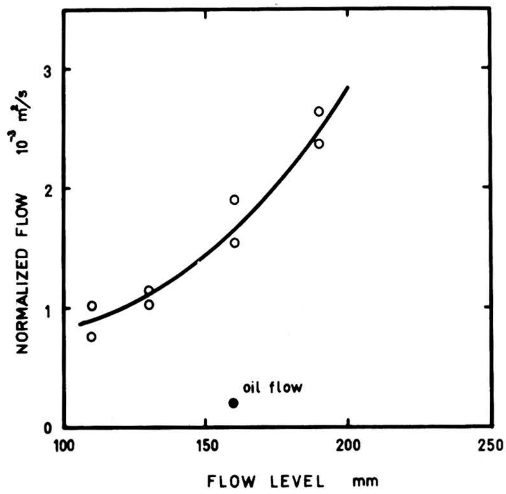

Figure 3. Water flow in Cell No. 1

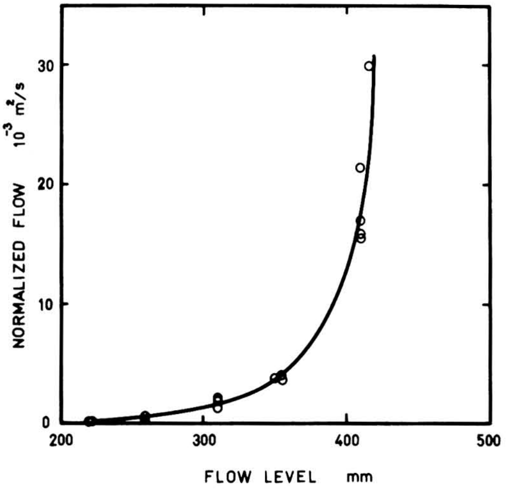

Figure 4. Water flow in Cell No. 2

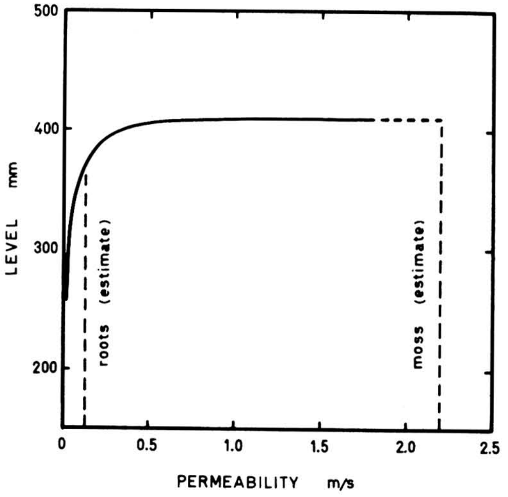

Figure 5. Permeability at Cell No. 2

July 1973. Measurements on this sample yielded the following values.

Moss layer:
porosity, $e = 0.9$
fiber diameter, $d = 0.5\text{mm}$
specific surface, $S = 4/d = 8 \times 10^3 \text{m}^{-1}$

Root layer:
$e = 0.85$
$d = 0.2\text{mm}$
$S = 20 \times 10^3 \text{m}^{-1}$

The respective permeabilities to water, estimated from the Kozeny relationship (*5*):

$$k = \frac{1}{5\mu} \frac{e^3}{(1-e)^2 S^2} \rho g$$

where

$\mu = 1.0 \times 10^{-3} \text{kgm}^{-1}\text{sec}^{-1}$
$\rho = 1000 \text{ kg/m}^3$
$g = 9.82 \text{ m/sec}^2$

are: moss layer, 2.2 m/sec; root layer, 0.13 m/sec.

These estimates are in fair correspondence with the measured permeabilities at their respective levels.

Observations on Oil Flow

In the water flow tests, there was an equilibrium saturation of the ground for each level of water at which flow through the test section was maintained. Capillarity caused material some distance above the level of flow to become wet—but not saturated.

A matter to be resolved with respect to the flow of oil was the possibility that the organic layers might tend to retain water and so prevent full access of oil to the flow passages. This did not happen. When a flow of oil was introduced to the test cell, water was displaced immediately, and the oil appeared to wet the surface of the fibers. Complete relative permeability of the organic layers to oil is indicated by the oil flow shown on Figure 3 which, if multiplied by the ratio of the viscosity of oil to that of water, a factor of about seven, is comparable with the flow of water.

Conclusions

A profile of permeability to the flow of water of a typical ground surface layer at Norman Wells is presented in Figure 5. The velocity of flow at a particular level is obtained from

velocity = (permeability) (hydraulic gradient)

where a viscosity of 1×10^{-3} kg m^{-1} sec^{-1} has been taken for water.

The ground is equally permeable to Norman Wells crude oil and the velocity of flow of oil is given by

velocity = (permeability) (hydraulic gradient) × [(viscosity of water)/(viscosity of oil)]

The simple in situ flow experiment described is suitable for rapid and routine measurement of surface permeability in any situation in which an impermeable basement, for example, permafrost, underlies an upper region of varying permeability. The method described enables a profile of permeability to be determined.

Nomenclature

d = fiber diameter, L
e = porosity
k = permeability, LT^{-1}
g = gravitational acceleration, LT^{-2}
s = specific surface, L^{-1}
ρ = density of liquid, ML^{-3}
μ = viscosity of liquid, $ML^{-1}T^{-1}$

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Thermal and Photochemical Reactions of NO_2 with Butyraldehyde in Gas Phase

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■ The rates of thermal and photochemical reactions of butyraldehyde with NO_2 were measured. The thermal rate constant was determined to be $10^{7.4}$ exp $(-12{,}400/RT)$ lm^{-1} sec^{-1}. The rate constant for the reaction of oxygen atoms with butyraldehyde was determined to be 1.5×10^8 lm^{-1} sec^{-1} at 25°C. These results are close to those for the lower-molecular-weight aldehydes and indicate that they may all be treated by means of one general mechanism.

This paper summarizes thermal reactions of CH_3CHO, C_2H_5CHO, and C_3H_7CHO with NO_2 and the photochemical oxidation of C_3H_7CHO in the presence of NO_2. It is one in a series (*1-5*) devoted to the study of the reactions of substances found in photochemical smog. Aldehydes are of considerable interest because they have been found in relatively high concentrations (~2 ppm) in urban atmospheres (*6*) and because they are relatively reactive compounds. Aldehydes are also among the products of the oxidation of olefins by O_3 and by (O^3P).

Earlier studies of the thermal reactions of formaldehyde (*7, 8*) and acetaldehyde (*9, 10*) were carried out at elevated temperatures and at different concentrations compared with those reported here. However, the products of the reactions and the rate laws agree in general with those determined in the present work.

The reaction of atomic oxygen (O^3P) with formaldehyde (*11, 12*) and with acetaldehyde (*13-16*) have also been investigated in photochemical systems. This paper extends the series of aldehydes to butyraldehyde and shows that all of these low-molecular-weight aldehydes can be treated by means of one general mechanism.

Results

The experimental procedures used in this work have been described in previous papers (*1-5*). In general, gases were purified and transferred by standard high vacuum techniques. The concentration of NO_2 was determined photometrically at 4358 Å where photolysis does not take place, and the products of the reactions were analyzed chromatographically.

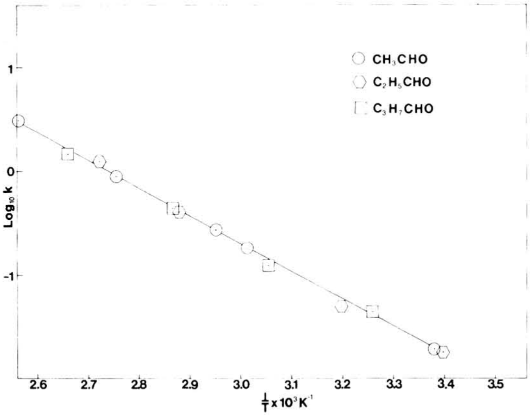

Figure 1. Arrhenius plot for some aldehyde $-NO_2$ reactions

Thermal Reactions. A series of reactions in which $[NO_2]$ was varied in the range 10^{-5} to $10^{-4}M$ and each aldehyde concentration (CH_3CHO, C_2H_5CHO, and C_3H_7CHO) was varied in turn in the range 10^{-4}–$10^{-3}M$, was carried out at room temperature.

Plots of the initial rates of loss of NO_2 as a function of the product, $[NO_2]_0[ald]_0$ yielded straight lines indicating a rate law of the form,

$$\frac{-d(NO_2)}{dt} = k_{expt}[NO_2]_0[ald]_0 \tag{1}$$

A second series of reactions was run for each aldehyde as a function of temperature between 22° and 117°C. By use of Equation 1, the specific rate constants were calculated and are represented in the Arrhenius plot shown in Figure 1. All three aldehydes gave the same results within experimental error. A least squares treatment of the data yields the relationship:

$$k = 10^{7.4}e^{-12400/RT} \tag{2}$$

in which k is in liter mol^{-1} sec^{-1}, and the activation energy is given in calories. Equation 2 may be compared with the relationship reported by Gray and Yoffe (*17*),

$$k = 10^7 e^{-13500/RT}$$

for acetaldehyde between 100° and 150°C. From Equation 2, one obtains the experimental rate constant at 25°C with a value of 2.0×10^{-2} l. mol^{-1} sec^{-1}.

Quantum Yields. Quantum yields for NO_2 loss were measured at 3660 Å where butyraldehyde does not photolyze so that changes in quantum yield with the ratio of aldehyde to NO_2 would be due exclusively to reactions with $O(^3P)$ atoms and subsequent free radical reactions. NO_2 concentrations were varied from about $8.9 \times 10^{-5}M$ to about $1.6 \times 10^{-4}M$ and the aldehyde concentration was varied from about $2.7 \times 10^{-4}M$ to about $2 \times 10^{-3}M$. The results of this series are represented in Figure 2 which conforms to the relationship:

$$\Phi_{NO_2} = A + B\frac{[C_3H_7CHO]}{[NO_2]} \tag{3}$$

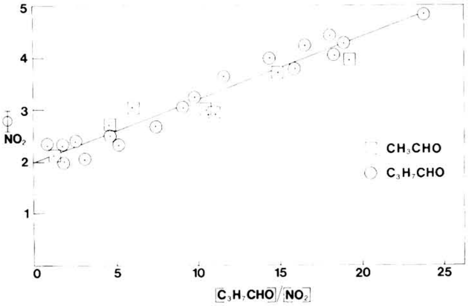

Figure 2. Quantum yields as function of $[C_3H_7CHO]/[NO_2]$

Table I. Initial Rates of Formation of Products for the Photochemical Reaction

Product	Initial rate, mol $l.^{-1}$ sec^{-1}
$C_3H_7NO_3$	4.2×10^{-11}
$C_3H_7NO_2$	1.9×10^{-11}
CO_2	9.5×10^{-10}
H_2O	8.7×10^{-10}
NO	2.8×10^{-9}

in which A equals 2, the quantum yield for pure NO_2, and B equals 0.12.

Product Analysis. The principal products of reaction found by chromatographic analysis were NO, CO_2, H_2O, $C_3H_7ONO_2$, and $C_3H_7NO_2$. Some C_3H_7ONO was also found but its rate of formation was not measured. The rates of formation of these products were determined by measuring the chromatographic peak areas as a function of irradiation time. The product concentration was fit to a least squares curve with the form $P = a + bt + ct^2$. The value of b represents the initial rate of formation of products since $(dP/dt)_{t \to 0} = b$. Table I summarizes those initial rates of formation.

Discussion

The results of this study are consistent with the combined mechanism for the dark reaction (*17*) and the photochemical reactions (*13, 15, 18, 19*) of NO_2 and aldehydes. It may be summarized by:

$$NO_2 + h\nu \longrightarrow NO + O \qquad (I_a)$$

$$NO_2 + O \longrightarrow NO + O_2 \qquad (4)$$

$$O + C_3H_7CHO \longrightarrow C_3H_7CO + OH \qquad (5)$$

$$OH + C_3H_7CHO \longrightarrow C_3H_7CO + H_2O \qquad (6)$$

$$NO_2 + C_3H_7CHO \longrightarrow C_3H_7CO + HNO_2 \qquad (7)$$

$$NO_2 + C_3H_7CO \longrightarrow C_3H_7CO_2 + NO \qquad (8)$$

$$C_3H_7CO_2 \longrightarrow C_3H_7 + CO_2 \qquad (9)$$

$$NO_2 + C_3H_7 \longrightarrow C_3H_7O + NO \qquad (10)$$

$$NO_2 + C_3H_7 \longrightarrow C_3H_7NO_2 \qquad (11)$$

$$NO_2 + C_3H_7O \longrightarrow C_3H_7ONO_2 \qquad (12)$$

The reaction:

$$C_3H_7 + C_3H_7CHO \longrightarrow C_3H_8 + C_3H_7CO$$

was not included in the mechanism, since it should be relatively slow compared with Reactions 10 and 11. By analogy, the rate of the reaction

$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO$$

is (*20*) 2.4×10^3 l. mol^{-1} sec^{-1} compared with (*21*) 1.7×10^9 and 3.3×10^9 l. mol^{-1} sec^{-1} for CH_3, NO_2 reactions analogous to Reactions 10 and 11.

The rate law derived from Reactions 7 through 12 and the usual steady state approximations is:

$$-\frac{d(NO_2)}{dt} = k_7\left(3 + \frac{k_{10}}{k_{10} + k_{11}}\right)[NO_2][C_3H_7CHO] \qquad (13)$$

Comparison of Equation 13 with Equation 1 yields for the dark reaction,

$$k_{expt} = k_7\left(3 + \frac{k_{10}}{k_{10} + k_{11}}\right) \qquad (14)$$

From the initial rates of production of $C_3H_7NO_2$ and $C_3H_7ONO_2$ in Table I and the theoretical rates of formation of these products from the mechanism, one obtains $k_{10}/k_{11} = 2.2$. Thus, with k_{expt} equal to 2.0×10^{-2} l. mol^{-1} sec^{-1}, k_7 equals 5.4×10^{-3} l. mol^{-1} sec^{-1}. This value is small enough to justify the deletion of Reaction 7 from the mechanism for the purposes of the derivation of the quantum yield expression for short irradiation times. The expression is:

$$\Phi_{NO_2} = 2 + \left(3 + \frac{2k_{10}}{k_{10} + k_{11}}\right)\frac{k_5}{k_4}\frac{[C_3H_7CHO]}{[NO_2]} \qquad (15)$$

This equation compares favorably in form with Equation 3 for which

$$B = \left(3 + \frac{2k_{10}}{k_{10} + k_{11}}\right)\frac{k_5}{k_4}$$

and helps to support the proposed mechanism. If one uses (*22*) $k_4 = 5.5 \times 10^9$ l. mol^{-1} sec^{-1}, and $B = 0.12$ from Equation 3, one obtains $k_5 = 1.5 \times 10^8$ l. mol^{-1} sec^{-1} which is not too far from 2.7×10^8 l. mol^{-1} sec^{-1} reported by Cadle and Powers (*13*) for the reaction of $O(^3P)$ with acetaldehyde, and close to 1.4×10^8 l. mol^{-1} sec^{-1} reported by Cadle and Allen (*16*) for propionaldehyde.

The quantum yield results indicate that the mechanisms and rate constants for the photochemical reactions of NO_2 with low-molecular-weight aldehydes (at least up to C_3H_7CHO) are all the same within experimental error. They depend on the aldehydic C—H bond energy and very little on the size of the R group in RCHO. A few points were determined for CH_3CHO and included in Figure 2 to help support this conclusion.

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Cation Solubilities of Lignite Fly Ashes

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■ Concentrations of Ca, Na, Mg, and Fe were determined in water extracts of four lignite fly ashes from three Northern Great Plains mines. The main mass of soluble cationic material released was represented by Ca and Na, although considerable variability existed among the four ashes in proportional and absolute amounts solubilized. Mg and Fe generally were solubilized at rates roughly one to two orders of magnitude less than Ca and Na. As the ratios of H_2O:ash were increased, generally greater relative amounts of Ca, Mg, and Fe and lesser relative amounts of Na were found in solution. Dust collector ash was higher in sulfate than electrostatic precipitator ash, as indicated by these tests. Approximately 50% of the cations solubilized by water from dust collector ashes appeared to exist as sulfates. It is believed that a considerable portion of the Ca, Mg, and Na exists in the ash as oxide, thus giving rise to high pH values for water suspensions.

In recent decades, use of lignites and subbituminous coals present in the Tertiary rocks of the Northern Great Plains has been largely limited to local institutional heating plants and moderate-sized (<500 MW) thermogenerators. Total annual consumption for these purposes is generally estimated at less than 10 million tons (T). However, because of rising energy requirements, priorities on petroleum and gas usage, and other factors, these beds of fossil fuels are quite likely to play a major part in energy production in the upper Mississippi and Missouri River areas for the next two to three decades. Fortunately, reserve supplies are large; one estimate (*1*) is a total of 438.5 billion tons in North Dakota and Montana, representing about 25% of the coal reserves of the United States. Several major thermogenerating units are in advanced planning to construction stages. Some of these plants will consume 7000 to 10,000 T/day, and larger plants are being planned.

These fuels are moderately high in total ash; one group of samples, ranging from 7–14% ash, on the dry basis, and with BTU values of 5000–7000/lb, will produce major quantities of ash. Known uses of coal ash include: partial aggregate requirements in asphalt paving, cement in certain concretes, deicing material for streets and highways, and bulk density—ameliorating materials in certain soils. Because of the large quantities of ash, the utility of the ash as an amendment in the amelioration of certain sodic claypan soil properties is being investigated. The possibility exists that some ashes may contain sufficient toxic factors to affect plant growth on certain soils. Ancillary to that investigation and because other potential uses of the ash may also depend on cation solubilities, a study was made of the water-soluble cation composition of some of the major ashes being produced by operating generating plants.

Procedure

Four lignite fly ashes from the Northern Great Plains were used in this study. These will be referred to by number and are: No. 1—ash from lignite taken from Gascoyne mine, N.D., fired at the Fergus Falls, Minn., power plant and collected from the electrostatic precipitators; No. 2—ash from lignite taken from Beulah mine, N.D., fired at the Fergus Falls, Minn., power plant and collected from the dust collectors; No. 3—ash from lignite taken from Gascoyne mine, N.D., fired at the Fergus Falls, Minn., power plant and collected from the dust collectors; No. 4—ash from Stanton, N.D., power plant collected from the dust collectors. The mine is adjacent to the plant.

Water solubilities of Ca, Mg, Na, and Fe were determined at H_2O:ash ratios by weight of 5, 25, 50, 75, and

Table I. Cations Solubilized from Four Fly Ash Samples by One Washing at Three Water:Ash Ratios

(Values based on dry wt. of ash)

Fly ash no.	Water: ash	Ca, ppm	Na, ppm	Mg, ppm	Fe, ppm
1	5	2,360	834	6	1.1
	50	11,200	955	36	11.7
	100	14,000	1,184	47	23.2
2	5	4,760	9,550	8	1.5
	50	14,800	10,300	71	17.4
	100	22,800	10,350	135	33.3
3	5	5,960	11,040	0	1.5
	50	11,800	11,720	30	11.7
	100	17,600	12,880	36	30.0
4	5	2,480	6,030	2	1.8
	50	7,000	6,490	36	16.7
	100	8,800	6,850	72	35.0

Table II. Cations Solubilized from Four Fly Ash Samples in Composite of Five Washings at Three Water:Ash Ratios

(Values based on dry wt. of ash)

Fly ash no.	Water: ash	Ppm solubilized from fly ash			
		Ca	Na	Mg	Fe
1	5	11,000	1,790	125	5.3
	50	28,000	1,820	461	54
	100	36,000	2,970	916	124
2	5	15,800	16,900	88	4.9
	50	38,000	12,400	369	65
	100	54,000	10,800	582	76
3	5	10,200	7,580	0	17.4
	50	32,000	9,350	56	9.3
	100	44,000	8,640	374	18.4
4	5	6,200	9,660	4	6.9
	50	18,000	8,420	126	42.1
	100	28,000	8,640	285	111

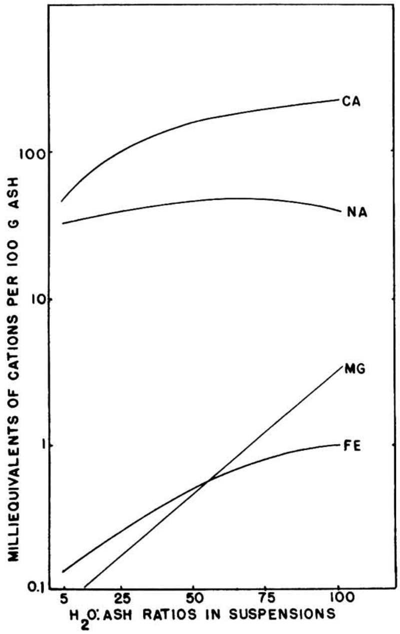

Figure 1. Release of cations by ash no. 3 to five composited extractions at $5 H_2O$:ash ratios

100 for 1, 5, and 50 washings. These ratios were obtained by adding the appropriate weight of ash to 25 grams of deionized water in plastic centrifuge tubes. Each washing consisted of shaking the suspension 30 min (15 min in the case of 50 washings), centrifuging, and decanting off the supernatant. This procedure was followed until the desired number of washings had been made.

All washings were done with H_2O temperatures of 22-23°C. Mg, Na, and Fe analyses were done by atomic absorption spectrophotometry. Ca was determined by EDTA titration. Potassium was not determined in these investigations. Total analyses of ashes from the Gascoyne lignite have been reported by Sondreal et al. (*2*) and indicate K contents ranging from 0.83–0.41%, and from the Stanton lignite, 0.17–1.2%. This is approximately an order of magnitude lower than the four cations chosen for analysis. Soluble K was presumed to be present in about the same relative amounts to total K as was the case with sodium compounds, and thus was not determined.

Results and Discussion

Tables I and II give the soluble cations released from four fly ashes at three H_2O:ash ratios for the first washing and a composite of washings 1–5, respectively. Ca solubilized from a given amount of fly ash increased with increased dilution of the system. Essentially an equal percentage of the total Na contained in the ash was soluble at all H_2O:ash ratios, although ash no. 1 tended toward an increased percentage of the total Na being released with increased H_2O:ash ratios in both the single and composite of five washings. [In the composite of five washings, ashes no. 2 and 4 had more Na solubilized at the H_2O:ash ratio of five than at other ratios (Table II).] In the composite of the five washings, ashes no. 2, 3, and 4 released a greater fraction of the total soluble Ca and Na in the first washing than did ash no. 1.

Amounts of soluble Mg and Fe were small, relative to Ca and Na. Both exhibited an increased percentage of the total element solubilized with increased dilution of the system.

Table III. pH, Total of Cations Determined and Sulfate Content of Supernatant from Composite of Five Washings at Three Water:Ash Ratios

Fly ash no.	Water: ash	pH supernatant	Total cations, meq/l.	SO_4, meq/l.
1	5	11.8	25.70	1.25
	50	10.5	6.16	0.64
	100	9.7	4.08	0.48
2	5	11.6	61.61	30.0
	50	10.7	10.02	4.3
	100	10.3	6.66	2.5
3	5	11.6	50.97	31.6
	50	11.1	8.98	4.5
	100	10.8	5.87	2.2
4	5	11.6	29.41	16.4
	50	11.0	5.26	1.6
	100	9.2	3.79	0.9

In 50 washings, solubilized Ca, Mg, Na, and Fe aggregated 5.35, 7.95, 6.74, and 5.10% of the original weight of ashes no. 1, 2, 3, and 4, respectively. The mass represented by Ca of total solubilized cations measured ranged from 82.5% for ash no. 1 to 68.9% for ash no. 4.

Releases of Ca and Na during the 50 washings can be summarized as follows:

1. Ashes no. 2, 3, and 4 had 78–91% of the soluble Na and 31–36% of the soluble Ca going into solution in the first five washings.
2. Ash no. 1 had 34% of the soluble Na and 50% of the soluble Ca going into solution in the first five washings.

Thus, the ash from an electrostatic precipitator investigated here appears to release soluble cations in a different pattern from the ashes from dust collectors. However, fly ash no. 1 may not be representative of all collections from electrostatic precipitators.

Fly ash no. 3 is used for Figure 1 to show the overall trend of the ashes collected from the dust collectors. All five H_2O:ash ratios are plotted vs. the milliequivalents of cations solubilized per 100 grams of ash for the composite of five washings. Generally, the same solubility characteristics as discussed for Table II are shown in Figure 1.

The pH, total of the four cations determined, and sulfate of the supernatant resulting from the composite of five washings of three H_2O:ash ratios are given in Table III. With increased dilution of the four ash samples, pH, total cation concentration, and SO_4 in the supernatant decreased. For ash no. 1, the percentage of the cations present in the form of sulfates is considerably less than for the other three ashes. Reactions of all ashes are alkaline, with pH values of first water suspensions ranging to 11.8.

Doran and Martens (*3*), using 15 fly ash samples from nine states, reported samples from the Northern Great Plains region to have acid-neutralizing capacities much larger than fly ashes from the eastern and southern United States. This high neutralizing capacity and the high pH, especially from lower fly ash dilutions, are largely the result of soluble compounds of Ca and Na. Ca and Na in the present study made up well over 80% of the soluble cations determined. The supernatant concentrations of Ca and Na are quite high at the lowest H_2O:ash ratios used.

Pozzolanic activity (tendency to set up as cement) was quite noticeable in the first five washings. The ash used in these washings was difficult to suspend in the next washing, but by the 20-30th washings, all pozzolanic tendencies disappeared.

Rainfall on open stockpiles of fly ash would bring about H_2O:ash ratios considerably less than five. At such ratios, runoff and leaching water would contain high salt concentrations, of which over 50% of the cations in most cases could be sodium (Table I, ashes no. 2, 3, and 4), and pozzolanic activity would be high. Thus, any application of ash to surfaces should be accompanied by concomitant mixing to prevent lump or crust formation on soils susceptible to crusting.

A possible use of lignite fly ash is as a soil amendment; either acid or sodic soils might be improved. As a soil amendment for the amelioration of sodic (alkali) soils, fly ash at 5 T/acre-furrow slice will give a H_2O:ash ratio of 100, and at 20 T/acre-furrow slice, will give a H_2O:ash ratio of 25, at a soil water gravimetric content of 50%. If we initially release high concentrations of salts, flocculation and permeability of sodic soils should be increased, and subsequent releases, made largely of Ca, could replace Na on the soil colloid exchange sites as the leaching process takes place. For example, a sodium adsorption ratio of 0.87 was observed in the equillibrium water-ash solution at the 5th washing of ash no. 3 with a water:ash ratio of 100:1. Such a sodium adsorption ratio would not impart sodium ions to clay systems, but rather remove sodium and add calcium. Independent soil column investigations in this laboratory have indicated such takes place; field studies are in progress (*4*).

Phosphorus reduction in lake waters and generating plant cooling waters is another possible use. Tenney and Echelberger (*5*), in a study of fly ash utilization in the treatment of polluted waters, stated that the degree of phosphate removal achieved by a fly ash dosage is determined by the water-extractable lime and gypsum obtained from the fly ash. Typical lignite fly ashes from the Northern Great Plains have been found to have water-soluble constituents of about 8.55% while a typical bituminous fly ash will have about 2.51%. However, it appears from Ksp values of ferric and aluminum phosphates that the soluble iron (ca 20 ppm) derivable from the ashes would have a considerable potential for reducing phosphates in solutions. Kardos (*1*) has proposed that aluminum from gibbsite may reduce soluble phosphate in soil-water systems by 99.98%. The ferric oxides in these fly ashes can supply at least as much soluble iron to combine with phosphates.

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Inhibition of Photochemical Smog Reactions by Free Radical Scavengers

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■ Several free-radical scavengers which appear to have potential as photochemical smog inhibitors have been studied in a series of smog chamber experiments. The inhibition of smog manifestations by the proposed compounds was investigated for pure hydrocarbons and also for synthetic auto exhaust. Particular emphasis in this investigation was placed on uncovering possible detrimental side effects resulting from the use of the inhibitors. In this regard, several of the compounds investigated, while demonstrating an inhibitory effect with respect to NO photooxidation and ozone formation, also yield remarkably large increases in light-scattering aerosol production. These findings have great significance in terms of the possible future use of smog inhibitors in the atmosphere.

The formation of photochemical smog, initiated by the rapid conversion of NO to NO_2, has long been thought to involve a chain mechanism for NO photooxidation. In such smog systems the chain carrier, which is both reactant and product in the NO conversion process, has been postulated to be the hydroxyl radical (*1, 2*). Such a mechanism involving butane and nitric oxide follows:

$$C_4H_{10} + HO\cdot \longrightarrow C_4H_9\cdot + H_2O \qquad (1)$$

$$C_4H_9\cdot + O_2 \longrightarrow C_4H_9O_2\cdot \qquad (2)$$

$$C_4H_9O_2\cdot + NO \longrightarrow C_4H_9O\cdot + NO_2 \qquad (3)$$

$$C_4H_9O\cdot + O_2 \longrightarrow C_3H_7CHO + HO_2\cdot \qquad (4)$$

$$HO_2\cdot + NO \longrightarrow NO_2 + HO\cdot \qquad (5)$$

A possible means of slowing the conversion of NO to NO_2, thereby inhibiting smog formation, has recently been suggested by Heicklen (*3*) and Gitchell et al. (*4*). It involves removal of the chain carrying HO radicals in such a way that the chain is not regenerated. Radical scavengers such as phenol, benzaldehyde, aniline (*4*), and naphthalene (*5*), were suggested because of their easily abstractable hydrogen atoms and because they have no hydrogen atom associated with the α-carbon atom, thus inhibiting chain regeneration.

Stephens et al. (*6*) investigated the effect of several possible smog inhibitors on aerosol formation in mixtures of 2 ppm pentene-2/1 ppm NO_2/0.5 ppm SO_2. Phenol and 4-*n*-hexylresorcinol slightly depressed aerosol formation, although another phenol, 2,6-ditertiary butyl 4-methylphenol, and pyrolidine enhanced aerosol formation. Still another phenol, 2,6-ditertiary butyl 4-methoxyphenol, along with pyrogallol and morpholine, had no effect on aerosol formation. Aniline and *N,N*-dimethylaniline increased aerosol formation at both the 0.5- and 5-ppm levels. *N*-Methylaniline depressed aerosol formation when it was present at 0.5 ppm but increased aerosol formation at the 5-ppm level.

These seemingly conflicting findings may be explained by the methodology employed. Aerosol formation was monitored by a forward-scattering smoke photometer in a stirred dynamic reactor having a residence time of 34 min. Stirring has been shown to adversely affect aerosol formation (*7, 8*), with the magnitude of the effect depending on the particular hydrocarbon system under study. Also, the short residence time coupled with the method of monitoring aerosols may lead to results which are difficult to interpret. For example, in certain chemical systems where nucleation follows an induction period, small aerosols might not have grown to light-scattering size because of the short residence time, but in other chemical systems such growth may have occurred earlier so that a larger fraction of the total aerosol surface was in the light-scattering size range.

Dimitriades and Wesson (*9, 10*) studied the reactivity of several aldehydes present in automobile exhaust and observed that addition of 0.5 ppm of benzaldehyde to an irradiated propylene/NO_x system reduced the rate of NO_2 formation by almost a factor of 2 and lowered maximum oxidant by about one third. Benzaldehyde addition also decreased PAN and CH_2O levels but increased PBzN formation. The addition of benzaldehyde thus inhibited many of the classical smog manifestations; however, the increase in the severe lachrymator PBzN is a very negative side effect. Aerosol formation was not monitored. A study by Kuntz et al. (*11*) has also shown the inhibition effect of benzaldehyde.

In a recent smog chamber experiment carried out in Battelle-Columbus' 610-ft^3 chamber, a trace quantity of phenol was found to yield a severalfold increase in aerosol production in a synthetic auto exhaust experiment. Because such a detrimental side effect as increased aerosol production would obviate the use of the proposed smog inhibitors in urban atmospheres, we initiated a program to more thoroughly investigate the effect of some proposed smog inhibitors under conditions more representative of polluted atmospheres than earlier inhibition studies, giving particular attention to adverse side effects.

Experimental

The Battelle 610-ft^3 smog chamber has been described previously (*12*). Light intensity measurements by NO_2 photolysis (*13*) and *O*-nitrobenzaldehyde photolysis (*14*) agree quite well when compared as described by Gordon (*15*). The value for k_d is 0.45 min^{-1}. Total hydrocarbon is determined by flame ionization, CO by NDIR, SO_2 by flame photometry, O_3 by chemiluminescence, NO and NO_2 by automated Saltzman and by chemiluminescence, PAN by electron capture gas chromatography, and light scattering and visibility by broadband (420–570 nm) integrating nephelometry.

The synthetic automobile exhaust was made up of 50% by weight of a high aromatic automobile fuel (simulating fuel-derived exhaust constituents) and 50% by weight of a C_1—C_4 hydrocarbon mixture (which simulates combustion-derived exhaust components). The composition of this "light-end" mix by volume is ethane 4.0%, ethylene 44.1%, acetylene 28.0%, propylene 16.0%, 1-butene 6.2%, and *trans*-2-butene 1.7%. Aniline was obtained from Baker; isooctane and benzaldehyde from Eastman; and naphthalene from Matheson, Coleman, and Bell. These compounds were used without further purification.

Results and Discussion

The results of our experimental program are shown in Table I. The first comparison is between Runs 1 and 8 which are essentially duplicate experiments, run to ensure that the chamber had not become contaminated with the low-volatility additives used in the experiments. Such contamination would be expected to greatly increase light scattering in subsequent runs. The similarity in Δb-scat values for these two runs indicates that contamination was minimal. A comparison of other reactivity parameters demonstrates rather good reproducibility, certainly within the variation generally exhibited in smog chamber experimentation (*16*).

Run 2 is similar to Runs 1 and 8, with the addition of 0.4 ppm aniline to test its efficiency and side effects as a smog inhibitor. As reported by Gitchell et al. (*4*), the maximum NO_2 level was decreased and the time to achieve this maximum was considerably lengthened. In addition, the maximum ozone level was almost halved and the PAN maximum was cut substantially. All of these beneficial effects, however, are more than offset by the phenomenal increase in light-scattering aerosol, as measured by Δb-scat. The detrimental effect on visibility of such greatly increased light scattering is demonstrated by the drop in visibility from about 17 miles to less than 0.3 mile.

In Run 3 we attempted to determine whether the increased light scattering was hydrocarbon-composition related; for example, is the increased light-scattering phe-

Table I. Smog Inhibition Experiments[a]

Run:	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Additive, ppm (v/v):		**Aniline, 0.4**	**Aniline, 0.8**	**Aniline, 0.8**	**Benzaldehyde, 0.4**	**Naphthalene, 0.4**	**Naphthalene, 0.4**	
Hydrocarbon, ppm C:	**Syn. exhaust, 16**	**Syn. exhaust, 16**	**Isooctane, 16**		**Syn. exhaust, 16**	**Syn. exhaust, 16**		**Syn. exhaust, 16**
NO, ppm	0.83	0.80	0.76	0.80	0.80	0.83	0.76	0.76
NO_2, ppm	0.19	0.20	0.20	0.20	0.20	0.20	0.21	0.20
SO_2, ppm	0.10	0.10	0.00	0.00	0.10	0.12	0.11	0.10
NO_2, max, ppm	0.72	0.44	No max	No max	0.62	0.72	No max	0.71
NO_2 *t*-max, min[b]	55	90	—	—	55	60	—	53
O_3 max, ppm	0.80	0.42	0.07	0.00	0.64	0.70	0.00	0.89
O_3 *t*-max, min.	150	140	240	—	135	165	—	140
PAN max, ppm	0.64	0.43	—	—	0.56	—	—	—
Δb-Scat., $10^{-4}m^{-1}$[c]	1.35	102	53.8	67.8	3.10	25.0	7.50	2.35
Final visibility, miles, approx. (*18*)	17.0	<0.3	0.53	0.43	9.0	1.1	3.8	11.0

[a] All experiments at 85°F, 40% relative humidity, and 40 ppm CO added. [b] t-Max. is defined as the time to maximum concentration in minutes. [c] Δb-Scat is the difference between initial and maximum light-scattering coefficient; therefore it provides a measure of aerosol in the light-scattering size range.

nomenon related to some synergism between aniline and the aromatic compounds in our synthetic exhaust mixture? Run 3 demonstrates that even with the paraffin isooctane, very high light-scattering values are obtained. In this experiment, the high aerosol levels were achieved while apparently very little else was occurring in terms of conventional smog manifestations. Another highly unusual feature of this experiment was the steady decrease of both NO and NO_2 throughout the irradiation.

Run 4 carried the aniline series of experiments one step further with the irradiation of aniline in the absence of other hydrocarbons. As in Run 3, virtually none of the classical smog manifestations were apparent. Interestingly, the aerosol levels with pure aniline as the reacting hydrocarbon were slightly higher than the binary mixture of aniline and isooctane of Run 3.

Runs 5 and 6 are similar to Run 2 with the exception that benzaldehyde and naphthalene, respectively, were the additives. The benzaldehyde experiment exhibited a slight drop in NO_2 and PAN maximum concentrations, a moderate decrease in maximum ozone level, and a very mild increase in light-scattering aerosol when compared to the baseline runs (Runs 1 and 8). The naphthalene run was very similar to the baseline runs with the exception of a rather large increase in aerosol. Run 7 showed many of the features of the pure aniline experiment (Run 4), without quite the same large increase in light scattering. The light-scattering value obtained was, however, well above that found in the baseline synthetic exhaust runs.

It seems rather important, from the standpoint of both inhibition studies and possible future gasoline modifications (or exhaust modification caused by catalytic mufflers) to understand the difference between phenol and aniline, on the one hand, and benzaldehyde on the other, which lead to such greatly increased aerosol production from the former compounds. The mechanism of inhibition of NO conversion by phenol is probably the reaction of phenol with hydroxyl to produce H_2O (*17*) followed by termination involving NO and NO_2:

$$HO\cdot + C_6H_5OH \longrightarrow H_2O + C_6H_5O\cdot$$

$$C_6H_5O\cdot + NO \longrightarrow C_6H_5ONO$$

$$C_6H_5O\cdot + NO_2 \longrightarrow C_6H_5ONO_2$$

The reaction with benzaldehyde is thought (*4*) to go through the following steps:

$$HO\cdot + C_6H_5CHO \longrightarrow H_2O + C_6H_5\dot{C}O$$

$$C_6H_5\dot{C}O + O_2 \longrightarrow C_6H_5C(O)O_2\cdot$$

$$C_6H_5C(O)O_2\cdot + NO \longrightarrow C_6H_5C(O)O_2NO$$

$$C_6H_5C(O)O_2\cdot + NO_2 \longrightarrow C_6H_5C(O)O_2NO_2$$

An increase in one of the major products predicted by the benzaldehyde mechanism, the potent lachrymator PBzN has, in fact, been confirmed by Dimitriades and Wesson (*10*) and Kuntz et al. (*11*).

The inhibiting reaction in the case of aniline is presumably,

$$C_6H_5NH_2 + HO\cdot \longrightarrow C_6H_5NH\cdot + H_2O\cdot$$

This reaction has been reported by Neta and Fessenden (*17*). Further reactions of the $C_6H_5NH\cdot$ radical are unknown.

It is difficult to speculate on further reactions of the $C_6H_5NH\cdot$ radical which might lead to increased aerosol formation. It is also difficult to explain how the inhibition mechanisms proposed for phenol and benzaldehyde might lead to such drastic differences in aerosol production. Because of the importance of these differences in aerosol production to our understanding the chemical basis for formation and growth of aerosol into the light-scattering size range, this is a fertile area for further research.

In summary, we have investigated the use of several free-radical scavengers which have been proposed as photochemical smog inhibitors. Our studies have been carried out under conditions more representative of the atmosphere than earlier inhibition work and have been aimed at assessing, insofar as feasible, both the positive and negative effects of these inhibitors on photochemical smog formation processes. The conclusion to be drawn from this work is that, while some important smog manifestations are reduced by the use of these inhibitors, other rather serious effects also result. Thus, while the possibility of chemical inhibition of photochemical smog may have potential, the choice of a suitable inhibitor and the documentation of its efficiency and possible side effects lie rather far in the future.

Acknowledgment

The authors would like to acknowledge the assistance of G. F. Ward in smog chamber operations.

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Air Quality Control Using Minimum Pollution Dispatching Algorithm

SIR: The correspondence by Deininger and Cohen [Deininger, R. A., Cohen, J. M., *Environ. Sci. Technol.*, 8 (7), 679–80 (1974)] quite rightly makes the point that minimum pollution dispatching as formulated by Sullivan and Hackett (*1*) is a quadratic programming problem, and that quadratic programming can also handle the more important case of constrained pollutant concentration. We wish to suggest yet another optimization method, one that takes full advantage of problem structure and also provides the dispatching information mentioned by Sullivan in his reply to Deininger.

Power dispatch problems are usually classed as separable, meaning that the objective and constraint functions are the sum of individual functions each involving a single independent variable. The method we have used and wish to offer for consideration is separable programming using Dantzig-Wolfe decomposition, as described in Dantzig (*2*) and Lasdon (*3*). This method is not restricted to quadratic functions, and so can solve not only quadratic minimum pollution dispatching but also the more general dispatch problem

$$\text{minimize} \quad \sum_{j=1}^{J} a_{ij} Q_j(P_j)$$

$$\text{subject to} \quad l_j \leq P_j \leq u_j \qquad j = 1, 2, 3 \cdots J$$

$$\sum_{j=1}^{J} P_j = P$$

providing only that all Q_j's, the functions relating SO_2 emission to power generation, are convex and piecewise differentiable (Deininger's notation is used throughout).

Separable programming has been used to solve problems with cubic and exponential Q_j (*4*). These problems could also have been solved by the Lagrange multiplier method used by Sullivan.

Separable programming can also solve Deininger's second problem, minimization of cost subject to limits on ground level concentration, which would be cumbersome at best using Lagrange multipliers. Again, separable programming allows both the cost and the constraints to be represented by any convex separable functions.

The dispatching information extracted by Sullivan from the Lagrange multiplier solution can also be obtained by separable programming. The sensitivity factors relating change in ground level concentration to the change in imported or exported power are directly available. This information is directly analogous to "incremental cost" in conventional power dispatch.

The "optimal linear control law" disucssed by Sullivan is usually implemented with participation factors. Each generator's share of a small change ΔP in load is determined by multiplying its participation factor by ΔP. Wollenberg and Stadlin (*5*) discuss calculation of unconstrained and constrained participation factors using separable programming.

Our computational experience with the power dispatch problem includes Lagrange multipliers, quadratic programming (Wolfe's method), and separable programming. We have found separable programming to be more versatile, more compact, and much faster than quadratic programming for problems with and without functional constraints. The Lagrange multiplier method is faster than either for simple minimum pollution dispatch, but should be avoided if the problem includes functional constraints. As Sullivan points out, this method of ambient air quality control is an on-line approach so time and memory requirements are more important than they might be for off-line study.

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Bruce F. Wollenberg

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Leeds & Northrup Co.
North Wales, Pa.

INDUSTRY TRENDS

Allied Air Products Co., Portland, Ore., received a $100,000 order from a plywood manufacturing concern for a central condensing unit to convert blue haze from three veneer dryers to a thick brown syrup. This order places the company strongly in the pollution control field.

Carus Chemical Co. has started expansion of its Cariox potassium permanganate plant at LaSalle, Ill. Carus is the sole producer of potassium permanganate in the Western Hemisphere.

Commonwealth Associates Inc. was retained by the City of Kalamazoo, Mich., to develop a coordinated transportation and land use program to ease traffic congestion and make the city's east central area more conducive to new development.

Consolidated Fibres, Inc., a subsidiary of Browning-Ferris Industries, Inc., has won approval from the City of Tucson Board of Adjustment to build a half-million-dollar paper reclamation plant next to Interstate Route 10, southwest of downtown Tucson, Ariz.

EcolSciences, Inc., Vienna, Va., has established a regional office in Mountain Lakes, N.J., to serve clients in Connecticut, New York, and eastern Pennsylvania.

Union Carbide Corp. and Biospherics Inc., Rockville, Md., signed a patent and technology agreement granting Union Carbide exclusive worldwide marketing rights for Biospherics' process for removing phosphorus from wastewater.

Publishers Paper Co., a subsidiary of Times-Mirror Co., will construct a paper recycling plant at Newburg, Ore. The plant will process 85,000 tons/yr of old newspapers into newsprint, and will cost about $9 million.

Rader Companies, Inc., Portland, Ore., has a $4-million contract from Union Electric Co. (UEC, St. Louis, Mo.) to supply UEC with a waste recovery system to process 8000 tons/day of garbage at two of UEC's generator plants.

The American Meter Div. of The Singer Co., Philadelphia, Pa., has entered the pollution control market with instruments to measure and control air, water, sewage, and noise pollution.

Reichhold Chemicals, Inc., White Plains, N.Y., is supplying polyurethane foam systems for insulating "hot oil" pipelines to meet safety and environmental requirements.

The Permutit Co. has supplied a PermuRO roughing demineralization plant to Allegheny Power System at Haywood, W.Va., to treat boiler feedwater.

B. F. Goodrich Chemical Co. has developed the "Catoxid" catalytic oxidation process to dispose of waste chlorinated hydrocarbons, reclaim chlorine values, and save energy.

Simpson Lee Paper Co., San Francisco, Calif., started to build a $10-million environmental improvement facility at its Shasta Mill, Anderson, Calif., to burn wood extractive materials, recycle pulping chemicals, and reduce particulates and odor.

Torit Div. of Donaldson Co., Inc., has supplied a magnesium oxide dust control system for Northern Malleable Iron Co., St. Paul, Minn.

New England Power Co. (NEPCO) has successfully tested the first unit of its Bear Swamp, Mass., pumped-storage hydroelectric facility, which cost over $100 million and will furnish 600 MW.

Dow Chemical Co. has incorporated Dow Chemical Japan Ltd., capitalized at 400 million yen (about $1.3 million).

Hydrocarbon Research, Inc. (HRI), a subsidiary of Dynalectron Corp., Washington, D.C., received an $8.1-million contract for a 600-ton/day coal liquefaction pilot plant using HRI's "H-Coal" process.

Monsanto Enviro-Chem Systems, Inc., St. Louis, Mo., will install its integral interpass absorption system for the Borden, Inc., sulfuric acid plant at Piney Point, Fla., for enhanced SO_2 control.

Approved Engineering Test Laboratories (AETL), Encino, Calif., is checking on earthquake response of a nuclear reactor core at El Centro, Calif., for General Atomic Co. Project value exceeds $100,000.

Tracor, Inc., Austin, Tex., will construct and install an aircraft noise monitoring system for the City and County of San Francisco at San Francisco International Airport.

The Belgian subsidiary of **Arthur G. McKee & Co.** will build a $15-million granular carbon plant in Belgium for Chemviron, S.A., a part of Merck & Co.

Chemical Construction Corp. (Chemico), New York, N.Y., is part of a consortium to build a $850-million natural gas liquefaction plant, the world's largest, in Algeria.

Calgon Corp. received a $330,000 contract to supply a custom-designed, automated polymer and ferric chloride feed and concentrated storage system for the 48-mgd sewage plant an Niagara Falls, N.Y.

WAPORA, Inc. has established a Modeling and Data Analysis Group at its Washington, D.C., headquarters to develop mathematical and computer methods to enhance company studies.

Normandeau Associates, Inc., Bedford, N.H., has done a year-long ecology-based assessment of the Merrimack River watershed for the U.S. Army Corps of Engineers, and recommends ozonation rather than chlorination to purify the water.

Halsted Press of John Wiley & Sons, Inc., New York, N.Y., will market and distribute Dowden, Hutchinson & Ross (DH&R) books. DH&R books emphasize biological, earth, and environmental sciences.

Metal Cleaning & Processing, Wilmington, Del., a detinner, will purchase all scrap steel cans recovered from the garbage-to-energy system of the City of Baltimore, Md.

Commonwealth Associates Inc. will design a 1400-MW gas-fired generating station to be built at Mazandaran, Iran, for the Iranian government. Caspian Sea water will be used for once-through cooling.

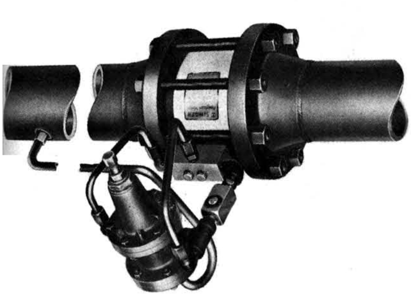
Sonic Development Corp. (SDC) has formed a Combustion Systems Div. to make industrial oil burners using SDC's patented Sonicore fuel atomizing nozzles. The atomizer, correctly used, can give 15–20% fuel savings.

Northern Research and Engineering Corp. (NREC), Cambridge, Mass., has a $1.65-million contract from the Federal Aviation Administration to determine if turbine engine emissions increase with extended use of the engines.

Dames & Moore, Los Angeles, Calif., will provide baseline environmental data on water catchment areas for the Parramatta and Port Hacking Rivers for the New South Wales (Australia) Department of the Environment.

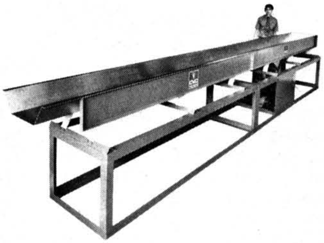
The Standard Oil Co. (Ohio) will participate in a privately financed experiment in solar heating and cooling of commercial buildings. Oliver Tyrone Corp. will be the managing participant.

NEW PRODUCTS



Axial flow valves
Designed to be substituted where noise of regulators and control valves in piping systems is an irritant or hazard, the axial flow valve lowers noise levels and achieves better regulation. Used primarily for control of gases, the axial flow valve is capable of handling most on-off, throttling, relief, and back-pressure applications. The Singer Co. **101**

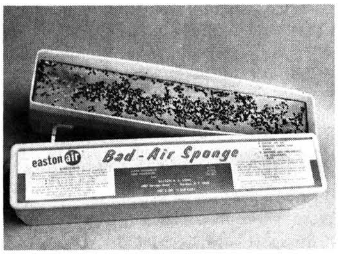
Discharge control system
Marine discharge control system removes oil from bilge and slops in compliance with the EPA and Coast Guard clean water standards. It filters the bilge water and provides a permanent record of the time, duration, and quality of water discharged. The total system is constructed for effectiveness and protection and ease of operation for an untrained crew. Gulf Oil Corp. **102**



Mechanical conveyor
Vibratory mechanical conveyor features quiet operating, semibalance electric powered drives, long-lasting fiberglass leaf spring isolation, and modular tray sections. The conveyors are available in a wide range of tray widths and types to accommodate varied conveying requirements. Special features include tray covers, dust-tight inlets and discharge, explosionproof drives, and stainless steel construction. Cleveland Vibrator Co. **103**

Liquid flocculant
High-molecular-weight liquid flocculant provides more efficient sludge reduction in industrial water and wastewater treating systems. Material is an anionic polyelectrolyte synthesized to work over a wide range of pH. It augments water clarification and reduces sludge volume by free water release. Petrolite Corp. **142**

Corrosion inhibitor
Synergistic blend of corrosion inhibitors and pH buffering agents are designed to provide better corrosion inhibition of metals used in closed cooling and heating recirculating water systems. The material is effective against corrosion with raw, softened, or demineralized make-up water, and is compatible with antifreezes. Zimmite Corp. **143**



Air sponge
A high-adsorbent, condensed paste resin with activated charcoal air sponge. Inert pollutants are physically attracted and many common gaseous air irritants are adsorbed, solubilized, and chemically neutralized by polymerization. The air sponge is receptive to both water- and oil-soluble air contaminates. Easton R/S Corp. **104**

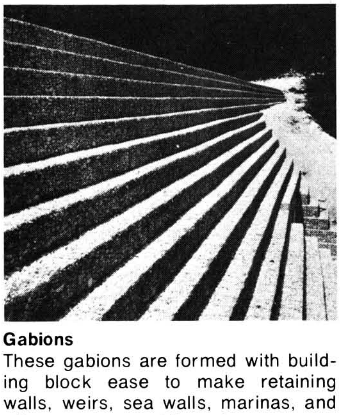
SO_2 analyzer
Pulsed fluorescent SO_2 analyzer measures ambient air concentrations while eliminating the need for flames, hazardous bottled gases, or consumable reactants. Model has full-scale ranges of 0.5, 1.0, and 5 ppm with precision to 1%. It demonstrates linear response through full sensitivity range, excellent stability, and freedom from interference. Thermo Electron Corp. **128**

Sound barrier
Noise controlling sound barrier is composed on 1-lb/ft^2 limp mass barrier layer bonded to ½-in. layer of acoustic foam. The foam acts as a sound absorber and vibration isolator. It is suitable for use in reducing floor noise in vehicular equipment. Foam is fire retardant. Heavy black vinyl skin can be laminated to barrier to provide a finished surface. The Soundcoat Co. **129**

Lead test kit
Simple and inexpensive test kit determines the presence of lead in gasoline. Use of the kit will help prevent contamination of unleaded with leaded gasoline. It consists of a treated paper that is sensitive to lead, a special solution, and various containers. The use of leaded gasoline in autos is prohibited beginning with 1975 models. The Standard Oil Co. of Ohio **130**

Biooxidation system
System fills need for equipment used in controlled bench scale experimentation in municipal and industrial waste treatment. It provides continuous flow for uniform organic loading, metered aeration, positive suspended solids control, and hydraulic loading to full-scale systems. Effective results are obtained through maximum control of liquid residence time, and other features. Cole-Parmer Instrument Co. **132**

Microfilm viewer
Hand-held microfilm viewer weighs only 13 oz and works on three double "A" batteries. Viewer has new, distortion-free magnification lens which permits easy viewing of aperture cards and 18× through 48× reduction microfiche. Device can be used in bright natural or artificial light, and can even be carried in a coat pocket. C.M.I. **141**

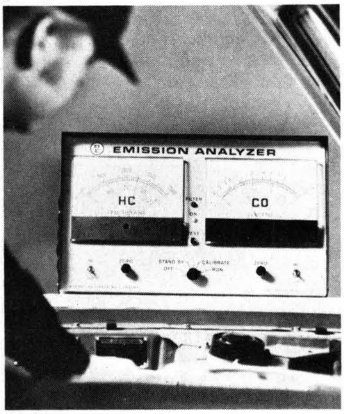


Gabions
These gabions are formed with building block ease to make retaining walls, weirs, sea walls, marinas, and other structures. They do not crumble or crack, become stronger with time, and gradually blend into the natural environment, according to the company. Maccaferri Gabions, Inc. **144**

Venturi scrubber
Dual-purpose venturi scrubber cleans incinerator exhaust gases and simultaneously concentrates black liquor for easier burning. Gases leaving the scrubber contain less than 0.07 g/scf, meeting pollution control codes. Liquor is used as scrubbing medium. Auxiliary fuel requirements are less than 4 gpm of No. 6 fuel oil. Swemco, Inc. **113**

Evaporator
New evaporator handles liquid chlorine, SO_2, and ammonia. Evaporation rate is self-adjusting, so proper liquid level is automatically maintained in the gas chamber. A weatherproof model for rugged outdoor service, even at power plants, is available. Gas chamber complies with all applicable codes. Pennwalt/Wallace & Tiernan **114**

Syringes
New gas-tight and liquid-tight syringes are available, primarily for high-pressure liquid chromatography. They are available in 50-, 100-, 250-, and 500-μl capacities, and will withstand routine inlet pressures from 2000–3000 psi. Hamilton Co. **115**



Auto exhaust analyzers
This line of infrared exhaust performance analyzers measures hydrocarbon and carbon monoxide content of internal combustion engines. The analyzers are easy to read, separate hydrocarbon and monoxide readouts, are fast and accurate, and can be used to determine compliance with emission regulations. Barnes Engineering Co. **116**

Calibration gases
Gases provide high-accuracy calibration standards for analysis of vinyl chloride monomer in industrial atmospheres. Disposable cylinders contain 14 liters of gas mixtures. Concentrations of 1, 10, 50, 100, and 1000 ppm vinyl chloride monomer in air are available from stock. Each is analyzed to ±2% accuracy. MG Scientific **117**

pH meter
Low-cost, portable industrial meter measures pH over the full 0–14 pH scale. All measurements are made with a new, rugged electrode, requiring no electrolyte refilling. Accuracy is ±0.01 pH unit. It operates from two standard 9-V batteries. The all solid state electronics comes complete with large 3½ in. direct reading mirror-backed meter. Ecologic Instrument Corp. **118**

Dilution-sampling system
Dilution-sampling system and sample-dilution probe are available as options for particulate concentration monitor. The two options greatly enhance the usefulness of the instrument system in applications involving emission of high particulate concentrations or wet particulates. Both devices are specially configured for each application to ensure better operation. Lear Siegler **119**

Aluminum recoverer
Melting furnace system is designed for maximum recovery of aluminum from scrap. The system includes an electric furnace to melt shredded cans and other aluminum trash to form solid metal rows suitable for further processing. Also included are a water-cooling system and a work platform. Charging and air-pollution accessories, molds, and tools are optional. Sola Basic Industries **120**

Filtration system
System features high filtration capacity and low operating cost. The compact, wheel-mounted system removes solid matter, down to ½μ, from nonviscous liquid flows to 40 gpm. Its design features noncorrosible plastic materials for safely handling a wide range of chemicals at temperatures up to 200°F. Designed for multiple industrial uses. Per Corporation **121**

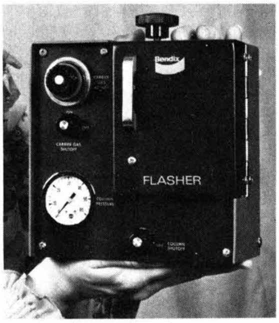
Dust control system
System protects the environment by suppressing dust before it becomes airborne. Special agents, on application, adhere to the dust-producing material to reduce secondary or downstream dust. It produces foams that consist of air, water, and a combination of safe surfactant materials. The need for vacuum collection systems, separators, cyclones, and bag plants are reduced. G. E. Doule Corp. **122**

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.

Water clarifier
Coagulant aid can be used as a prime coagulant in raw water clarification replacing inorganic coagulants, such as aluminum or iron salts. Effective in both high- and low-turbidity waters, the clear, colorless liquid is very stable in the presence of oxidizing agents such as chlorine. Also, the quality of the sludge produced is such that it is easier to dewater. Drew Chemical Corp. **123**

Multiple point chlorinator
Device is designed for water and wastewater treatment applications requiring more than one point of chlorine injection. It allows chlorine feed rates to be varied at each point of application, without affecting the feed rate of any other point. Separate metering tubes are panel mounted and contain individual rate adjustments. Economical, simple to install. Capital Controls Co. **124**

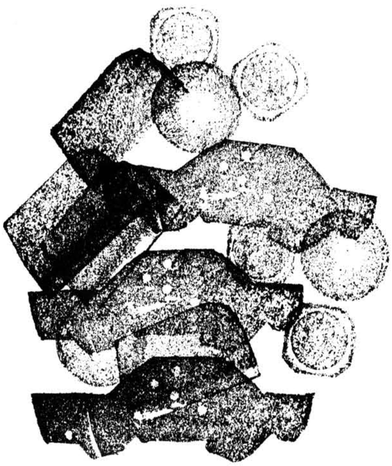
Particle remover
System removes or recovers particles entrained in air or gas. The device features high particulate removal efficiency (to 0.1 μ), low power consumption (2 hp/1000 cfm), and low water use ($^1/_2$ gal/1000 ft^3 of air or gas). There are no fans, blowers, moving parts, packing, or impingement targets. RP Industries, Inc. **125**



Vinyl chloride detector
In this device, an electrical flasher provides energy to flash a collected sample from an adsorption tube into the gas chromatograph for analysis. The system can monitor vinyl chloride to concentrations as low as 50 ppb, well below the 1-ppm standard now proposed by the Occupational Safety and Health Administration. Bendix Process Instruments **126**

Signal simulators
This device was developed to determine the source of erratic readings generated from pH electrodes or thermocouples. It is a hand-held, battery-powered simulator employed to generate easily a mV signal representing a given pH or temperature, and can quickly isolate the cause of an erratic reading. Weight is 8 oz. Electrofact **127**

SOLID WASTES-II



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Cleaning Our Environment
The Chemical Basis for Action
249 pages, (1969), Paperback, $2.75

Supplement to Cleaning Our Environment
20 pages, (1971), Paperback, $1.00

NEW LITERATURE

pH and Science Supply News. Issue of this 44-page publication covers Ohaus balances, Waring blendors, and Beckman's audio-visual programs. pH measurements, electrophoresis, and enzymology are fully covered, as are many other science supplies. Markson Science Inc. **151**

Effects of foam. Company bulletin lists seven harmful effects of foam on effective wastewater treatment. Bulletin also describes the company's approach to foam control in wastewater treatment, and an electronic instrument that controls antifoam feed by sensing foam levels. Nalco Chemical Co. **152**

Water checklist. Checklist describes 200 publications on water now available from the firm. There is much material on pollution and environmental protection. Unipub, Inc. **153**

Fish facilities. New brochure covers plan and design of fish facilities, including hatcheries, spawning channels, ladders, intake structures, and related subjects. Harza Engineering Co. **154**

NO_x monitoring. Brief catalog and two companion bulletins picture and describe a full line of NO/NO_x and ozone-monitoring instruments which detect through the chemiluminescent detection principle. Measurement is in ppb to 1% concentration. McMillan Electronics **155**

Sludge conditioning. Four-page brochure covers sludge conditioning, including sewage, petrochemical wastes, and other pollutants. The brochure tells how to accelerate sludge flow, even if sludge has difficult materials in it, including cans. Franklin Miller, Inc. **156**

Water sterilizer. Brochure describes Steritron ultraviolet water sterilizer which destroys up to 99.9% of waterborne bacteria, viruses, spores, and fungi without chemicals or heat. Canrad-Hanovia, Inc. **157**

Environmental services. Brochure describes company's capabilities in air, water, meteorology, noise, combustion, computer programming, engineering management, and custom-designed continuous monitoring stations. York Research Corp. **158**

Dry polymer preparation. Revised handbook describing the company's "Omega Polypak" system is now available. System, through initial wetting action eliminates troublesome agglomerates caused by clumping of partially wet polymer particles. BIF **159**

Instruments and reagents. A 16-page bulletin, numbered 297, lists instruments and reagents for laboratory personnel interested in water, wastewater, or industrial wastes analysis. Fisher Scientific Co. **160**

Biological research equipment. Catalog 174 describes EcoloGen mixed culture apparatus, airborne contamination monitors, and other equipment useful in sophisticated biological laboratories. New Brunswick Scientific Co., Inc. **161**

Molecular sieve. Technical bulletin No. C-2 describes a geometric molecular sieve with proprietary manner of providing for maximum desiccant density for any given space configuration. Coast Engineering Laboratory **162**

Carbon monoxide detector. Technical bulletin describes the AGC-211M which catalytically converts carbon monoxide to methane, so that flame ionization detection for ppb measurement of carbon monoxide in the atmosphere becomes possible. Carle Instruments, Inc. **163**

Publication list from IAEA. Catalog lists publications from the International Atomic Energy Agency (IAEA) covering peaceful uses in medicine, farming, environment, industry, and power. Unipub, Inc. **164**

Organic vapor analyzer. Two-page brochure explains a new instrumental technique, using a battery-operated photoionization analyzer, to detect organic vapors, including vinyl chloride. h·nu Systems Inc. **165**

Dustless process. New process which makes powdery materials essentially dustless is discussed in depth in the 12-page publication, "Harshaw dustless process." Harshaw Chemical Co. **166**

Portable recorders. Twelve-page catalog provides features, photos, and detailed specifications on the company's entire line of medium-frequency, portable recorders. Gulton Industries, Inc. **167**

Incinerator systems. Four-page bulletin highlights the company's factory-packaged, pollution-free incinerator systems for solid waste disposal. Ask for Bulletin 410-B. Sunbeam Equipment Corp. **168**

CO monitoring. Brochure describes the company's "Ecolyzer 3100 Alarm" system for monitoring carbon monoxide. Features, specifications, and a partial customer list are given. Energetics Science Inc. **169**

Smoke/opacity monitor. Company describes device which monitors particulates in stack gas round-the-clock, and features an automatic daily calibration check. Baldwin Electronics, Inc. **170**

Spectrophotometers. The company's 700 Series catalog describes the 700 series spectrophotometers and a number of accessories in detail. GCA Corp. **171**

Centrifugal pumps. Heavy-duty plastic centrifugal pumps for many uses, which obviate metallic contamination, are described in catalog 11.0. Seal specifications, dimensions, and performance curves are given. Vanton Pump and Equipment Corp. **172**

Reverse osmosis. Bulletin WC-147 describes company's Rosep system which demineralizes boiler feed water and high-purity process water at reduced costs. The system can also be used for metal waste concentration and recovery, nuclear radwaste, and cooling towers. Up to 90% ion removal is possible. Graver Water Conditioning Co. **173**

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.

Laboratory supplies. September 1974 catalog describes a complete list of nuclear, biological, chemical, and environmental laboratory supplies. Interex Corp. **174**

Sludge pumping. An eight-page article describes a new technique for pumping, through pipe, filter cake, and centrifuge discharge, sludge with solid content up to 65%. Ask for "Handling high solids content non-Newtonian fluids." Robbins & Myers, Inc. **175**

Infrared spectrophotometers. New series of five infrared spectrophotometers, with many applications, is described in Bulletin 7263. Instrument is computer compatible. Beckman Instruments, Inc. **176**

Water monitors. Bulletin 740 covers company's pH, ORP (Redox), and conductivity monitors for pollution abatement and process control work. Company's GLI model 60 and 70 line of analyzers is also discussed. Great Lakes Instruments, Inc. **177**

Hydrogen measurements. Bulletin 0103 describes the company's AGC-111H gas chromatography system with the firm's breakthrough hydrogen transfer system, offering quantitative accuracy with operational simplicity. Carle Instruments, Inc. **178**

Pressure instrumentation. Transducers, indicating systems, and transmitters are described and illustrated in a catalog. All specifications, prices, and ordering information are given. YSI-Sostman **179**

Gas transfer. Brochure describes company's new static aerator which incorporates gas transfer principles in a diffused air system efficiently and economically. A comprehensive design manual is included. Device contains no moving parts. Aqua-Aerobic Systems **180**

Organic reactions. Booklet, "Reactiones organicae—a technical introduction," describes a punch-card system designed to describe chemical reactions in terms of reaction Centers and conditions. Sadtler Research Laboratories, Inc. **181**

Business guide. A guide to over 5 million U.S. business and industry firms, the NBL directory is classified by type of business activity using the 4-digit standard industrial classification system. National Business Lists, Inc. **182**

Odor-control technology. Report entitled "Odor modification and masking" discusses chemical, petrochemical, food processing, sewage treatment, feedlot, leather tanning, textiles, and plastics applications. Rhodia Inc. **183**

Fluid containment. Advertising folder illustrates flexible membrane linings used as fluid containment and corrosion control vehicles. "Specialty" jobs are listed. Unit Liner Co. **184**

Total energy systems. Article discusses logical, economical, and efficient alternative power source for use in any large new school construction project. Heat recovery becomes more efficient. Envirodyne Energy Services **185**

Pumps. A 48-page catalog features a complete line of tubing, metering, positive pressure, specialty pumps, and drive systems. Many different types of pumps with numerous applications are described. Cole-Palmer Instrument Co. **186**

Wastewater handling. Brochures describe the company's line of environmental products dealing with solutions to industrial wastewater problems. Company's Equalization Basin pretreats from 50,000 to 100 million gpd. Sampling systems are also described. ETS Products **187**

Electrodes. A 20-page product catalog covers the complete line of the company's Electrofact pH and ORP electrodes. Very useful in monitoring mine wastewater and industrial waste, as well as high-temperature pH. Electrofact **188**

Compactors. Publication contains brief specifications and photographs of landfill compactors, steel wheel and pneumatic compactors, and other types of compactors and rollers. Hyster Co. **189**

Scrubber corrosion. "How to avoid scrubber corrosion" is the title of an 18-page paper which describes gases causing corrosion, alloys resistant to corrosion, and related topics. Swemco, Inc., 470 Park Ave. South, New York, N.Y. 10016. Write direct.

Boiler efficiency. Company will send charts that plot stack temperature against combustion efficiency to help make proper burner adjustments for boilers. Perhaps 10–15% of fuel can be saved. Fuel Efficiency, Inc., 131 Stuart Ave., Newark, N.Y. 14513. Write direct.

Ultrafiltration. Publication No. 413A describes a compact, self-contained system for concentration or desalting biological solutions to volumes as low as 0.1 ml. Amicon Corp. **190**

Wastewater treatment. New process design manual for upgrading existing wastewater treatment plants. Treats subject exhaustively. Technology Transfer, U.S. Environmental Protection Agency, Washington, D.C. 20460. (Write direct.)

BOOKS

Air Pollution and Atmospheric Diffusion. M. E. Berlyand, Ed. vi + 242 pages. Halsted Press, 605 Third Ave., New York, N.Y. 10016. 1974. $26.75, hard cover.

This book is a compendium of air pollution articles written in the U.S.S.R. It covers comparisons of automatic gas analyzers using SO_2, influence of meteorological conditions on the content of contaminants in city air during summer, studies of aromatic impurities in air, aerosols, urban air pollution, dust problems, and many other very pertinent related topics.

Proceedings of the National Conference on Municipal Sludge Management. 210 pages. Information Transfer, Inc., 1625 Eye St., N.W., Suite 622, Washington, D.C. 20006. 1974. $15, hard cover.

This compendium freely discusses problems concerning all aspects of municipal sludge management. Papers included in the book also discuss the all-important matter of cost. Solutions are presented for various unit processes and total systems. Toxicity, resource recovery, intermedia pollution control associated with incineration, land disposal, composting, and recycle are included.

Livestock and the Environment. Ralph H. Ramsey. v + 357 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1974. $3.50, paper.

This book is a compendium of titles and abstracts dealing with the subject of livestock and its environmental effects. It is an updated and revised extension of the Bibliography of Livestock Management EPA-R2-72-101, and was compiled to speed the information flow in this environmental matter. Ask for EPA-660/2-74-024; the EPA's Office of Research and Development sponsored the preparation of this book.

Recent Advances in Air Pollution Control. 530 pages. American Institute of Chemical Engineers, 345 E. 47th St., New York, N.Y. 10017. 1974. $15 ($7.50 for AIChE members).

Describes technological advances toward purifying the environment and achieving national standards on air quality. Two sections cover national emission standards and their impact on industry; three discuss emission species; and the remaining covers miscellaneous topics, including pollution control as a process design variable. Ask for S-137.

The Geothermal Steam Story, or A Hot Tip from Mother Earth. R. J. Birsic. iii + 120 pages. R. J. Birsic, Publisher, 1487 Skyline Drive, Fullerton, Calif. 92631. 1974. $5.95, paper.

Describes geothermal energy activities in New Zealand, Italy, Japan, the U.S., and other countries. The book contains over 70 pictures and charts from all of the leading countries. It also discusses in detail, and answers the question, "Can you make money on $team?"

Energy and the Environment: A Collision of Crises. Irwin Goodman, Ed. 272 pages. Publishing Sciences Group, Inc., 411 Massachusetts Ave., Acton, Mass. 01720. 1974. $14.95, hard cover.

Discusses matters covered by a four-day conference of 18 leading energy experts and 22 seasoned journalists. Examines interwoven energy/environment/foreign policy problems and their implication for the trade balance, industrial development, and public health. Each article is followed by a question-and-answer section.

The Liquid Metal Fast Breeder Reactor. Thomas B. Cochran. 271 pages. Johns Hopkins University Press, Baltimore, Md. 21218. 1974. $6.95, paper.

This work is subtitled, "An environmental and economic critique." It finds economic arguments for the liquid metal fast breeder reactor (LMFBR) open to serious questions, and finds no environmental advantages for the LMFBR over presently operating light water reactors or developing high-temperature gas reactors. An analysis of costs, uranium supplies, environmental impacts, and safety aspects is given.

9th Intersociety Energy Conversion Engineering Conference (1974 Proceedings). 1343 pages. American Society of Mechanical Engineers, 345 E. 47th St., New York, N.Y. 10017. 1974. $70, paper.

These proceedings introduce new developments and unique concepts for solving basic and related problems of power generation and energy conversion. Among the many subjects covered are solar power, hydrogen energy systems, MHD power generation, coal and shale utilization, biomedical power systems, and energy conservation engineering. Ask for Book #H-26.

A Guide to Water Cleanup Materials and Methods. Arthur D. Little, Inc./Learning Systems. 350 pages. New Boston House, 114 Lowell St., Andover, Mass. 01810. 1974. $29.95, hard cover.

Represents first central data engineering base for water pollution control equipment, and provides timely information about preventive and remedial pollution control efforts. The book lists all important domestic and foreign producers of water cleanup equipment, and describes 500 products in terms of function, properties, dimensions, performance characteristics, applications, and compatibility with other equipment.

Geochemistry and the Environment, Vol. 1, The Relation of Selected Trace Elements to Health and Disease. NAS Printing and Publishing Office, National Academy of Sciences, 2101 Constitution Ave., Washington, D.C. 20418. 1974. $8.50.

Report of a workshop on possible links between the geographic distribution of certain elements and patterns of disease in animals and humans. Considers elements such as fluorine, cadmium, zinc, lead, iodine, chromium, copper, selenium, and tellurium. The workshop was held in 1972 under the auspices of the National Research Council.

Environmental Statements and Water Resource Planning in North Carolina. Maynard Hufschmidt. xiii + 127 pages. Water Resources Research Institute of the University of North Carolina, 124 Riddick Building, North Carolina State University, Raleigh, N.C. 27607. 1974. $3.00, paper.

This report discusses how well the environmental review and clearance procedure is working in North Carolina. It also shows how the quality of environmental statements for projects affecting water resources in the state, initially poor, have been steadily improving, and where further improvement is needed.

Waste Oil Recovery and Reuse. vi + 418 pages. Information Transfer, Inc., 1625 Eye St., N.W., Suite 622, Washington, D.C. 20006. 1974. $17.50, hard cover.

Scope includes identification of the known available sources of waste oils, their characteristics, and the most up-to-date technology for processing waste oils for reuse. Also discussed are industrial and institutional needs—all to assist responsible management and agencies in implementing effective waste oil recovery and reuse programs.

American Indian Food and Lore. Carolyn Niethammer. xxx + 191 pages. Macmillan Publishing Co., Inc., 866 Third Ave., New York, N.Y. 10022. 1974. $7.95, hard cover.

The American Indians truly appreciated the values of nature and a pure environment. Here is a delightful compendium of recipes, amply illustrated, for dishes made from products of the environment and nature itself.

Efficient Use of Fuels in Process and Manufacturing Industries. 350 pages. Institute of Gas Technology, 3424 South State St., IIT Center, Chicago, Ill. 60616. 1974. $25, hard cover.

Book covers the symposium covering various methods of reducing fuel consumption in process and manufacturing plants. Also covers heat pipes, space heating, low-Btu gas from coal, and many other pertinent topics.

Processing and Management of Agricultural Wastes. Cornell University. Agricultural Waste Management Program, Riley-Robb Hall, Cornell University, Ithaca, N.Y. 14850. $15.

Book contains proceedings of the 1974 Conference on Waste Management. It emphasizes information related to federal effluent guidelines and their effect on the livestock industry; control of nonpoint diffuse pollution sources; and waste stabilization, treatment, and disposal of a variety of animal wastes.

Human and Ecologic Effects of Nuclear Power Plants. Leonard A. Sagan, Ed. xix + 536 pages. Charles C Thomas, Publisher, Bannerstone House, 301–327 East Lawrence Ave., Springfield, Ill. 62703. 1974. $34.50, hard cover.

This book is directed toward an exposition of human and ecologic effects of nuclear plants, of which more will probably be built at an accelerated pace. Over half of the book is dedicated to a description of reactors and the uranium fuel cycle. Particular emphasis is given to sources and quantities of radioactivity that enter the environment.

Stevens Water Resources Data Book. Leupold & Stevens, Inc. 160 pages. Leupold & Stevens, Inc., P.O. Box 688, Beaverton, Ore. 97005. 1974. $4.00, paper.

This data book is a handy text for the novice, or reference for a seasoned hydrologist. It covers the hydrologic cycle, water level measurements, float wells and instrument shelters, measuring flows in manholes, well measurement, telemetering, and errors in float operated devices. Circular dimension tables, metric system tables, and handy conversion tables are also given. Book is plastic comb-bound so that it will lie flat when opened.

Environmental Impact Statement: A Reference Manual for the Architect/Planner (EIS). Kaiman Lee. 265 pages. Environmental Design & Research Center, 938 Park Square Bldg., Boston, Mass. 02116. 1974. $52, hard cover.

A complete guide in environmental impact analysis for the building type. This manual contains a detailed procedure and content requirements for writing an environmental impact statement. The impact analysis task is broken down into inventory, goals, analysis, and evaluation. An environmental information matrix of 600 elements is included.

Sanitary Landfill Technology. Samuel Weiss. 300 pages. Noyes Data Corp., Mill Road at Grand Ave., Park Ridge, N.J. 07656. 1974. $18, hard cover.

This publication surveys all the latest technical information on the subject of sanitary landfills. It is based primarily on studies conducted by industrial or engineering firms, under the auspices of the EPA. Elements of design, site planning, pollution of subsurface water, and management are among the many topics covered. Particular cases in the U.S. and Germany are discussed in depth.

Unreal Estate. Anthony Wolff. 280 pages. Sierra Club Books, 1050 Mills Tower, San Francisco, Calif. 94104.

This book has been prepared as an "exposé" of "one of the biggest swindles" of present times—the subdivision and sale of "chunks of the U.S. by greedy entrepreneurs to gullible consumers." The book describes how "the selfishly cunning are succeeding in foreclosing our national mortgage." The author covers the "lowdown" on "land hustling."

Be Informed on Pollution. New Readers Press. 40 pages. New Readers Press, Box 131, Syracuse, N.Y. 13210. 1974. $0.75, paper.

This book is aimed at students in the middle grades of school. It offers a comprehensive picture of environmental pollution, energy, and recycling in terms that "kids" can easily understand. In addition to well-illustrated text, eight pages of learning exercises are included. This learning aid also has a very significant chapter called "What can I do?" The book exhorts the student to "be informed, get involved."

N.U.K.E.E.: A Novel. Don Widener. v + 218 pages. Hawthorn Books, Inc., 260 Madison Ave., New York, N.Y. 10016. 1974. $6.95, hard cover.

Timely novel with a frightening core of truth at its base. N.U.K.E.E. is a giant nuclear power plant, a far-out follow-up to the controversial breeder reactor type that is now being constructed. The book demonstrates what might happen in such cases where nuclear technology develops beyond man's ability to understand or control it. Startling ending.

The Urban Organism. Spenser W. Havlick. x + 515 pages. Macmillan Publishing Co., Inc., 866 Third Ave., New York, N.Y. 10022. 1974. $12.95, hard cover.

Examines the state of America's natural resources, where they are, and what is happening to them. With an original approach that focuses on the urban area, the book provides a survey of current national resource problems and practices. It seeks to make the reader aware of his own impact on the country's stock of natural resources.

Battle for the Wilderness. Michael Frome. ix + 246 pages. Praeger Publishers, 111 Fourth Ave., New York, N.Y. 10003. 1974. $10, hard cover.

Optimistic book attempts to show how wilderness can provide new generations a link with the spirit of adventure and exploration at the heart of our nation's history. Part I tells how our primitive lands have inspired many of America's foremost artists and authors. Part II traces the emergence of the conservation philosophy to present-day conservation struggles.

Introduction to Environmental Science and Technology. Gilbert M. Masters. xii + 404 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1974. $13.50. hard cover.

Considers population, pollution, and resource depletion as primary factors limiting the range of alternatives still available to mankind. The book first discusses basic principles of ecology. In a second section, water pollution is discussed. Section three deals with problems associated with air pollution. A final section discusses energy and raw materials.

MEETING GUIDE

November 17–21 New York, N.Y.
Winter Annual Meeting. American Society of Mechanical Engineers

Includes environmental and energy discussions. *Write:* M. Jones, ASME, 345 E. 47th St., New York, N.Y. 10017

November 18–22 Puerto Rico
Tenth American Water Resources Conference. American Water Resources Association

Write: AWRA, 206 E. University Ave., Urbana, Ill. 61801

November 18–22 Atlantic City, N.J.
First Annual Meeting. Federation of Analytical Chemist and Spectroscopy Societies

Theme will deal with energy and the environment. *Contact:* Hal Ferrari, Lederle Labs, Pearl River, N.Y. 10965

November 19–22 Madison, Wis.
State Energy Systems—Modeling and Planning Workshop. The Energy Systems Research Group/University of Wisconsin Extension

Problems of state and regional energy modeling examined and the Wisconsin Regional Energy Simulation Model (WISE) introduced. *Contact:* Dr. R. C. Lutton, Admin. Director, UW-Extension, Engineering Dept., 432 N. Lake St., Madison, Wis. 53706

November 21 Chicago, Ill.
Annual Meeting. Institute of Gas Technology

Includes presentation, "Pipeline Hydrogen—The Fuel for the Nuclear Age." *Contact:* H. R. Linden, Institute of Gas Technology, IIT Center, Chicago, Ill. 60616

December 1–5 Washington, D.C.
Sixty-seventh Annual AIChE Meeting. American Institute of Chemical Engineers

Contact: Joel Henry, AIChE, 345 E. 47th St., New York, N.Y. 10017

December 2–4 Dallas, Tex.
Texas Water Quality Technology Conference. American Water Works Association

Theme is "Action Now in the Water Laboratory." *Contact:* J. Layne, AWWA, 6666 W. Quincy Ave., Denver, Colo. 80236

December 2–4 Coral Gables, Fla.
Remote Sensing Applied to Energy Related Problems. Miami Clean Energy Research Institute

Employs modified short-course format. *Write:* T. N. Veziroglu, Director, Clean Energy Research Institute, U. of Miami, Coral Gables, Fla. 33124

December 4–5 Washington, D.C.
Industrial Water Cooling Tower Design and Technology. American Institute of Chemical Engineers

Advanced wastewater treatment course held at the same time. Other courses concerning the environment will be offered at different locations. *Write:* AIChE, Continuing Education, 345 E. 47th St., New York, N.Y. 10017

December 4–6 San Diego, Calif.
Third National Bicycle/Pedestrian Planning, Design and Implementation Seminar. Metropolitan Association of Urban Designers and Environmental Planners, Inc., and others

Among topics included is "Role of Bicycle/Pedestrian Facilities in Today's Environment." *Write:* MAUDEP, P.O. Box 722, Church St. Station, New York, N.Y. 10008

December 5–6 Clemson, S.C.
Tenth Annual Air and Water Pollution Control Seminar. Clemson University

Latest developments in air and water pollution control as applied to industrial operations. *Write:* Dr. F. C. Alley or Dr. A. R. Abernathy, Continuing Engineering Education, 116 Riggs Hall, Clemson University, Clemson, S.C. 29631

December 5–7 Atlanta, Ga.
Mill Yard Superintendents' Workshop. TAPPI

Of special interest to paper mill yard superintendents. *Contact:* S. J. Hayes, TAPPI, 1 Dunwoody Park, Atlanta, Ga. 30341

December 8–13 Pacific Grove, Calif.
Conference on Earthquakes & Lifelines. Engineering Foundation

Contact: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

December 9–10 New York, N.Y.
National Urban Mass Transportation Conference. U. of Chicago Center for Continuing Education

Economic, environmental, social implications of transportation planning. *Contact:* Ms. H. Kaplan, New York Management Center, Dept. 14NR, 360 Lexington Ave., New YorK, N.Y. 10017

December 10–13 San Diego, Calif.
Workshop on Reactor Licensing and Safety. Atomic Industrial Forum, Inc.

Technical and policy issues important to reactor licensing. *Write:* Conference registrar, Atomic Industrial Forum, Inc., 475 Park Ave. South, New York, N.Y. 10016

December 12–17 San Francisco, Calif.
Fall Annual Meeting. American Geophysical Union

Write: M. Walt, Lockheed Palo Alto Research Laboratory, Dept. 52-10, Bldg. 201, 3251 Hanover St., Palo Alto, Calif. 94304

December 16–20 Tarpon Springs, Fla.
Total Loss Control Management Conference. International Safety Academy

Write: H. E. O'Shell, Director International Safety Academy, 1021 Georgia Ave., Macon, Ga. 31201

January 12–17 Pacific Grove, Calif.
Engineering Problem Areas Interfacing with Rheology Conference. Engineering Foundation

Contact: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

January 13–17 Washington, D.C.
Annual Meeting. Transportation Research Board of the NAS/NRC

Contact: H. M. Gillespie, Public Information Officer, Transportation Research Board, 2101 Constitution Ave., Washington, D.C. 20418

February 1–6, 1975 New Orleans, La.
Annual Convention. National Asphalt Pavement Association

Includes environmental topics. *Write:* G. C. Goggin, NAPA, 6811 Kenilworth Ave., Riverdale, Md. 20840

February 23–28 Pacific Grove, Calif.
Coping with Environmental and Safety Regulations in the Food Industry. Engineering Foundation

Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

February 24–26, 1975 New York, N.Y.
Annual Meeting. TAPPI

Theme is "60 Years of Service to TAPPI Members Around the World." *Write:* S. J. Hayes, TAPPI, 1 Dunwoody Park, Atlanta, Ga. 30341

March 9–13, 1975 Williamsburg, Va.
Annual Scientific Meeting. Society of Toxicology

Write: R. A. Scala, Society of Toxicology, Exxon Research and Engineering Co., P.O. Box 45, Linden, N.Y. 07036

April 2–4, 1975 Chicago, Ill.
Annual Industrial Pollution Conference and Exposition. Water and Wastewater Equipment Manufacturers Association

Write: C. Novak, WWEMA, 744 Broad St., Rm. 3401, Newark, N.J. 07102

April 8–11, 1975 Burlington, Canada
Symposium on Environmental Biochemistry.

Emphasis is on aspects of biochemical processes as they pertain to the human environment. *Contact:* J. O. Nriagu, Canada Centre for Inland Waters, 867 Lakeshore Road, Burlington, Ont., Canada L7R 4A6

Courses

November 18–22 Austin, Tex.
Advanced Water Pollution Control and Environmental Impact. Continuing Engineering Studies/The University of Texas

Fee: $275. *Write:* Engineering Institutes of the College of Engineering, Cockrell Hall 2.102, The University of Texas at Austin, Austin, Tex. 78712

November 25–26 Las Vegas, Nev.
Workshop on Thermal Plume Prediction. U.S. Environmental Protection Agency

Write: Mrs. B. Kennedy, Thermal Pollution Branch, Environmental Protection Agency, 200 SW 35th St., Corvallis, Ore. 97330

December 2–5 Washington, D.C.
Management of Municipal Solid Waste. The George Washington University

Fee: $340. *Write:* Director, Continuing Engineering Education, The George Washington University, Washington, D.C. 20006

December 2–6 Cleveland, Ohio
Industrial Noise Control Seminars. B&K Instruments, Inc.

Fee: $200. *Write:* Bill Rhodes, Director of Communications, B&K Instruments, 5111 W. 164th St., Cleveland, Ohio 44142

December 2–6 Oak Brook, Ill.
Stack Sampling Training School. Nalco Chemical Co.

Write: Nalco Chemical Co., 2901 Butterfield Rd., Oak Brook, Ill. 60521

December 5–6 Las Vegas, Nev.
An OSHA Checklist for the Construction Engineer. National Society of Professional Engineers.

Write: NSPE/PEC OSHA Seminar, 2029 K St., N.W., Washington, D.C. 20006

December 9–10 Madison, Wis.
Geothermal Energy Utilization. University of Wisconsin-Extension

Fee: $100. *Contact:* R. C. Lutton, P.E., University of Wisconsin-Extension, Engineering Dept., 432 N. Lake St., Madison, Wis. 53706

December 9–13 Madison, Wis.
Advances in Wastewater Treatment and Disposal. University of Wisconsin

Fee: $300. *Write:* U. of Wisconsin Extension, Dept. of Engineering, 432 N. Lake St., Madison, Wis. 53706

December 9–13 Washington, D.C.
Solar House Heating and Cooling. The George Washington University

Fee: $435. *Write:* Director, Continuing Engineering Education, The George Washington University, Washington, D.C. 20006

December 14 Gaithersburg, Md.
Instrumental Methods for Air and Water Measurements and Monitoring. IEEE Nuclear and Plasma Sciences Society, Atomic Energy Commission, Environmental Protection Agency, National Bureau of Standards

Write: R. B. Johnson, Materials Bldg., B-348, National Bureau of Standards, Washington, D.C. 20234

December 16–20 Washington, D.C.
Mathematical Models for Environmental Sciences: Application of Mathematical and Probabilistic Techniques to Environmental Problems. The George Washington University

Fee: $395. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20006

December 17–19 New Brunswick, N.J.
Industrial Noise Exposure and Control. Rutgers University—The State University of New Jersey

Contact: Prof. J. J. Soporowski, Jr., Dept. of Environmental Science, Cook College, Rutgers University, P.O. Box 231, New Brunswick, N.J. 08903

International

November 18–23 London, England
Biennial Public Works and Municipal Services Exhibition, British government and others.

Write: The Municipal Agency Ltd., 178/202 Great Portland St., London WIN 6NH, England

November 25–29 London, England
Petroleum and the Continental Shelf of Northwest Europe. Institute of Petroleum and others

Discussion of environmental risks to the North Sea and monitoring requirements of oil spills. *Contact:* Jill de Wardener, Institute of Petroleum, 61 New Cavendish St., London W1M 8AR

December 2–4 New Orleans, La.
International Conference on Effluent Variability from Wastewater Treatment. International Association on Water Pollution Research and others

Contact: Prof. A. J. Englande, Dept. of Environmental Health, Tulane Riverside Research Labs., Belle Chasse, La. 70037

December 9–13 Stockholm, Sweden
Ecology 1975. U.S. Department of Commerce

Will cover products in the air and water pollution control fields, solid waste treatment and noise abatement. *Contact:* P. G. Combs, Northern Europe Div., Office of International Marketing, U.S. Dept. of Commerce, Washington, D.C. 20230

Call for papers

November 15 deadline
Second Annual Research, Design and Development Conference. Environmental Engineering Division, American Society of Civil Engineers.

Conference will be held July 21–23, 1975, in Gainesville, Fla. *Contact:* P. L. Brezonik or J. P. Heaney, Dept. of Environmental Engineering Sciences, University of Florida, Gainesville, Fla. 32611

November 30 deadline
Fourth National Symposium on Radioecology. Atomic Energy Commission and others

Conferences will be held May 12–14, 1975, in Corvallis, Ore. Emphasis on increasing role of nuclear energy in the total energy picture, and upon the radioecological implications of energy resource development. *Submit to:* C. E. Cushing, Jr., Ecosystems Dept., Battelle, Pacific Northwest Labs, Richland, Wash. 99352

December 1 deadline
Annual North East Regional Antipollution Conference (ANERAC). University of Rhode Island

Conference will be held July 9–11, 1975, in Kingston, R.I. Theme is "Energy Conservation and Pollution Control." *Write:* Prof. D. Sussman, Bliss Hall, University of Rhode Island, Kingston, R.I. 02881

December 1 deadline
Summer Computer Simulation Conference. AIChE, AMS, ISA, SCS, SHARE

Conference will be held July 21–23, 1975, in San Francisco, Calif. Emphasis on simulation as a tool for problem solving; environmental and energy applications will be covered. Submit 3–5 page summary to S. I. Schlesinger, The Aerospace Corp., P.O. Box 92957, Los Angeles, Calif. 90009

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AUSTRALIA

PUBLIC SERVICE OF VICTORIA
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FISHERIES AND WILDLIFE DIVISION
PROJECT LEADER (THREE POSITIONS)
Position No. 1—Westernport. Ref. No. (H/04)
Position No. 2—Gippsland Lakes. Ref. No. (H/05)
Position No. 3—Port Phillip Bay. Ref. No. (H/06)

Yearly Salary: $A14,520

Duties: To be responsible for the supervision and direction of research activities conducted by the Marine Pollution Studies Section in the Westernport Bay, Gippsland Lakes and Port Phillip Bay Environmental Studies. To assist in the co-ordination of research activities and to maintain liaison with other groups participating in environmental investigations. To prepare reports and recommendations. Other duties as directed.

Qualifications: An approved degree in Science or an equivalent qualification; preferably a higher degree. Demonstrated ability and extensive experience in marine ecological research and in the supervision of scientific staff. To be capable of working with multi-disciplinary groups and to have report writing experience.

Note: Separate applications must be submitted for these positions.

Applications quoting appropriate reference number should be addressed to the Secretary, Public Service Board of Victoria, State Public Offices, No. 1 Treasury Place, Melbourne, 3002, Australia, by not later than 9.30 a.m. on Wednesday 20th November 1974, together with statements of experience and qualifications and date and place of birth.

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AUSTRALIA

PUBLIC SERVICE OF VICTORIA
MINISTRY FOR CONSERVATION
PROJECT DIRECTOR (THREE POSITIONS)
Position No. 1—Port Phillip Bay. Ref. No. (H/07)
Position No. 2—Westernport Bay. Ref. No. (H/08)
Position No. 3—Gippsland Lakes. Ref. No. (H/09)

Yearly Salary: $A16,393—Scientific Officer
$A16,207—Engineer

Duties: Subject to the Director of Environmental Studies, to be responsible for the general direction and co-ordination of the Port Phillip Bay, Westernport Bay and Gippsland Lakes Environmental Studies. To maintain liaison with, and co-ordinate, the activities of the Government, University and other groups participating in such Study. To summarise and report on activities of participating groups and to assist in the application of research activities to environmental management.

Qualifications: An approved degree in the physical or biological sciences, or an approved degree in engineering or other qualification admitting to Membership in the Institution of Engineers, Australia, or other appropriate qualification; a higher degree desirable. Demonstrated ability at a senior level to plan, develop and lead inter-disciplinary investigations. Experience in the practical application of research findings to management and a knowledge of the working of Government, University and Industry desirable. Experience in a marine science an advantage.

Note: Separate applications must be submitted for these positions.

Applications quoting appropriate reference number should be addressed to the Secretary, Public Service Board of Victoria, State Public Offices, No. 1 Treasury Place, Melbourne, 3002, Australia, by not later than 9.30 a.m. on Wednesday the 20th November 1974, together with statements of experience and qualifications and date and place of birth.

CLASSIFIED SECTION ■ POSITIONS OPEN

AUSTRALIA

PUBLIC SERVICE OF VICTORIA
MINISTRY FOR CONSERVATION
FISHERIES AND WILDLIFE DIVISION
PROJECT CO-ORDINATOR
(FRESHWATER BIOLOGY)
(REF. NO. H/10)

Yearly Salary: $A13,660

Duties: To co-ordinate the participation of the freshwater fisheries staff in environmental studies. To be responsible for and participate in freshwater biological investigations in such studies and to maintain liaison with Government Departments, Universities and other groups conducting similar investigations. To prepare reports and recommendations.

Qualifications: An approved degree in Science or Agricultural Science or an equivalent qualification; preferably a higher degree. Ability to plan, lead and co-ordinate activities involving multi-disciplinary research groups. Appropriate experience in freshwater biology and proven research ability. Experience in report preparation.

Applications quoting reference number (H/10), should be addressed to the Secretary, Public Service Board of Victoria, State Public Offices, No. 1 Treasury Place, Melbourne, 3002, Australia, by not later than 9.30 a.m. on Wednesday the 20th November 1974, together with statements of experience and qualifications and date and place of birth.

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ENVIRONMENTAL ECONOMIST
REF. NO. (H/11)

Yearly Salary: $A13,660

Duties: To be responsible for the development of the most effective means of applying economic theory and practice in environmental studies. To co-ordinate the activities of major environmental studies from an economic viewpoint and, in particular, to assist in the application of economics to environmental management. To prepare reports and to make recommendation.

Qualifications: An approved degree with economics as a major; preferably a higher degree. Proven ability to work effectively in multi-disciplinary scientific investigations and wide experience in the application of economics to environmental investigations. Demonstrated ability at a senior level assisting in the planning and development of inter-disciplinary investigations.

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AUSTRALIA

PUBLIC SERVICE OF VICTORIA
MINISTRY FOR CONSERVATION
ENVIRONMENTAL MODELLER
REF. NO. (H/12)

Yearly Salary: $A13,660

Duties: To assess the role of mathematical modelling in environmental investigations and to be responsible for the implementation of modelling techniques. To assist in the co-ordination of environmental studies and in particular, of the interplay between environmental modelling and other aspects of environmental understanding. To maintain liaison with governmental agencies and other groups and to promote an understanding of the use of models as an aid to decision making.

Qualifications: An approved degree in the physical or biological sciences, or an approved degree in engineering or other qualification admitting to Membership in the Institution of Engineers, Australia, or other appropriate qualification; a higher degree desirable. Considerable experience in environmental modelling and demonstrated ability in the application of modelling techniques to inter-disciplinary investigations. Experience in the practical application of modelling to conservation or environmental management an advantage.

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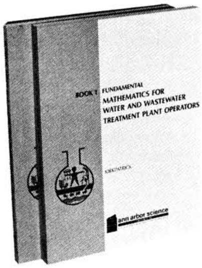

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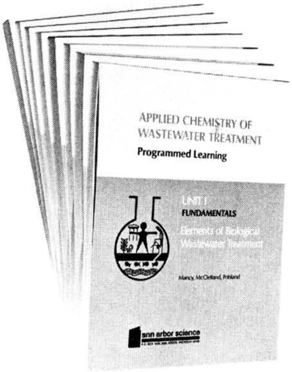

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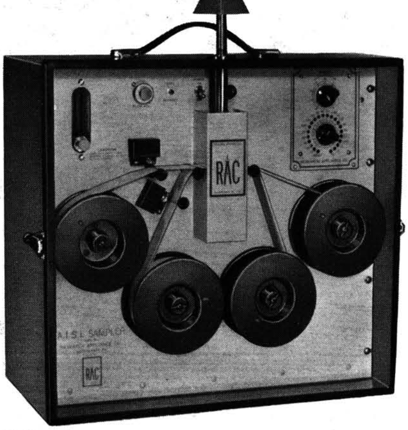

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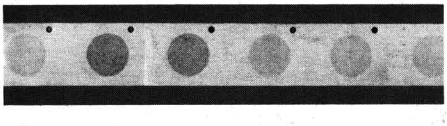
G2-T-600
Monitor



Section of filter tape showing typical 1" dia sample spots.

this line of versatile, precision samplers & monitors provides a wide range of capabilities to meet air sampling requirements

RAC offers a variety of portable, automated, timer-controlled instruments designed to sample/monitor airborne *particulate matter*—to **ASTM D1704** specs—by means of filter tapes. Particles down to 3.4 microns (and smaller) are collected automatically and accurately during preset sampling cycles. In addition, RAC particle samplers can be easily adapted to sample *hydrogen sulfide gas* (H_2S) in concentrations ranging from 0.02 to 20 ppm. *Fluorides,* both gaseous and particulate, are sampled simultaneously with a dual-tape instrument.

Engineered to operate unattended and with optimum repeatability, these precision designs are among the most versatile, adaptable devices available for both indoor and outdoor air sampling/monitoring operations. RAC **monitor** configurations automatically evaluate sample spots by means of an integral densitometer, and provide an output signal that can transmit the densitometer readings to a remote data collection device or station.

The scope of application for RAC tape instruments depends largely on users' needs and ingenuity. They can be used to detect air pollutants, to indicate the rate and frequency of change in ambient pollution concentrations, to provide data for determining source and distribution of atmospheric contaminants, to check the efficiency of dust collection and air filtration equipment, to plot traffic flow/density patterns, to correlate wind direction with ambient pollution levels, and for similar types of air sampling/monitoring operations.

Ten different models . . . plus a variety of specialized options . . . are available to meet virtually any air sampling/monitoring requirement within the capabilities of RAC filter tape designs.

For details on particle & H_2S samplers, send for BULLETIN 2300.
CIRCLE 14 ON READER SERVICE CARD

For details on dual-tape fluoride sampler, send for BULLETIN 2356.
CIRCLE 15 ON READER SERVICE CARD

STACK SAMPLING SEMINARS
Since 1970, RAC has sponsored an annual series of 2-day, technical, practical seminars on stack sampling parameters & procedures (EPA methods). **Write for descriptive folder.**

CIRCLE 16 ON READER SERVICE CARD

RAC

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