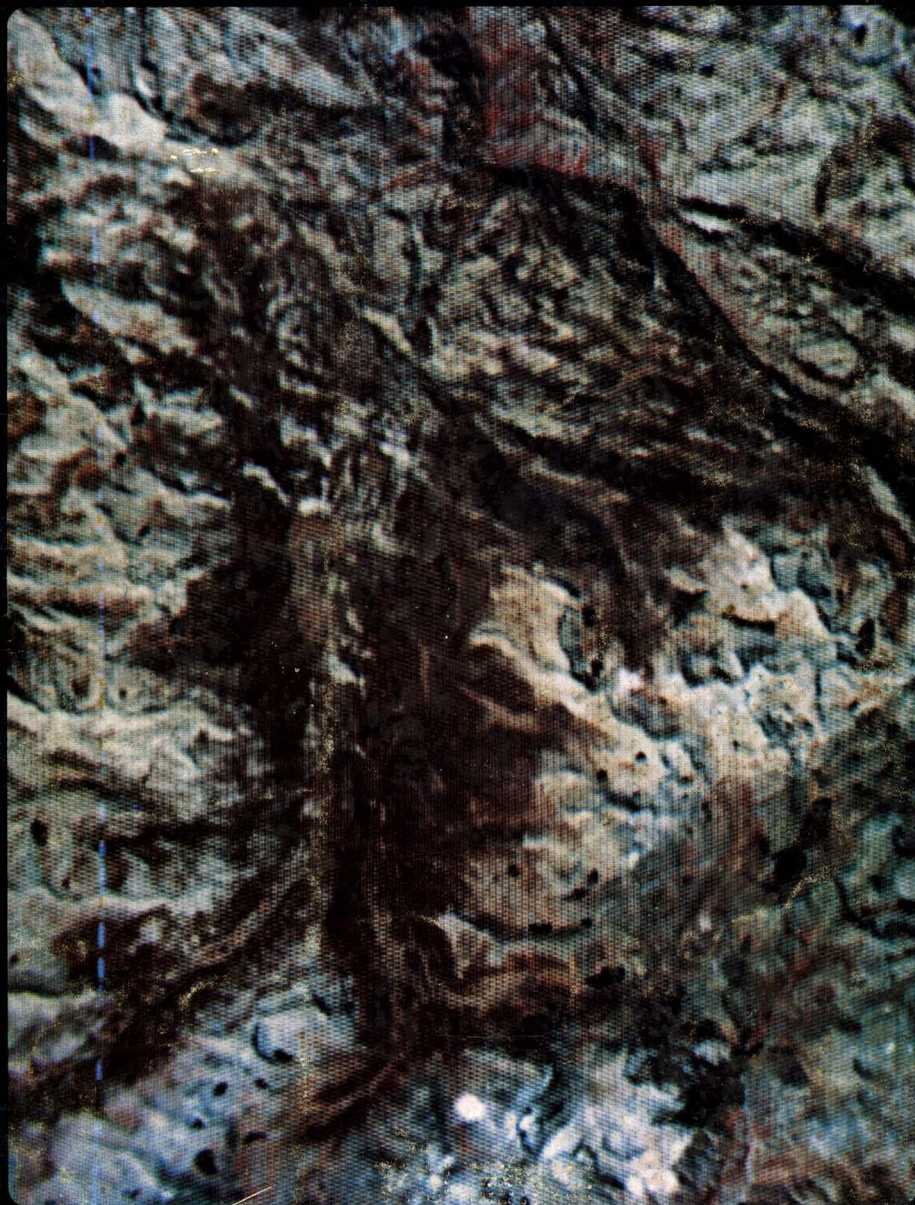


Environmental

Science & Technology

AUGUST 1975



Zooming in on remote sensing 714-725



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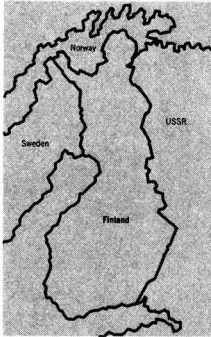
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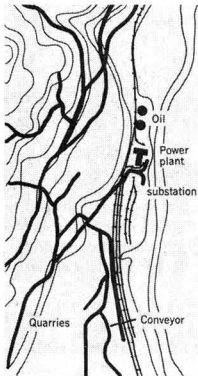
Science & Technology

Volume 9, Number 8, August 1975

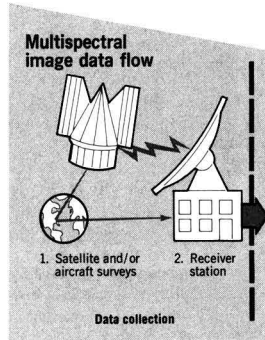
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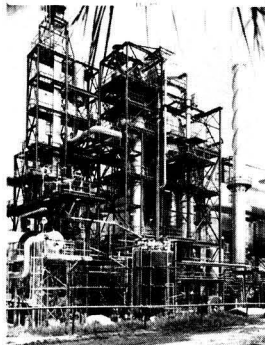
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Volume 9, Number 8, August 1975 695

CURRENT RESEARCH

Adsorption of poliovirus onto activated carbon in wastewater 727

C. P. Gerba,* M. D. Sobsey, Craig Wallis, and J. L. Meinicke

Effects of pH and dissolved organics on poliovirus adsorption to activated carbon were determined. Virus removal was improved by lowering pH or reducing organics. In column studies, removal was dependent on rate of hydraulic loading and column length.

Hydrocarbon consumption and synergistic effects in photooxidation of olefins 732

C. K. K. Yeung and C. R. Phillips*

Mixtures of ethylene, propylene, *cis*-2-butene, and nitrogen oxides were irradiated in air. The data demonstrate the existence of synergistic effects in the photooxidation of olefins. The kinetics of the photooxidation of ethylene is briefly discussed.

Accumulation and elimination studies of four detergent fluorescent whitening agents in bluegill (*Lepomis macrochirus*) 738

C. R. Ganz,* Janos Schulze, P. S. Stensby, F. L. Lyman, and Kenneth Macek

Bluegill were exposed to water containing one of four sulfonated stilbene fluorescent whitening agents. Exposure periods were from 35–70 days. Little evidence of accumulation and no metabolites of the FWA's were found.

Removal of dissolved molybdenum from wastewaters by precipitates of ferric iron 744

G. R. LeGendre and D. D. Runnells*

High levels of molybdenum present in industrial wastes can be removed from aqueous effluents by adsorption or coprecipitation with ferric oxyhydroxide at low pH. This process occurs naturally in a mining stream in Colorado, precipitating a mixture of iron compounds enriched in Mo.

Formation and emission of nitric oxide in fluidized bed combustion 749

D. J. Parks and E. A. Fletcher*

NO formation in fluidized beds was studied at various temperatures, flow rates, air-fuel ratios, particle sizes, bed depths, and amounts of fuel-bound nitrogen. Levels of NO formed were higher than equilibrium levels with stoichiometric and rich fuel mixtures, and lower with lean mixtures. Powdered Ni almost eliminated NO from the products of rich mixtures.

Fate of trace metals in Los Angeles County wastewater discharge 756

F. M. M. Morel,* J. C. Westall, C. R. O'Melia, and J. J. Morgan

An equilibrium model for the speciation of trace metals in LA County sewage is presented. A study of the oxidation and dilution of the sewage by seawater shows that most metals tend to be solubilized in the ocean. It is argued that sewage particulates are mobilized at the outfall, and that nearby sediments are a mixture of natural sediments and sewage.

New Orleans drinking water sources tested by gas chromatography-mass spectrometry. Occurrence and origin of aromatics and halogenated aliphatic hydrocarbons 762

B. J. Dowty, D. R. Carlisle, and J. L. Laseter*

Low-molecular-weight organics were extracted from water and analyzed by GC-MS. Compounds in numbers 60–70 were commonly found, but they varied considerably from day to day. Commercial artesian water and deionized-charcoal filtered water were analyzed. Both contained a wide variety of organics.

NOTES

Trace elements in corn grown on long-term sludge disposal site 765

M. B. Kirkham

Corn plants grown in soil treated with municipal sludge for 35 years were analyzed for trace metals. Results indicated that the elements did not accumulate much in the grain when compared to a control crop. Roots and leaves, however, did show higher than normal levels.

Chromium and lead in colored printing inks used for children's magazines 768

D. F. Eaton, G. W. A. Fowles,* M. W. Thomas, and G. B. Turnbull

Lead and chromium at high levels are extracted with dilute HCl from printing inks used in some children's comics. Magazines from the United Kingdom, Spain, and Austria were investigated.

Credits: 706 (two photos), ES&T's Julian Josephson; 710 (upper), Nyblin Atelier (Helsinki); 710 (lower), Ari Ojala, Lehtikuva OY (Helsinki); 718, Calspan Corp.; 721, General Electric.

Cover: General Electric. LANDSAT-1 satellite image of September 16, 1972 shows approximately 325 square miles of the Yosemite National Park in the California Sierra Nevada Mountains from which it was possible to inventory the number of acres of timber and identify forest stands damaged by mountain pine beetle.

* To whom correspondence should be addressed.

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

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Neither method is practical for continuous, automatic monitoring.

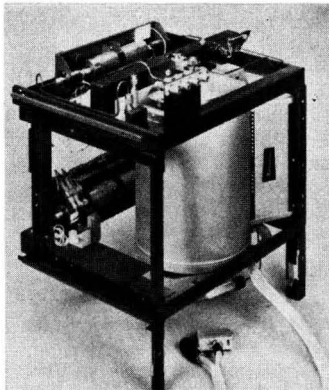
This one is

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Inside view showing the 2 zirconia tubes and the combustion oven.



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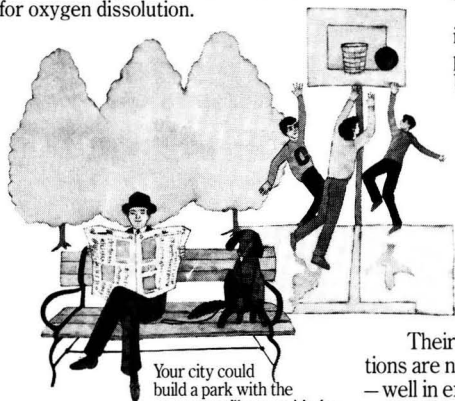
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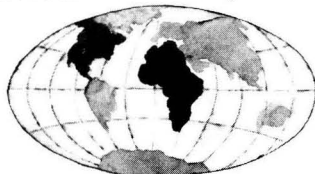


Your city could build a park with the money you'll save with the UNOX System.

Of course, power is required for on-site oxygen production. This power is usually equal to or slightly greater than the power for oxygen dissolution. So the total power to operate an oxygen activated sludge system will generally be about 30% less than the power needed for an air system.

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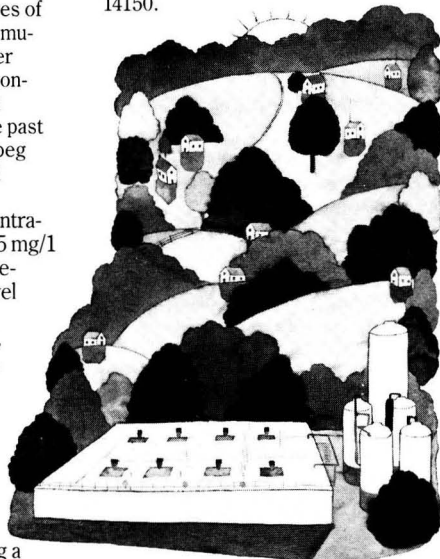
water pollution problem for an air pollution problem.

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

A closer look from afar

Remote sensing has come a long way, from the launching of ERTS-1 (July 23, 1972) to the recently launched LANDSAT-2 (Jan. 22, 1975). These identical satellites take pictures every day, make 14 passes each day, and photograph the same spot on the earth every 18 days.

In 1973, the prime contractor for the Earth Resources Technology Satellite (ERTS-1), General Electric, came up with a multispectral analysis (MSA) system. In MSA, the responses to man-made as well as natural objects on the ground are different; these differences can be assigned color themes and used to point out differences visually.

In all of this image analysis work it is first necessary to establish ground truth information. Ground truth involves knowing precisely the identity of objects on the ground. Then, correlation of the known information with colored items in the satellite photo is possible. What is simply fantastic about MSA is the extrapolation possible from the small area of ground truth information to the remainder of the area encompassed by the satellite picture, perhaps as much as 13,000 sq mi, or more than 8 million acres. And all this for less than a tenth of a cent per acre.

Its use today has been referred to as the laboratory notebook of the future, although 90% of today's users employ 10% of the capacity of the MSA system. Certainly, MSA is the real-time data logger of the future.

In a recent real-time experiment, a satellite photo revealed differences in the quality of water in the Gulf of Mexico. In less than 12 hours the images were relayed by satellite to Captain Jacques Cousteau's ship Calypso. Then, his divers sampled and analyzed the Gulf water, thus establishing ground truth information. From this information, extrapolation of the entire water quality in the entire satellite photo could be accomplished.

What is proving today to be exceedingly useful in the environmental monitoring field may tomorrow be useful in the medical field for disease diagnosis; the meteorological field for weather reporting and forecasting; and the resources area for energy and mineral resources location.



What's important for you in a water monitor?

Accuracy

How do you rate your data for accuracy?

What kind of accuracy do you expect from a field monitor?

Calibration

How often do you calibrate to insure accurate data?

Do you perform single, two-point or multi-point dynamic calibration?

Do you correct for variation in temperature of the sample—and also for variation in temperature between water sample and calibration solution?

Cleaning

How frequently do you clean your water sensor elements?

How much algae build-up can you tolerate on your sensors?

How long does it take before solids encrustation and sedimentation affect sensor reading?

Maintenance

How often do you have to send out field crews for monitor maintenance?

Can you *schedule* your maintenance?

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

Accuracy

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

Calibration

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

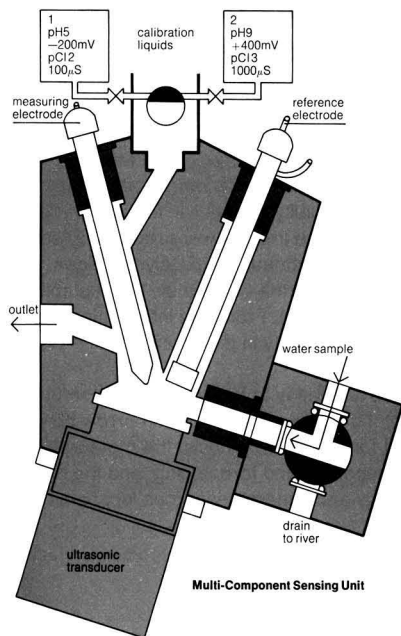
Cleaning

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

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CIRCLE 9 ON READER SERVICE CARD

LETTERS

Slow water year

Dear Sir: The following remarks to the editorial (*ES&T*, April 1975, p 291) must be considered as my own and not to be considered as officially those of the City. I am a chemist in charge of the Environmental Division, which encompasses waste water treatment, noxious aquatic weed control of Winter Park lakes and the laboratory. This is a combination that constantly involves the P.L. 92-500, the EPA, the Florida D.P.C., the Orange County Pollution Control and the East Central Florida Planning Council. For some years we have been subject to varying regulations and alternatives lacking in unified thinking.

It becomes obvious that there is a need for continuing research to prove the need for certain actions seemingly based on rationale rather than fact. Certain actions are taken because the parameter can be controlled but not proven any need to control. What started with Federal money to upgrade all treatment plants to an acceptable discharge level has degraded to optimum finances such as the Regional Plant concept, which centralizes rather than disperses effluents. From mandatory "no discharge" by 1979 thinking is now that AWT effluent may be permitted into lakes, rivers and streams. The phosphorus level being a limiting nutrient is open to question. Reducing phosphorus to 1.0 ppm in effluents first requires assumption that the receiving body of water be in such volume that the dilution factor will nullify that element and secondly that background data does not reflect a natural high phosphorus such as in the state of Florida. Where one lake is undergoing an algal bloom blamed on a 3.0 ppm phosphorus level from effluent discharge another nearby lake with no discharge has an equal bloom and a heavy infestation of hydrilla yet contains only 0.05 ppm phosphorus.

Land inundation of effluents has produced many problems yet to be solved. Transfer of viruses, degree of saturation, depths of saturation, acres required to absorb 50-90 MGD, water table levels, availability of land, equal acres during drying periods, land prices and even feasibility are considerations without adequate known facts, Regional AWT plants at the proposed 5.0 mg/liter level would actually discharge a greater tonnage on a point source than a smaller plant with only secondary treatment.

The alternatives set forth in certain

planning schedules leaves the contributor in a state of confusion regarding advance engineering plans for interceptors from a phased-out plant to the regional plant, shared interceptors, land rights, costs, dates and above all else governmental decisions that are finalized but based on scientific facts.

As you state in your editorial "—mandate will have been refocused, re-defined, reoriented, retrofitted and rewritten." We feel this will be true making plans nearly impossible to formulate without excessive expenditures where reimbursement from the governmental funds is not known.

Many of us believe we are going too fast, that harbingers of doom are pushing where discretion would better suit, that pollution should be better defined, research completed and any needed action definite and fully financed properly.

W. L. McClintock

City of Winter Park
Winter Park, Fla. 32789

Water quality instrumentation

Dear Sir: The feature article, "Instruments for Water Quality Measurements" (*ES&T*, March 1975, p 214) contained inaccurate and misleading information as to the products of my company.

Astro Ecology Corp. does not manufacture manual laboratory analyzers as indicated in table 2 of the subject article but does manufacture both automated laboratory and field analyzers for the measurement of TC, TOC, and TOD, which are not properly credited.

Several brochures describe our TC, TOC, and TOD analyzers, including our models 1500 and 1600, which measure TOC and TOD simultaneously in a single instrument. It should be noted that these analyzers have been on the market for four years and have been utilized in numerous applications in the USA, Japan and Europe by leading corporations, governments, and municipalities.

Alfred Cohen, President

Astro Ecology Corp.
Houston, Texas 77058

In the editorial processing *Environmental Science & Technology* incorrectly labeled Table 2. The table caption "Manual laboratory analyzers" should be replaced by "Typical commercially available analyzers."

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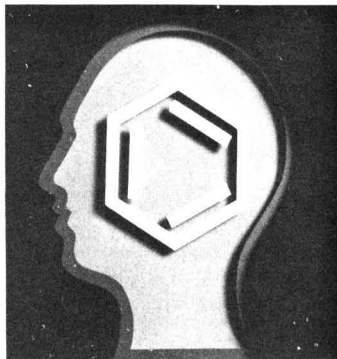
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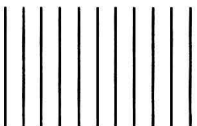
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CURRENTS

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EPA's deputy administrator John R. Quarles predicted an increase in the cost of potable water to consumers to ensure the protection of public health. In a speech delivered before the annual meeting of the American Water Works Association, Quarles said that moderate increases would result from implementation of the Safe Drinking Water Act of 1974. On a related matter, EPA's Office of Toxic Substances recently submitted a report to Congress delineating agency programs to identify the nature, sources and extent of contamination of the U.S.' drinking water by suspected chemical carcinogens. Preliminary results of the National Organics Reconnaissance Survey of 80 U.S. cities, begun last November, were also included in the report.

EPA has suspended the parking-related portions of the indirect source regulations; not covered by this indefinite suspension were those provisions pertaining to highways and airports. Originally promulgated at the instigation of a Federal court order, the indirect source regulations, covering large shopping centers, apartments, office buildings and parking garages, require that a facility constructed on or after January 1, 1975 be subject to an air quality review. The EPA now believes that preconstruction reviews can be more effective when incorporated into state and local government planning, zoning and permit-issuing mechanisms. To date, EPA has approved the indirect source regulations of Ala., Fla., N.C., Ky., Wash., Idaho, Nev., and the Territory of Guam.

The National Research Council released a report on air quality and automobile emissions. Prepared for the Committee on Environmental Decision Making, the report concluded that there is no evidence to justify relaxation of existing ambient air quality standards for the regulated pollutants. Further, adherence to statutory emission standards for hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NO_x) should occur with no significant increases in ambient concentrations of sulfuric acid and acid sulfates. Specifically, HC and CO

emission standards for 1978 and later model year cars at current statutory levels are feasible and should be maintained. Catalyst technology will probably permit achievement of the statutory emission standard for NO_x (0.4 gm/mi) in 1978. If the NO_x standard is relaxed, a two-car control strategy should be implemented.

EPA has signed an agreement to use NASA's research center to conduct standardized tests for product noise emissions. EPA's planned test facilities at NASA's Lewis Research Center near Sandusky, Ohio, are to be operational by January 1976. Tires, motorcycles, light trucks, and automobiles are some of the products to be tested as mandated by the 1972 Noise Control Act.

A new Office of Land Information and Analysis has been established by the U.S. Geological Survey, Dept. of the Interior. Operating under a budget of about \$15.3 million, and headed by Dr. James R. Balsley, the unit will consolidate existing land resources and environmental impact programs, including the Earth Resources Observation Systems (EROS) program.

A recent IMOS task force report stated that there is "cause for concern" that fluorocarbon -11 and -12, used as refrigerants and aerosol propellants, are damaging the earth's ozone layer. The Inadvertent Modification of the Stratosphere task force report was released by H. Guyford Stever, Chairman of the Federal Council for



Federal Council's Stever

Science and Technology, and Russell W. Peterson, Chairman of the Council on Environmental Quality. It recommended that Federal regulatory agencies restrict fluorocarbon uses if a study by the National Academy of Sciences, to be completed next Spring, confirms the current task force assessment. Another recommendation was that aerosol products containing fluorocarbons be so labelled.

Three U.S. Navy scientists postulated that vegetation contributes heavily to smog in urban areas. Naval Research Laboratory scientists R. A. Saunders, J. R. Griffith and F. E. Saalfeld analyzed rainwater collected in Washington, D.C., a city with little industrial activity, following a sustained smog alert in mid-August 1973. Gas chromatographic/mass spectroscopic analyses identified unsaturated hydrocarbons, but no aliphatic hydrocarbons in the water samples. The scientists concluded that this smog alert could have been caused by hydrocarbons volatilized from Appalachian vegetation, and that automobile emissions probably played a minor role.

STATES

California restores while Florida delays the SO₂ ambient air quality standard. The Calif. Air Resources Board restored the stringent 0.04 ppm for 24 hr standard for SO₂. Citing evidence of effects on visibility and plant damage at levels below 0.10 ppm for 24 hr, the Board rescinded an action taken by the former Air Resources Board in October 1974. The new Board plans to reconsider the SO₂ standard for 24 hrs and to consider other time intervals as well. The Florida Pollution Control Board voted to delay implementing the July 1, 1975 standard for SO₂ emissions from existing fossil fuel steam generators for two years. The delay was instituted to relieve consumers from rising electrical rates and to acquire additional data on SO₂ levels and their effects.

Louisiana was among the first states to have its territory mapped by land use types by the U.S. Geological Survey's (USGS) new office of Land Information and Analysis under a five-year nationwide program. Louisiana officials used the computerized USGS land use maps along with flood-time images taken by NASA's LANDSAT earth resources survey satellites to determine the number of acres of various types of land—urban, farm, upland forests and wetland forests, for example—undated by spring floods this year. This was the first time that satellite imagery has been used on a non-

experimental, operational basis, and the first time land use maps have been used to determine the various acreage of land use types flooded.

Oregon's first nuclear generating station is scheduled to go on-line by late 1975 or early 1976. The \$405 million Trojan Nuclear Plant, near Portland on the banks of the Columbia River, will generate 1.13 million kilowatts of electric energy. The plant's hot water effluent will be used by the Oregon Game Commission to breed salmon and trout. The air, vegetation, soil, fish and public drinking water surrounding the site are continuously monitored. In a related matter, the Tennessee Valley Authority authorized a continuation of studies, through mid-1980, to develop beneficial uses for heated discharged water from power plants. Ultimately to be created is the Southeastern Waste Heat Research Center at Browns Ferry Nuclear Plant in Alabama.

The control estimate cost of construction of the Trans-Alaska Pipeline, to be completed by late 1977 to an initial design capacity of 1.2 million barrels/day, has been revised upward to \$6.375 billion. In October 1974, the control estimate was \$5.558 billion. According to Alyeska Pipeline Service Co., the increase "resulted from construction experience since that date (October 1974), . . . and compression of the construction schedule to meet the planned July 1977 startup date."

The Illinois EPA has granted a construction permit to Granite City Steel to install two coke oven pushing emission control systems at its coke oven batteries. The company has also applied for a patent on its "one-spot coke receiving system," which realizes the objectives of full enclosure of the coke push and capture of the emissions during pushing. Emissions to the air occur when finished coke is pushed from an oven into the air. The Granite City Steel's system can be incorporated into the design of new batteries, or it can be retrofitted to existing coke oven batteries. According to the company, the system requires less energy to operate and initial costs are lower than alternative control methods such as stationary sheds and traveling hoods.

The Minn. Pollution Control Agency (MPCA) will conduct a chemical wastes disposal demonstration project in the Minneapolis-St. Paul area. The estimated cost of the five-year project is \$5.41 million; the U.S. EPA will provide \$3.72 million with the remainder

coming from the MPCA and other local sources. The facility will consist of a specially designed, lined landfill into which the chemical wastes will be deposited. The liner, possibly made of concrete, asphalt, clay or plastic, will prevent seepage and subsequent contamination of ground water. Some of the chemical wastes will be chemically fixed, encapsulated or neutralized before disposal.

N.Y. City's Mayor Abraham Beame dedicated the first upgraded sewage treatment plant in the city's \$2.4 billion water pollution control program. The complete program, underway since the early 1960's and to continue through the early 1980's, involves the upgrading of 12 sewage treatment plants, including this first one, the 26th Ward, and the construction of two new plants. The completion of the 26th Ward plant is the first step in the restoration of clean water to Jamaica Bay; this plant can now treat 85 mgd of sewage generated from an area of 6,000 acres with a population of 5 million. The New York State Dept. of Environmental Conservation has recently submitted, under Section 208 of P.L. 92-500, a grant application for \$8 million to develop an Areawide Waste Treatment Management Plan for N.Y. City.

MONITORING

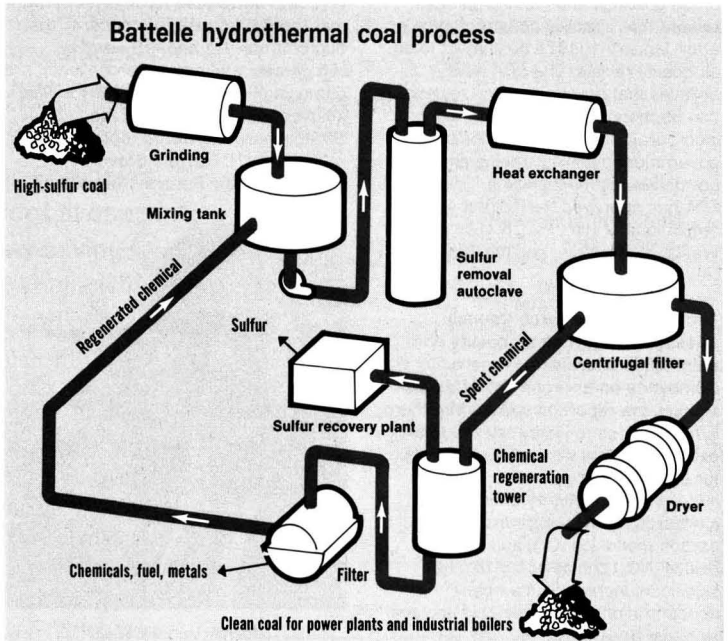
Charting total ozone distribution in the earth's upper atmosphere will be done on a daily basis with a new

spectrophotometer to be launched in 1978 with the Nimbus G satellite. This spectrophotometer is being developed by Beckman Instruments, Inc. (Fullerton, Calif.) under contract with NASA. At present, ozone determinations are being made once every seven days by a Beckman spectrophotometer launched with the Nimbus 4 satellite five years ago. The ozone measurements could help scientists resolve the current controversy concerning what depletion effects aerosol fluorocarbons may have on the ozone layer.

Portable CO samplers called "Ecolyzers" were used to ascertain 1-hr personal CO exposures experienced by commuters in the Boston, Mass., area. The Ecolyzers employ an electrochemical sensing method. These portable samplers demonstrated that fixed location monitors significantly underpredict one-hour personal CO exposures experienced by the commuters.

TECHNOLOGY

Removal of 99% of pyritic sulfur and 70% of organic sulfur from coal can be accomplished by the Hydrothermal Coal Process developed by Edgel Stambaugh of Battelle (Columbus, Ohio). The raw coal is first ground; it is then heated in a slurry of water and chemical leachant at moderate temperatures and pressures, and finally dried. Sulfur and many toxic metals are removed, and the coal would produce



less than one lb/million Btu of SO_x. However, the "clean" coal is treated with alkali to inhibit SO_x production even more. The process is believed to be 20% less costly than any alternate means of "cleaning" coal. Process modifications can enhance coal gasification, liquefaction, or depolymerization.

Reduction of solvent emissions to the atmosphere by 2400 t/yr and natural gas savings equal to 1.6 trillion Btu result from use of new water-based coatings for the beverage containers made by American Can Co. The previous procedure was to use hydrocarbon solvent-based coatings, and vent the solvent to the atmosphere; however, Clean Air rules called for oxidizing solvent fumes before venting. This entails high capital and operating costs. The new water-based coatings are about 53% water, 36% solids, and 11% non-smog-producing hydrocarbons. For this process, American Can won the Packaging Institute's Ecology Award.

Removal of phosphorus (P) in wastewater sometimes can be done with waste from another plant. The City of Marion, Ind., was required to remove 80% of wastewater P content or achieve less than 1.0 mg/liter P in the final effluent, whichever is less. The waste used for P removal was ferric chloride (FeCl₃) from an etching process, discharged in large quantities by the Marion RCA Industrial Plant. Results indicate that with 800 lbs/day of FeCl₃ or more (P discharges 81–310 lbs/day), the P effluent requirement is met. If commercial FeCl₃ were used at 800 lbs/day for 1 yr, increased costs could be \$400,000. Also, RCA may be entitled to a cost rebate for the waste FeCl₃.

Detoxification of cyanide wastes is possible with the Cyanil Process, which operates by electro-oxidation. Cyanide, mostly from plating and metal finishing, is reduced to less than 1 ppm; lower capital and operating costs are incurred than those of alkaline chlorination and hypochlorite processes, and the system is safe and easy to operate, compact in size, and almost maintenance-free. It was developed by the University of Waterloo (Ont.) and by B&W Heat Treating (1967) Ltd. (Kitchener, Ont.), and received the first Chemical Institute of Canada Environment Improvement Award. The system will be marketed by Cyanil Co., a part of B&W Heat Treating Ltd. (Kitchener, Ont.).

INDUSTRY

Radian Corp. (Austin, Tex.) will assess, select, and develop pollution control techniques for synthetic fuel plants based on coal, pursuant to an 18-month contract, worth over \$420,000, with the U.S. Energy Research and Development Administration (ERDA). Radian will identify process waste streams (gas, liquid, solid) from planned coal conversion plants, and their potential pollutants, and propose sampling and analysis methods for possible development. More specifically, Radian will concentrate on various state-of-the-art processes now being developed for the production of clean energy from coal, and will take into account coal feedstock as well as process wastes.

Israel Proler, chairman and president of Proler International Corp. (Houston, Tex.), one of the world's leading processors of metals for recycling, forecast "very significant growth" of his company in the next five years. He told



Proler—metals for recycling

Proler stockholders that the firm has budgeted \$12 million for capital expansion this year in preparation for the increased demand for scrap metal, which he foresees. Proler predicted that 300 million tons of new steel-producing capacity will be needed to meet world demand by 1980, and that much of this capacity will stem from construction of electric furnaces capable of using 100% scrap. He also foresees profits for his company despite recent softening of scrap prices.

Varian Associates (Palo Alto, Calif.) has announced success in developing a new gallium arsenide (GaAs) solar cell. Only 1/8 in. in diameter, and 20% efficient, the cell produced 10 W of electricity directly from sunlight. According to Ronald Bell, Varian's Solid State Laboratory director, other solar energy materials, such as silicon, require 1000 times the surface area to

produce the same amount of electricity. Cells can be connected in series so that 100 cells will generate 1 kW. Varian is testing a GaAs cell generator consisting of a concave reflector that collects sunlight and focuses it on the cell array. Light is concentrated by a factor of 1000. GaAs is a low-cost semi-conducting material used in electronics.

The Du Pont Co. (Wilmington, Del.) warns that the stringent 1983 requirements of the Federal Water Pollution Control Act Amendments of 1972 will cost tremendous amounts of money, energy, and other vital resources without significantly improving the usefulness of the nation's waterways. In a new booklet, "Water Pollution Abatement: Are We Getting Our Money's Worth?" Du Pont considers the 1977 requirements to be "generally necessary and economically sound," but calls for a reassessment—very soon—of the 1983 goals. The company foresees having to spend at least \$500 million for water pollution control facilities between 1977 and 1983, and estimates that 65% of this disbursement will bring about no real water improvement, but could potentially cost 125,000 jobs.

Samuel Johnson, chairman of Johnson Wax (Racine, Wis.) has announced that his company has removed all fluorocarbon propellants from its production lines in the U.S., and is reformulating its product ingredients worldwide to achieve the same goal. He said that indeed, over the past 3 years, his firm had been using fluorocarbons in less than 5% of the total propellants in its products, for Johnson Wax had invented the "water-base" aerosol system about 15 years ago. Johnson also said that in addition to better environmental acceptability, water-base formulations using propellants other than fluorocarbons are less expensive.

Otis Elevator Co. is providing two battery-powered 20-passenger electric buses for use in New York City's Roosevelt Island community where automobiles are forbidden. Each bus is powered by one 72-volt battery that can power the bus for 4–5 hrs between battery exchanges; such exchanges are a 5-min, one-man operation. According to the company, battery-operated buses are extremely reliable, with no combustion engine or transmission. Moreover, the bus is a material saver, since it is expected to last 20 yrs, while gasoline-powered buses last five yrs, and diesel buses 12 yrs.

Pollution control at textile plants

Charlotte, populationwise the largest city in North Carolina, is one of the textile centers of the world. Thus, it was appropriate that the American Association of Textile Chemists and Colorists (AATCC, Research Triangle Park, N.C.) should have held its fourth Textile Technology/Ecology Interface Symposium there in late May. Symposium chairman Harry Zika of Union Carbide Corp. told the meeting that the textile industry was in difficult times. He pointed out that in addition to profit and inventory problems, new regulations concerning water pollution control (wpc), air pollution control (apc), solid waste disposal, and the Occupational Safety and Health Administration (OSHA) present formidable challenges.

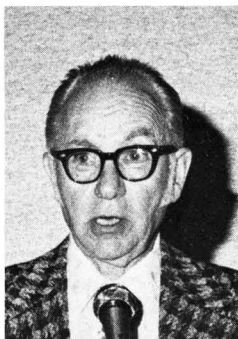
A federal case

Indeed, the challenges presented by at least the wpc rules led to a federal case. F. Sadler Love, secretary-treasurer of the American Textile Manufacturers Institute (ATMI, New York, N.Y.), complained that the EPA 1983 best available technology economically achievable (BATEA) guidelines "pushed too far," and said that the ATMI therefore sued for injunctive relief. Nevertheless, the ATMI will work on a cooperative study with the EPA in order to evolve "reasonable" guidelines. As Love put it, the textile industry will "go the mile, but not the extra mile."

What, however, would have motivated the ATMI to sue? Perhaps one answer to this question might be found in what Robert Miki, director of the Office of Environmental Economics, U.S. Department of Commerce (Washington, D.C.), told a symposium luncheon session. He said that environmental standards should be consistent with the objectives of economic growth and stability, "rather than the pursuit of an idealistic maximum which would involve excessive or disproportionate sacrifices by segments of the economy."

What those sacrifices, excessive or not, may be, cannot be exhaustively quantified at this juncture, Miki pointed out. For openers, many guidelines have yet to be promulgated. Numerous new source performance standards (NSPS) still need to be ascertained. Also, while

fragmentary cost estimates, within each compartment, for air, water, solid waste, and noise rules have been made, combined costs to industry of all environmental regulations (and to those, one should probably add OSHA standard compliance) have not yet been determined, he said.



Symposium chairman H. Zika
"Rules present formidable challenges"



Dan River vice-president Goodson
Assessed regulation cost impact

Miki did give some numbers, however. For 1973-1982, he gave an estimate of total environmental control expenditures of \$194.8 billion (1973 dollars), of which industry's share would be \$156.8 billion and government's share \$32.7 billion, with the remaining \$5.3 billion for land reclamation, radiation, and noise. By contrast, textile executive L. Aubrey Goodson, Jr., vice president of Dan River Inc. (Danville, Va.), estimated wpc costs alone at \$300 billion

over the next decade. Perhaps an indication of future costs to the textile industry could be found in the fact that its capital spending for pollution control in 1974, \$25 million, was 2.9% of industry's total capital spending.

Possibly, a principal factor behind ATMI's suit was the industry's uncertainty in process management and investment planning, in view of the piecemeal nature and the timing of environmental regulations. These factors, among others, have motivated Miki to advocate that the formulation of environmental regulations take into account

- careful examination of achievable technological alternatives available to industries
- pursuit of the least costly way of cleaning up the environment
- provision for minimizing adverse economic impact before dislocations appear.

Overregulation?

"Are we legislating ourselves out of business?" was the topic of a presentation by Dan River's Goodson. He said that although the textile industry recognizes "reasonable regulatory needs," and is willing to work with government in fact-finding to accomplish "what is really reasonable," the regulatory process is fast getting out of control. He acknowledged that "regulators are good civil servants seeking to accomplish their assigned tasks, and convinced that their agency objectives are valid and important." However, he said that collectively, they "change from a Dr. Jekyll to a Mr. Hyde," and that the costs of meeting their requirements can hobble an industry.

Goodson also explained how these costs could hit the public. If EPA-required wpc costs are to be \$30 billion/yr, the impact on 56 million American families could, in turn, be \$527/yr. That impact could, in its turn, cause families to reduce apparel expenditures; he estimated the resultant cost of wpc alone to the textile industry of \$3.192 billion/yr in lost trade. By the same token, he pegged OSHA costs at \$239-563/yr per family (depending upon final OSHA standards); product safety at \$53-105/yr per family; more for apc rules;

The industry readily acknowledges the need for clean air and water, and safe, healthy working conditions. However, spokesmen warn of severe economic problems if environmental and OSHA regulations are complicated and overzealous

and even more to meet non-environmental regulations. These legally mandated costs could effectively price textiles—and other products, perhaps—beyond what many families can afford to pay.

Goodson also cited a negative impact on technology in that "so many R&D dollars are now spent coping with the demands of the regulators. Cost-reduction opportunities and new product possibilities have to be put off." While pointing out that none were opposed to a clean environment, or to job and product safety and quality, he noted that the cost and paperwork loads of present regulation are well-nigh disastrous. Moreover, he said, the federal regulatory budget—direct cost to the taxpayer—was \$1.3 billion in 1972, and could be \$2.2 billion in 1975, representing a 69% growth in three years.

What can costs to the industry (1974 dollars) be to meet best practicable control technology currently available (BPCTCA, 1977) and BATEA (1983), for example? Edwin Barnhart, president of Hydrosience Associates, Inc. (Emerson, N.J., *ES&T*, January 1975, p 22), made some estimates. He told the symposium that total costs to meet BPCTCA that set the textile industry back \$416.4 million; for BATEA, installation costs could be \$150 million, costs to meet standards \$262 million, and annual capital and operating costs \$293 million. With direct discharge, the industry might face annual operating costs of \$300 million for BPCTCA, and \$580 million for BATEA. Barnhart warned that just for achieving BPCTCA, a 3.7% price increase to the textile consumer would result.

EPA and OSHA

One of the views expressed at the symposium was that pure cost/benefit analysis would not justify pollution control except in rare cases. This view was stated by Howard Zeller of EPA Region IV (Atlanta, Ga.), who also said, "Environmental controls cost 0.1% of the Gross National Product." He also pointed out that the EPA is aware of the economics and cost of pollution control. However, he remarked that EPA operates "in a fishbowl," and is beset not

Category	Approximate rated capacity (thousands of lbs/day)	Cost, \$/lb of production	Total cost (millions of dollars)	Annual capital and operating costs (millions of dollars)
Carpet	1,200	\$ 1.50	\$ 1.8	\$ 2.0
Commission house	2,700	17.00	45.9	57.0
Dry finishing	2,000	3.00	6.0	1.0
Knit finishing	2,350	10.00	23.5	17.0
Stock and yarn dyeing	2,000	7.00	14.0	11.0
Wool finishing	550	18.50	10.2	4.0
Wool scouring	500	30.00	15.0	7.5
Woven finishing	24,000	12.50	300.0	194.0
Total			\$416.4	\$293.5

Source: Hydrosience Associates, Inc.

only by industry, which accuses EPA of being "unkind," but also by extremist action groups who threaten court suit if the EPA does not immediately move to shut down what these groups feel to be offending facilities.

Zeller said that as of the time of his talk, EPA Region IV had issued 6000 National Pollutant Discharge Elimination System (NPDES) permits, with 3000-4000 left to issue to "minor dischargers." About 10-15% of these permits went to the textile industry. The present move, Zeller explained, is to shift the emphasis from permit issuance to enforcement, and he noted that 50% of his regions' permittees were in violation of their permits. He also expressed the feeling that BPCTCA is a "good level," and that all dischargers "should be brought to that level by 1977." However, he "accepts the ATMI suit" concerning the 1983 BATEA.

Sam Morekas of EPA (Washington, D.C.) said that as far as hazardous wastes—especially solid wastes—are concerned, his agency has no regulatory authority at present. However, he hopes to see the legislative process start during this Congressional session toward regulating these wastes. He visualizes a P.L. 92-500-type approach, possibly with a permit system, guideline enforcement by states, and actions against "imminent hazards." And Tom Sargent, also of EPA (Athens, Ga.), reminded the symposium that the agency and its predecessors put \$3.4 million in public funds into textile industry pollution control since fiscal year 1969.

George Dominguez, manager of Ciba-Geigy Corp.'s EN-CAS Systems (Greensboro, N.C., *ES&T*, April 1975, p 302), alerted the meeting to forthcoming OSHA standards. First ones will entail cotton dust, noise, arsenic, bis-chloromethyl ether, and vinyl chloride. Others will come not too much later. He estimated total cotton dust control costs alone, over 1975-1977, at \$447 million.

Also presented were textile industry approaches to attacking pollution problems from in-house. These covered the gamut from heavy metal removal, advanced and biophysical waste treatment methods, and dye waste studies to hazardous waste disposal or incineration and complete water recycle.

A philosophical view

Charlotte is not only the symposium site, but also the home of the world-famous author and raconteur, Harry Golden (*For 2¢ Plain*). He told *ES&T* of his philosophy regarding the environment in general, and his remarks would also have bearing on the textile industry with which, as a long-time resident of Charlotte, he is familiar. Golden said that despite present economic and energy problems, the movement for environmental cleanup "is here to stay." He sees clean air, streams, and rivers as a "good investment for the consumer and his children and grandchildren," and hopes that the textile industry and industry in general, which, after all, also consists of consumers, will take this view to heart.

JJ

Water reuse reconsidered

Complete reutilization of treated waters for potable and nonpotable purposes is receiving increased attention

Workmen called dew gatherers who used instruments termed dew precipitators were common features to the inhabitants of the planet Arrakis (*Dune* by Frank Herbert). Fortunately we earthlings need not go to these extremes just yet. But, that water and the "pollutants" removed from it are precious commodities to be used prudently was the theme of the Second National Conference on Complete WateReuse. Organized by Lawrence K. Cecil, the conference was sponsored jointly by the American Institute of Chemical Engineers and the Environmental Protection Agency.

According to hydrologist Jack R. Lohman, the goal of P.L. 92-500, zero discharge of pollutants into the nation's waters, is noble but not possible. The conference, on the contrary, stressed, not zero discharge but better planning, management and use of water. Ses-

sions covered:

- water reuse and its attendant problems
- water's interface with air and land, and the modification of these interactions by the imposition of energy
- heavy metals in the environment and methods for their removal.

Pollutants as resource

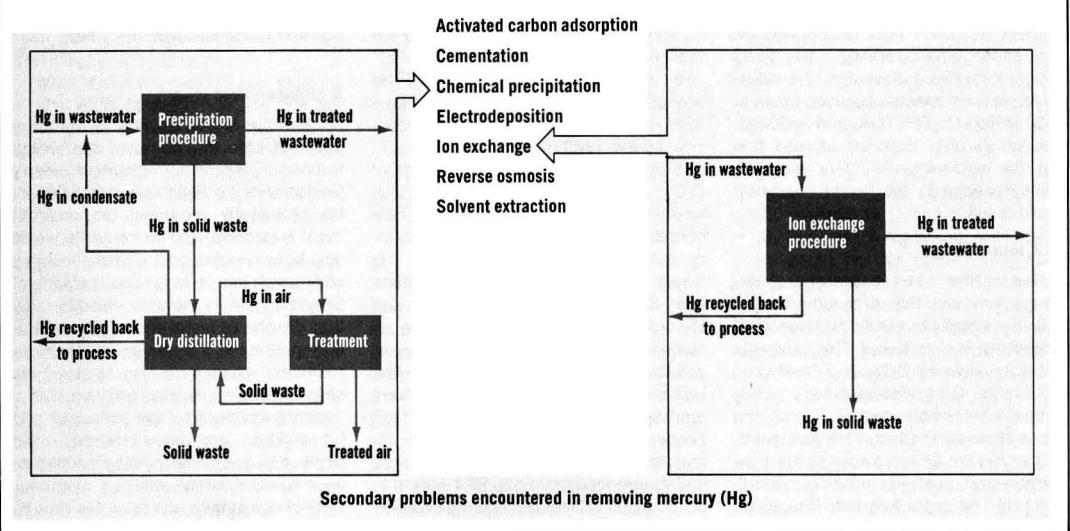
Since the pollutants in water, once recovered, do have a value as does the reclaimed water, industries may realize an overall profit in an optimized water and waste management system in which cost credits are allowed for recovered by-products and water. Industries are finding and will continue to find that over the long-term, abatement of water pollution and water conservation are economically compatible.

Heavy metals of immediate concern—

cadmium, cobalt, copper, chromium, iron, lead, manganese, mercury, nickel and zinc—are responsive to removal by practical treatment methods. These methods include activated carbon adsorption, cementation, chemical precipitation, electrodeposition, ion exchange, reverse osmosis and solvent extraction; they have been used in water purification and metal recovery industries.

An alternative method for the treatment and disposal of municipal wastewater is direct land application. Land may be used as a dumping ground, loaded to its hydraulic capacity, or it may be treated as a resource recovery area to harvest crops. Infection from spray irrigation-aerosols containing virus pathogens that are not destroyed by chlorination is slight. Studies show the spray site to be at least as safe as other confined public environments.

Practical methods to remove metals in wastewater include:



Back to roots

Going back to roots, Greek roots that is, Beatrice Willard, member of the Council on Environmental Quality, reminded her audience that the word ecology comes from the root oikos meaning home or habitat, and that the practitioner of this science is the ecologist. She went on to stress the necessity for a close working relationship between the engineer and the ecologist, particularly in the area of water reuse where substantial monetary savings to communities, and benefits to the land can be achieved.

Willard felt that sound planning and managing of man's activities in harmony with ecological principles, which she enumerated, involve the participation of the economist as well as the engineer and ecologist. Contributions from these three professions would bring man back into his ecological niche, a niche affected by and interrelated to everything else in the ecosphere.

In addition to the professional input discussed by Dr. Willard, the informed citizen has a vital role to play in bringing man's activities more in balance with the physical and biological laws controlling his environment.

Professional and lay people, with knowledge of and interest in water resources and related land use, can ask the questions and provide the value judgments required in sound planning at all government levels. Effective public participation, after becoming properly informed, means gaining access to appropriate agencies and participating in public hearings. One nongovernmental group of informed citizenry, the League of Women Voters, was represented at the conference by Edith C. Chase.

Dilemma

The increased urbanization of our expanding population, and decreased "virgin" protected water supplies has increased the pressure on municipalities to consider the use of treated water for potable purposes. According to Daniel A. Okun, professor of environmental engineering at the University of North Carolina, "In the United States, for example, about one-third of the population traditionally drinks water that, in fact, comprises wastewaters that only hours earlier had been discharged from municipal or industrial sewers."

The use of previously contaminated waters for potable purposes poses serious threats, for even with conventional treatment, the fate of water-borne viruses is uncertain, and the ultimate effect on humans ingesting the water is unknown. Further, each year witnesses the introduction of hundreds of new chemicals into the environment. Conventional water treatment is only partially effective in removing these chemicals from wastewaters. The long-term effect

of ingestion of low-levels of these chemicals is difficult to assess.

Most water utilities in the U.S. are too small to economically supply the manpower, operation and monitoring needed to assure the continuous high-level performance required of treatment plants using sources of water that are highly contaminated. Also, the technology for analysis and routine monitoring of these treated waters is not yet available to assure a continuously safe potable supply.

Dual water supply

So, what to do? The answer according to Okun may lie in the use of a dual water system where one system supplies potable water and the other would be adequately disinfected though not sufficient for potable purposes. The



CEO's Willard
"harmonizing man's activities with the ecosystem"

planned use of water such that no higher quality is used for a purpose that can tolerate a lower quality would be a concomitant to the dual supply system. For example, only 10% of the total public water supply is required for high purity purposes—drinking and cooking. Yet, pure waters are being wasted on uses such as urban irrigation and toilet-flushing that could tolerate water reclaimed from polluted rivers or from industrial or municipal wastewaters.

In a dual water system, the use of reclaimed water for lower quality water needs could reduce the costs of water pollution control, and would reduce environmental damage and the risk to the public from long-term ingestion of contaminants present in polluted water. Further, the use of reclaimed water would eliminate the cost of developing high-quality fresh water sources for purposes not requiring high-quality water.

Successful examples

The only planned direct reuse of wastewaters for potable uses is at Windhoek, Southwest Africa and, then, only when the chlorine demand can be met. The water reused is cycled through a complex advanced treatment facility

manned by highly qualified supervisors. The treatment facility receives no significant amount of industrial wastewater, and it makes up only a third of the city's potable water supply.

Closer to home, Colorado Springs, Colo., is passing about a third of its biologically treated wastewater through sand filters and subsequent disinfection. This reclaimed water is then stored for later dissemination through a secondary distribution system for sale as irrigation water to large-scale users. A portion of this reclaimed water is further treated to remove phosphates and organic chemicals, and is then sold to industrial users. The reclaimed water sells for two thirds the price of the higher quality potable water.

A philosophical view

Consider for a moment the proposition that there is no such thing as pollution. That in nature "pollutants" are simply different forms of matter undergoing constant change. With this premise operative, what then is pollution control? What curbs must man place on his technological activities?

If, as C. A. Caswell of Datagraphics Inc. (Carnegie, Pa.) does, you view the limiting factor of pollution control as the assimilative capacity of pre-existing physicochemical systems, then you see the human race faced, in the very near future, with the necessity for stabilizing industrial growth in order to stabilize the conversion of matter from one form to another. And, whether actions will be taken voluntarily or enforced upon societies by the physical laws governing the various natural cycles, the social dislocations will be great.

Present technology merely shifts the pollutant from one system to another; in a wastewater treatment plant, for example, from water to land, air and/or water. In the environmental sense, then, it is not the specific material produced that constitutes pollution but, rather, it is the rate at which it is being produced and introduced into a repository—air, water, land—that presents the problem. If pollution is defined as the addition of matter to air, water or land that adversely affects the beneficial utilization of these environmental compartments by life forms, then the measure of pollution is the extent to which the beneficial uses have been so affected. Reduce the production of a material to a level at which the receiving system can efficiently handle it and you have in a sense effected pollution control.

The decisions regarding pollution control will be technical, political/social, and legal. The engineer can describe the problem; the physical scientist can explain the underlying principles; but only society, through political mechanisms, can decide what to do about pollution control. LRE

Finland's cleanup campaign

Improved quality of life, as well as resource conservation, are both motives and goals of that country's stepped-up environmental programs

That the International Bank for Reconstruction and Development (World Bank, Washington, D.C.) would grant a 15-yr loan of \$20 million is not, of itself, big news. What is news is that this loan is being floated in support of a water pollution control (wpc) program in Finland, and is the first pollution control loan ever granted by the World Bank.

Proceeds from the loan will help to finance about 65% of the foreign exchange costs of wpc expenses to be incurred by Finnish industry between this year and 1977. The Mortgage Bank of Finland Oy (Helsinki) is the official borrower, and it, together with the National Board of Waters (NBW, Helsinki, under the Ministry of Agriculture and Forestry) would appraise and supervise sub-loans to 20-30 industrial companies. These industrial sub-borrowers must meet specific targets, set by the authorities, for reducing the amount of effluent they discharge.

Land of Lakes

About 10% of Finland is covered by inland waters that consist mainly of "watercourses"; that is, lakes joined together by narrow channels, short streams, and canals. There are more than 55,000 lakes, of which only two are over 100 miles deep. Average lake depth is about seven miles; such relatively shallow waters can often contain pollution-developing humus. Moreover, during the country's long, cold winters, ice cover reduces the ability of watercourses to receive wastewaters.

Simo Jaatinen, president of the NBW, which is in charge of Finland's fresh and coastal waters and wastewater, notes that his country's water consumption and wastewater production per capita are among the highest in the world. The reason is that Finland has large forest products and pulp and paper industries that use much water. These industries

are spread over many parts of the country, particularly in the lake regions. Thus, environmental pollution caused by urbanization and industrialization has been reflected principally in water pollution.

Jaatinen points out that the Finns "highly appreciate their lakes," and ex-

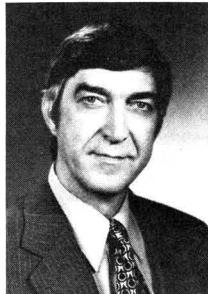
pect water quality and usability to increase despite expanding industrialization. Therefore, "water protection is generally regarded as No. 1 priority in the field of environmental pollution control," Jaatinen said.

Water cleanup funding

On the municipal front, Finnish authorities spend the equivalent of \$56 million/yr (based on 1 Fmk = \$0.28) on water protection. Jaatinen foresees that at this funding rate over the next five years, 90% of municipal wastewater will be very effectively cleaned. He also predicts that the municipal waste load discharged into waterways in 1980 will be only half of what it was in 1972. Indeed, from 1970 to 1974, the equivalent of \$98 million was expended on constructing treatment plants. By the end of 1973, over 400 municipal sewage plants served about 60% of the population.

Over the 10-yr period 1974-1983, industry faces wpc costs of \$503 million. Of this sum, the cost to the wood processing and pulp and paper industry could be \$329 million. The source of this capital will be the Mortgage Bank of Finland for 38.5%, the government-owned Postipankki (which handles the bulk of the Treasury's dealings with the public) for 38.5%, and self-financing, partly from "polluter pays" legal provisions, for 23%. Part of this capital would come from proceeds of the World Bank loan.

The wpc total spent by communities and industry is about the equivalent of \$112 million. The bulk of this money is spent on investments in machinery and equipment. While most of this hardware is used domestically, a considerable amount—much of it very sophisticated—is exported. Some Finnish companies that manufacture this equipment dis-



NBW president Jaatinen
"Water protection No. 1 priority"



DEP head Ojala
"More standards needed very soon"

cussed their capabilities, along with technical considerations, at an Embassy of Finland/Environmental Protection Seminar held at Rosslyn, Va., in February. Among topics covered were new processes and equipment, for which \$20.16 million are budgeted; "off-the-shelf" technology, to cost \$42.56 million, and monitoring, for \$420,000.

Water cleanup action

In Finland, water use and cleanup are regulated by its Water Act of 1962, which prohibits blocking, changing, or spoiling (including polluting) water-courses without a permit granted by the National Board of Waters. The Act also provides for Water Courts in which those who have been damaged by water pollution may sue for compensation.

The NBW is administering a water cleanup program over 1974-1985, with 1980 and 1985 goals that stress BOD₇, phosphorus (P), and nitrogen (N). By 1980, care must be taken to prevent discharge of toxic materials to water-courses, and all sewage factors causing water pollution will have to be sharply reduced. For industry other than wood processing, fertilizer, and foodstuffs, in wastewater not run through a municipal sewage system, BOD₇ must be 10 tpd or less, and P less than 0.1 tpd. The same must hold true by 1985, and by then, pollution will have to be limited so that it is mostly local, with prevention of operational accidents and disturbances, and provision for fast cleanup in case of an accident.

Water monitoring

The NBW conducts a monitoring program for discharges and ambient water quality, and has over 6000 sampling stations plus 7500 check points. In keeping with their discharge permits industries, too, must monitor. In some cases, a company may have to report on over 12 parameters. All industries, with two exceptions, use consulting firms approved by the NBW, of which there are about 15, to do their monitoring. These industries report 35,000-40,000 water quality readings, total, under existing permits, and can be called upon to report BOD, suspended solids, N, P, toxic materials, temperature, oil, dissolved oxygen, chloride ion, pH, oxidation-reduction potential, conductivity, flow velocity, and turbidity.

Several Finnish firms are doing brisk domestic and international business in monitoring and in water and wastewater treatment equipment and systems, as well as in consulting. Some of these firms were represented at the seminar, at which A. Ahlström Osakeyhtiö (Noor-markku), the DEVECON Group (Helsinki), Jaakko Pöyry & Co. Oy (Helsinki) and Oy Yleinen Insinööritoimisto (YIT, Helsinki) participated.

Air, noise, solid waste

Environmental matters other than those concerning water come under the Ministry of the Interior's Division for Environmental Protection (DEP), which started its work on March 1, 1973. The head of the DEP is Olli Ojala, who has to deal with problems of air, noise, solid waste, and outdoor reaction. Ojala explained that while water protection has top priority in Finland at present, air pollution control (apc) "is also badly needed." He also said that in cities and towns, as well as working places, "Noise abatement is given the highest priority by the majority."

Ojala noted that there are no environmental standards (aside from those for water) in Finland. However, certain recommendations on air pollutants and noise have been given by the National Board of Health, according to the Public Health Act of 1965. An Air Protection Act and a Noise Abatement Act are now being drafted by the DEP for consideration by the Finnish Parliament.

Nevertheless, Ojala is very concerned about the paucity of environmental standards. The feeling at the DEP seems to be that these standards need to be promulgated, with "teeth," as soon as possible; that much new legislation is needed fast; and that older laws need a major overhaul and revision. For example, the Forest Protection Act and the Nature Conservation Act date back to 1922 and 1923, respectively; however, for these laws, revision might soon be in the works.

There is no law on the books to deal with the management of solid waste. However, a Waste Management Act is being drafted for the Parliament's consideration. As for other pollutants, laws regarding oil damages, environmental poisons, and biocides are in force. Also in the statutes is the Work Security Act of 1958, which deals with in-plant occupational safety and health.



Nevertheless, a few private companies are active in the air protection field. One of these companies, Outu-kumpu Oy (Helsinki), principally in mining and metals, was represented at the Embassy seminar. However, the paper industry, probably Europe's largest in the business (Sweden is larger in pulp), is also very concerned with apc.

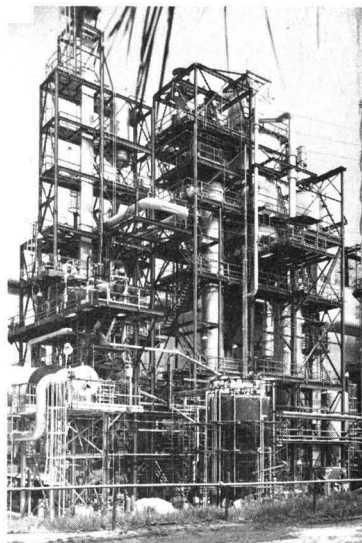
Conserving energy

While the environmental cleanup effort in Finland is in answer to social needs, more efficient use of energy and materials is a principal underlying factor. One very cogent reason is that Finland has little by way of indigenous fossil fuel resources, and wants to minimize its fuel import bill. The same holds true for a number of raw materials.

Nonetheless, the more completely fuel, materials, and heat are used in process, the less waste matter and energy get out to the environment, and the lower the operating costs. In Finland, this truism is being well applied, witness projects to recover and use waste heat from industry and other sources to provide space heating for buildings in certain districts of Helsinki, Finland's capital. Also, about 25% of industry's energy comes from recovered waste heat. However, as a rule, the Finns have never seen virtue in waste and prodigality; thus, the national trend to conserve, plus the effort to satisfy health and social needs, point to clean air and a high quality of life. JJ

Dry scrubbing of utility emissions

Foster Wheeler process of flue gas desulfurization is now underway at a Florida utility; demonstration started this May



Second generation flue gas desulfurization (FGD) systems may still be in their infancy, but at least seven systems are being investigated (*ES&T*, April 1974, p 306). Although the dry adsorption process was listed in the developmental category then, considerable new results are paving the way for the use of this process on utility boilers. In that same listing, four regenerable processes were listed as commercially available.

The dry adsorption process is applicable to all fossil fuel-fired utilities. Primary application is found in the area of large coal-fired boilers because of the established capability of the system to handle all three pollutants associated with such boilers. The process could also be used in large size refinery units as well as chemical process plants and metals smelting operations.

Mr. G. O. Layman, manager of power production for Gulf Power Co., an affiliate of the Southern Company, says that construction on the Foster Wheeler process started on February 15, 1974; the construction was at the Scholz Steam Plant, a 40 MW plant (Chattahoochee, Fla.). The testing program began this May.

Two years earlier, in January 1973, the Southern Services Company awarded a contract to Foster Wheeler Corp. to build a 20 MW prototype dry adsorption system. The actual contract called for the design, engineering, and construction and testing of a system that would accept 50% of the flue gas produced by a 40 MW boiler firing coal with 3% S, 14% ash, and a heating value of 12,400 Btu/lb.

The system at the Scholz plant consists of a 20 MW adsorber section and a 47.5 MW regeneration and RESOX (reduction of SO₂ to elemental sulfur) section. RESOX is a trademark of the

Foster Wheeler Energy Corp. The 20 MW adsorber is designed to accept 50% (half of the boiler flue gas flow) when the coal fired boiler is operating at a nominal 40 MW load.

This Scholz FGD unit is designed to meet the Florida Code for SO₂ emissions, which is 1.2 lbs/million Btu. The unit can handle coals with sulfur content as high as 5% because of the oversized design requirements of the regeneration and RESOX sections, and the inherent flexibility of the system.



Gulf Power's Layman

"regeneration—using coal to reduce SO₂ to elemental sulfur—is a real breakthrough"

Layman says that Southern Services, a private investor utility that relies on coal for more than 90% of its power generation, chose the system because it had already accomplished a very successful and lengthy pilot plant operation.

"One of the most important features of the system that has great long-range potential is the RESOX section. In this reduction step, coal directly reduces the SO₂, adsorbed by the front end of the system, to elemental sulfur." Layman adds, "It's a real breakthrough."

He explains that "all other systems ... for reduction of SO₂ to elemental sulfur require hydrogen in some form, usually natural gas, as well as catalysts. Foster Wheeler's unique approach to using coal to act as the reductant avoids the use of a costly and scarce natural resource."

In addition to FGD, the process has the potential for NO_x and fly ash removal. Also, it produces a commercial grade elemental sulfur as a by-product from the regeneration section (see box).

The process

Foster Wheeler, a designer and manufacturer of steam-generating equipment and a process plants contractor, has been licensed for the dry adsorption SO₂ removal process. The removal process was developed by Bergbau-Forschung (B-F), the central research institute for the German coal mining industry. Bench scale work at B-F began in 1966. Based on this pilot plant work, SO_x removal of up to 95% has been achieved. But Foster Wheeler independently developed the backend system, RESOX, for the reduction of SO₂ to elemental sulfur.

A second dry adsorption unit has been installed by Bergbau-Forschung, the licensor, at the Kellerman Power Plant of STEAG in Lünen, W. Ger. The unit will treat 10% of the flue gas from a 350 MW unit that will be burning coal of about 2% sulfur content. Here, a modified Claus unit will be used to process the SO₂-rich off gas. RESOX was developed by Foster Wheeler after B-F had gone ahead with the decision to install the modified Claus unit.

How it works

The adsorption section is based on the well-known suitability of activated char as an adsorption and filter media.

Dry scrubbing removes SO₂, fly ash, and NO_x^a

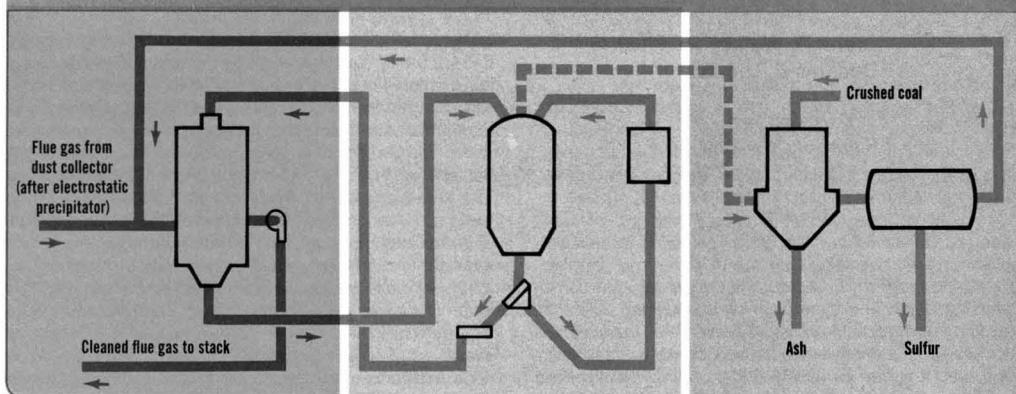
The steps:

Adsorption of dilute SO₂ on char

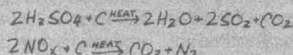
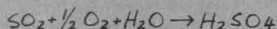
Regeneration of the char with the resultant production of SO₂-rich off gas

Reduction of SO₂ (RESOX) to elemental sulfur using coal

The flow sheet:



The equations:



^aRemoval efficiency: 95%—SO₂, 90-95%—fly ash, 40-60%—NO_x

The adsorber consists of vertical columns of parallel louvre beds that support and contain the char. The char moves slowly downward in mass flow while the pollutant-laden gases pass through the adsorber char bed in cross flow at 250–300°F. Sulfur dioxide, oxygen and water vapor contained in the flue gas are adsorbed into the char pores. Adsorbed SO₂ then reacts with the O₂ and H₂O to form H₂SO₄, which is firmly retained in the interior pore system of the char pellets. Oxides of nitrogen are also adsorbed by the char pellets. Clean gases, which are unchanged in temperature, are exhausted to the stack via an induced draft fan.

As the char progresses slowly down the adsorber, it becomes saturated and must be regenerated. It is heated in the regenerator vessel to 1200°F in an inert atmosphere. Sand at 1500°F is mixed with char to bring the char to 1200°F. All the reactions that have occurred in the adsorber are reversed at this elevated temperature (see box). Sulfuric acid is reduced to SO₂, oxides of nitrogen dissociate to oxygen and nitrogen, and CO₂ is produced as a result of chemically combining carbon in the char with the oxygen liberated from the reduction reactions. The regeneration

section yields adsorbed SO₂ in concentrated form, approximately 20% by volume. This SO₂-rich gas stream is sent to the RESOX section for reduction to elemental sulfur.

In the RESOX section, a Foster Wheeler proprietary process, SO₂-rich gas is passed through a vessel containing crushed coal. Here, SO₂ is reduced to gaseous elemental sulfur and the liberated oxygen combines with a portion of the coal to form carbon dioxide. Reduction in the RESOX reactor is done at 1200–1500°F. The gases leaving the reactor enter a condenser where gaseous sulfur is condensed and the tail gas recycled back to the adsorber to remove residual sulfur values, thus providing a closed-loop system.

This dry scrubbing process offers a number of advantages over conventional wet scrubbing. These include:

- significant NO_x and fly ash removal
- no slurry handling or pH controls required
- no stack reheat is required; the flue gas enters and leaves at the same temperature
- reduced power requirements stemming from the special size and shape of the char pellets, and the ad-

sorber louvres design gives low pressure drop on the gas side

- the char adsorbing material used in the process has a high ignition temperature of about 700°F that ensures safe operation in the 250–300°F designed temperature range
- a regenerable system with a saleable by-product (The char can be used for many cycles, the average life of a pellet being six months. Commercial grade sulfur is produced by the RESOX system)
- less space (The system uses considerably less space than a wet scrubbing system by virtue of its vertical integration concept and absence of sludge conditioning requirement.)

How much does it cost?

Installed capital costs are somewhat sensitive to the sulfur content of the fuel and the SO₂ percent removal to meet local codes. However, they range from \$25–35/kW for low sulfur level that requires a low removal efficiency to \$70–75/kW for high sulfur fuel that requires a high removal efficiency. Costs are competitive with wet scrubbing systems and may be lower depending on the price of recovered sulfur and the final cost of sludge disposal.

Measuring environmental stress

John E. Walker
Douglas B. Dahm

Calspan Corp.
Buffalo, N.Y. 14221

The environment radiates and reflects energy that can be detected remotely. The eyes of animals and man utilize this energy to assess the environment. The camera, the oldest remote sensing instrument, collects and converts this energy into a format that can be assimilated by man as information. The energy collected by the camera and recorded on film is normally of the same frequency as that detected by the eye. However, man's eye is not particularly sensitive to the energy in the longer wavelength, infrared (IR) spectrum.

Just beyond the frequency band we perceive as visible red (about 0.7μ) is the near IR band; it is part of the direct radiant energy from the sun. Moisture in the atmosphere and terrestrial bodies of water absorbs various amounts of energy in the near IR band. Some species of vegetation reflect large amounts back to the sky, whereas others reflect very little. Some species transmit almost as much as they reflect from their leaves, and absorb very little. Reflected energy does not represent thermal energy, which occurs more typically in the $10\text{--}100 \mu$ frequency range.

Because near IR energy is reflected, and there are materials used in film emulsions that are sensitive to near IR energy, a picture of this energy can be taken with a conventional

camera using special film. Radiant thermal energy in the $8\text{--}14 \mu$ band, however, must be detected by special mechanical scanning or detector array equipment, because films sensitive to this frequency band would be exposed by the heat accumulated in the mechanical parts of the camera.

Just beyond the near infrared is a transition band. Some of the energy from $1.0\text{--}2.0 \mu$ can be photographed if special techniques are used. The procedure, however, is very unwieldy and seldom used to photograph the environment.

Immediately beyond the transition band is the $3.0\text{--}5.0 \mu$ band that was initially used in mechanical scanning instruments to make terrain pictures. At this frequency band there is an atmospheric "window" that allows the energy to travel from features of the terrain to the scanner without major absorption by the atmosphere. A picture taken in this range does not portray the temperature or heat energy of the terrain features. Since the remote measurement of temperature of bodies of water is of primary environmental interest, this band is not as desirable as the far infrared band of $8\text{--}14 \mu$.

Recent advances in technology produced detectors for the mechanical scanner that operate in the $8\text{--}14 \mu$ "thermal" band and that are cooled by liquid nitrogen. This band is now utilized almost exclusively for remote sensing of water body temperatures for power plant work and other applications.

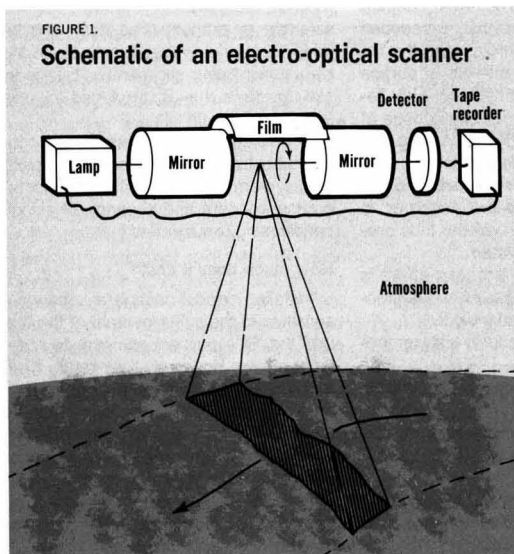
Energy thus can be separated into the visible spectrum: blue, green, and red light; the near infrared spectrum; reflected, non-visible infrared light; the middle infrared spectrum that is partially reflected, partially emitted infrared light and the far infrared spectrum which is essentially totally emitted thermal energy. Remote sensors—cameras and film or electro-optical mechanical scanner and film—are for the most part commercially available, reliable precision instruments. Present analysis technology, however, is only adequate to extract a fraction of the important environmental information that is recorded.

Energy recorders

The camera records near IR images directly on infrared-sensitive film. A between-the-lens shutter is physically located at a position in a compound lens system where all of the exposing light rays converge to a point before diverging to form images on the film in the focal plane. Therefore, the entire focal plane is exposed simultaneously and uniformly by a leaf type between-the-lens shutter. Repeatability from exposure to exposure is very good.

The other camera component that is important with respect to collection of near infrared energy for photometric analysis is the lens and its field of view. The most common lens for use with a $9 \text{ in.} \times 9 \text{ in.}$ or $4.5 \text{ in.} \times 4.5 \text{ in.}$ format is a 6 in. focal length; 3 in. lenses are more common for use with 70 mm film format cameras.

In an electro-optical scanner system, as shown in Figure 1, energy impinges on a very small metallic detector, which in turn converts the energy to a voltage that is either recorded on magnetic tape or used to modulate the intensity of a lamp that "paints" a picture of its intensity variation on film, as the film is moved along the flight path perpendicular to the direction of scanner rotation. The latent image can be created indirectly in the scanner or on the ground, after collection, by



Infrared remote sensors plus photometric interpretation and digital data analysis are being used to record the stresses on air, water, vegetation and soil

playing back the time-varying signals on special image-forming equipment.

The electro-optical scanner normally used for IR mapping at the longer wavelengths is essentially a panoramic camera. It usually covers a look angle of $\pm 60^\circ$ either side of the nadir. When used to collect visible, near infrared, middle infrared and far infrared energy of terrain features (multispectral scanners), the subjective interpretation type of analysis can be conducted cost-effectively by using film. However, for quantitative photometric analyses, computerized data handling is a must. As yet, no computerized data handling or analyses are available that include sufficiently accurate photometric calibrations of collected energy to make automatic photometric analyses cost-effective.

Some manufacturers of thermal scanners make electro-optical scanner heads that record only on magnetic tape. This increases the cost of the collection, but it makes the collection task easier. Magnetic tape allows more latitude for incorrect sensor operation than does direct film recording; it also increases the cost of the ground analysis equipment for users who want to do either a subjective analysis or an accurate photometric analysis. The latter is defined as isotherm mapping to $\pm 1^\circ\text{F}$ with geometric accuracy equivalent to U.S. Geological Survey $7\frac{1}{2}$ minute quadrangle sheets.

The simplest of the far infrared remote sensors available are the fixed radiation thermometers. These instruments do not produce "pictures" of the heat patterns, but they do provide temperature data which, when used in conjunction with the scanner imagery, allow accurate absolute water surface temperatures to be measured.

Energy records

The basic energy record of both cameras and scanners is film, with an option of interim recordings on magnetic tape for scanners. The visible and photographic region of the electromagnetic spectrum from blue light through near IR, including green and red light, can reveal the majority of stresses imposed on the environment. Only three major stress parameters are not clearly evident, namely, heat, noise, and concentrations of colorless liquids with unique absorption and transmission properties in the ultraviolet and beyond the near infrared. Even these regions can be "photographed" using electro-optical scanners.

Evidence of the environmental health of air, water, vegetation and soil is normally desired in map form, and then quantitatively assessed in terms of area and degree.

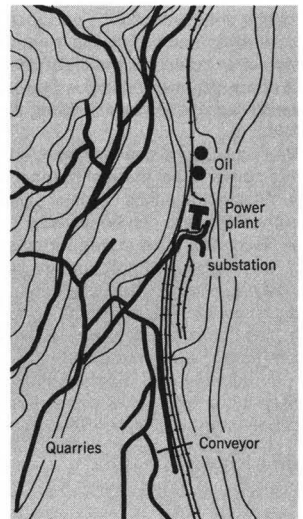
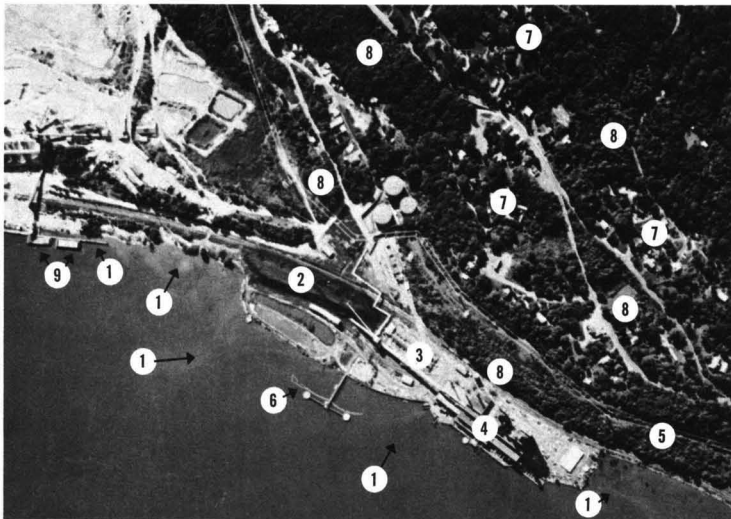
In the case of air quality, man can often observe emissions from industrial stacks and vehicles, dust from construction projects, smog and haze. The presence of hydrogen sulfide and other gases are often detectable also, but not visually. When concentrations of pollutants reach the point where they can be observed by man, they can also be photographed and the same subjective judgments concerning their significance drawn from interpretation of the photographs. However, it has now been proven that concentrations of particulates below man's direct observation threshold are recorded on film and measurable by photometric means.

In the short wavelength region of the spectrum (blue-light) scattering of energy in the optical path between the ground and camera is very large compared to the longer wavelength

FIGURE 2.

Power plant

Trained interpreter can extract salient ground features from aerial photograph



region (near infrared). Even so, the scattering is still measurable at the longer wavelengths and must be accounted for in quantitative analyses of environmental stress.

Thus, conventional aerial cameras and film can be used to monitor large areas of air pollution from day-to-day and with spectral measures of additive light (β_{λ}) and attenuated light (α_{λ}) in the air path. The relative amounts of $\alpha_{\lambda 1}/\beta_{\lambda 1}$ is a measure of the air path scattering properties and the relationships of $\alpha_{\lambda 1}/\alpha_{\lambda n}$ and $\beta_{\lambda 1}/\beta_{\lambda n}$ measures of the spectral nature of the scatters. With these measures of the scattering properties of the air path established, image densities recorded on the aerial film are relateable to the spectral ground reflectance properties of water bodies, soils, vegetation, paved surfaces, and any other object imaged on the film. Thus, other environmental stresses can be measured.

In the case of water pollution, an analysis technique has been developed that identifies chlorophyll, lignins, and organic material and delineates increasing and decreasing concentrations over entire water bodies relative to concentrations at a reference location.

In the case of vegetation stress, a unique measure is now available, namely, the ratio of near infrared reflectance to red reflectance. When vegetation is stressed to the point of chlorosis, the leaves stop absorbing energy in the red region of the spectrum. The near infrared band changes very slightly with stress, but as leaf area shrinks and the vegetation defoliates, a major energy change will occur. The remaining spectral reflectance levels and ratios relate to the vegetation type and crownal structure, that is, light scattering, absorption, transmittance and reflectance properties.

In the thermal region, atmospheric attenuation of energy from the surface of water bodies is present, and must be considered in mapping such pollution features as discharge plumes. Another advanced calibration technique has been developed (Calspan Corp. U.S. Patent Disclosure No. 1459. A Technique for Calibration of Infrared Thermal Imaging Systems) for thermal data collected from aircraft, which established this correction factor calibrating the output isothermal map to within 1°F; the relative values of the isotherms are on the order of 0.5°F.

Most conventional direct recording thermal scanners generate an image that is not spatially correct. In the direction of flight, linear scale distortions are caused by changing heat, tail, and cross winds. Across the flight direction, the scale varies as a tangent function from true vertical. Scanners with velocity/height (v/h) ratio sensors that automatically correct ground speed errors and even tangent errors are feasible, but would be very expensive. Tape recorded raw data with nadir position sync and v/h signals recorded, could be readily corrected after collection and during the generation of the film. In fact, there are also analogue devices that will correct these geometric collection errors during the isothermal map preparation.

By combining a conventional aerial camera and color film with a conventional thermal scanner in a single aircraft:

- All spectral bands of major significance in monitoring environmental stress can be covered.
- Resolution is optimized for classic subjective interpretation, where levels of pollution are sufficiently high for man to identify them easily, and photometric calibration can be accomplished accurately.
- The equipment costs for collection, processing and analysis of data are minimized.
- Accurate maps of environmental stress can be generated without expensive digital data handling and analysis equipment, or highly specialized and expensive manpower.

Display formats

The overhead view of the environment is becoming a familiar sight as a result of the satellite and high-altitude programs of the National Aeronautical and Space Administration

(NASA) over the past decade.

No article on remote sensing of environmental stress would be complete without illustrating the raw data film records of remote sensors. Figure 2 shows a conventional color aerial photograph of a fossil-fuel power plant on a river. The scale of the photograph is 1 in. = 500 ft. An individual trained to interpret aerial photographs of the environment can extract much information by using this classic technique. In conjunction with the photograph, the individual generally has a topographic map of the area that identifies salient ground features. A portion of such a map is shown in the insert.

Additional information extractable from the photograph by an inexperienced interpreter includes:

1. discolorations in the water, related to water quality
2. the coal supply for the plant
3. the substation transformer yard and distribution point to the transmission lines
4. the power plant proper and its stacks
5. a new transmission line
6. floating booms, probably for oil retention during unloading at pier
7. residences in the hills
8. grass areas and trees
9. barges

To a subject category photointerpreter, such as a power plant interpreter or forester interpreter, who has many years of experience, additional information may be extracted from associations he has established between his numerous observations of photographic images and investigations on the ground (ground truth). Such interpretations begin to involve very subtle image clues such as relative color or brightness. Furthermore, sensor optics, the atmosphere, film processing technology, film emulsion characteristics, and illumination conditions cause subtle color shifts that are easily misinterpreted as being real changes in objects under analysis. Therefore, the more man attempts to extract information through the subjective interpretation process, the more errors he can expect. An advanced photometric interpretation technology (U.S. Patent No. 3,849,006. Method for Extracting Photometric Information from Aerial Photography. Calspan Corp., K. R. Piech and J. E. Walker, Nov. 1973) is available that allows man to extract additional useful information from both color and IR film by recognizing subjective limitations and subtracting spurious inputs from other system variables.

To illustrate the limitations under which classic subject category interpreters work, consider the areas of discoloration in the water, annotated (1) on the photograph. Any of the discolorations could be interpreted as pollution from the power plant. However, a power plant interpreter would note where the power plant proper (4) was located and realize immediately that the discoloration near the barges (9) was not caused by the power plant because over 1000 ft of discharge pipe would be necessary to discharge in this area. Furthermore, the water behind the pier, and along the shoreline to the coal pile, is also discolored in the same fashion. Therefore, it is more likely that this discoloration stems from the nearby quarry operation.

With subjective judgment alone, no measures of suspended material concentrations, or identification of material in the discolorations are possible. An industrial subject category interpreter could probably identify the quarry activity from the complex conveyor system and the material excavating procedure and equipment being used. It is most likely this discoloration is a result of surface run-off from the barge-loading piers.

The two discolorations, either side of the long dimension of the plant proper, would most likely be cooling water discharges of the plant. Since the discoloration of the water is significantly less bright than those previously discussed, the suspended material either differs in type or concentration. A complex area of discoloration also occurs near the shore

FIGURE 3.

Strip-mining operation

In this color IR aerial photograph, cyan indicates bodies of green water, black indicates clear waters, red indicates vegetation

**Color IR photograph**

Figure 3 shows a color infrared photograph of a strip-mining operation in the midwest, first published in the September 1974 issue of "Photographic Applications in Science, Technology and Medicine." The typical "red vegetation" images are striking. The photograph was analyzed by classic subjective interpretation by consultants in mining and mine reclamation. An overlay of sixteen areas, designated by land-use type such as drag-line operation, power shovel operation, natural revegetation, partially graded area, spoil ridge top rounding area, complete spoil ridge regrading and revegetation, water surfaces, and mining area under preparation were extracted. The boundaries of the areas were selected by subjective judgment, and acreages of each land use type were probably computed. However, such an analysis only scratches the surface of useful information that can be extracted from color and color infrared film, when advanced photometric interpretation technology is applied.

area. There are rather unique islands of darker tones throughout the area. Since the map shows that this area is significantly shallower than other near shore locations and the darker tone islands get lighter from near to far shore, these could easily be weed beds developing and the discoloration a bottom effect.

Classic interpretation alone cannot provide the answer in either of the above cases. A ground and boat sampling survey would provide useful point data for a specific circumstance. Such surveys, however, have the inherent dilemma of requiring many field personnel to sample simultaneously because discharges are dynamic, rapidly changing conditions. Surveys by boat also have the problem of achieving accurate position location and compensating for mixing effects of propeller screws. Thus, ground and boat survey techniques are usually costly.

In the above examples, simultaneously exposed conventional color film and color infrared film would be preferred. Since water is a very strong absorber of near infrared energy, the water tonal qualities in the near infrared band are surface reflectance only, whereas in the blue, green and red regions, the reflectance is both a result of surface suspended material and, depending upon water depth, bottom effects.

First of all, except for a few small water bodies that are cyan (greenish-blue) in color, the majority of the water bodies are black, indicating essentially no exposure on the film, and therefore, that the majority of the water bodies are unpolluted clear water. The cyan-colored water bodies indicate that a green color is present, probably chlorophyll. With a simultaneously exposed conventional color film of this area, the optical water quality could have been assessed quantitatively, and future photographic missions to monitor results of reclamation quantitatively compared to this data. For example, the optical properties of the water bodies could be used to reflect the reduction in turbidity created by run-off from regrading and revegetation efforts, as well as rate of organic or nutrient material build-up as a result of old revegetation efforts or crop fertilization efforts.

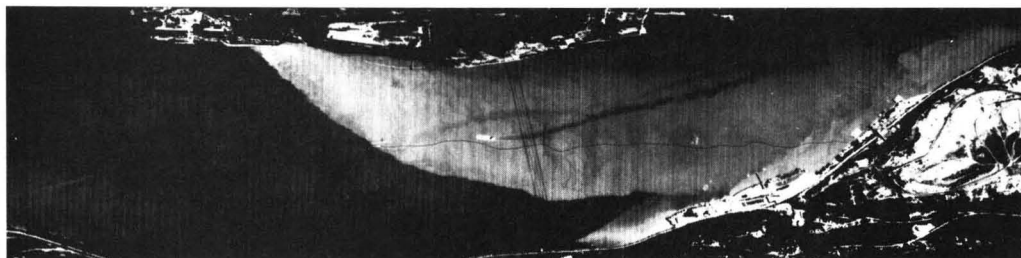
The real value of this unique near infrared film type relates to stress on vegetation. Because the landscape is predominantly covered with vegetation and the interpreter's eye is not optimized to differentiate shades of red, stress on vegetation is not easily detected on this film type by direct observation of subtle changes in red images. When vegetation is highly stressed, its image on this film type will shift to green for reasons discussed earlier.

Color infrared film with its near IR sensitivity adds signifi-

FIGURE 4.

Thermal discharges

The white area indicates hot water discharges, the dark gray area cold



cantly to the capability of remote sensing to solve vegetation stress and typing problems over large areas. When properly exposed, the near IR information can be used with advanced technology, both in air and water quality analyses from space satellites. Because of the very large area coverage, atmospheric attenuations are not constant over the picture format as they are from lower altitude aerial photographs with less coverage. At satellite altitudes, the exposing energy from water bodies in the near infrared band is primarily all atmospheric noise since water is such a strong absorber in this band.

An illustration of a typical thermal infrared (8–14 μ) image of a power plant discharge is shown in Figure 4. Very little information is extractable from this picture by subjective judgment alone. It can be said that there are hot water discharges from two sources, one on either side of the river, which do merge on one bank. Since the geometry is not spatially correct, it is not possible to readily compare the areas of the discharges and only relative judgments of the hottest (white) to the coldest (dark gray) water surface locations can be made. The upwelling cold water of an old boat wake, and the darker gray wake behind the boat imaged are apparent and illustrate how thermal surveys from boats must be made very carefully to avoid measurements being taken in such artifact areas.

However, a thermal photograph can be corrected for geometry, calibrated, and compiled into a useful isothermal map display.

Directly recorded photographic information has been, and most likely will continue to be, the most effective recording media for remote sensing because it is image shape, pattern and contrast that contains the information sought about the objects being sensed. Tape recording of attenuated object energy will continue to be processed to form the visual display that activates man's subjective interpretation process.

Advanced interpretation technology

The most well-publicized advancement in remote sensing of the past decade has been the development of remote sensing from space. However, in November 1974 a significant advancement in the interpretation of remote sensing data was made by researchers. The advancement is a patented technique for *photometric* calibration of remote sensor imagery. The technique allows the interpreter to derive an accurate measurement of all the additive and attenuating energy effects of the numerous variables inherent in a remote sensing system and thus obtain an accurate, quantitative measurement of the true reflected or emitted energy properties of the ground objects that are being imaged.

Experimental hardware was developed in 1973 and a facility for environmental application of this technology completed in January of this year. A photograph of the facility is shown in Figure 5; the facility is located at Calspan Corp. in Buffalo, New York, where the technology was developed. The facility

FIGURE 5.

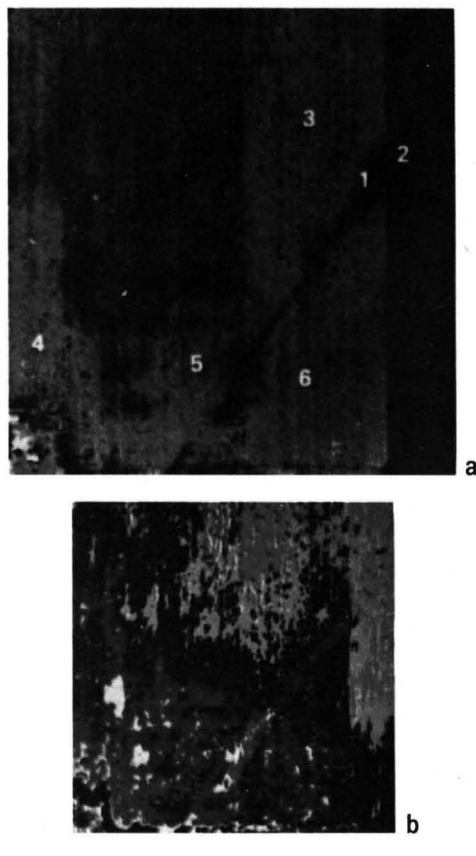
Calspan's photometric interpretation facility



FIGURE 6.

Stressed vegetation

A progressive shift of the near infrared to red energy ratio indicates the degree of disease

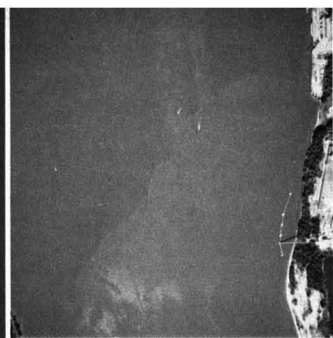
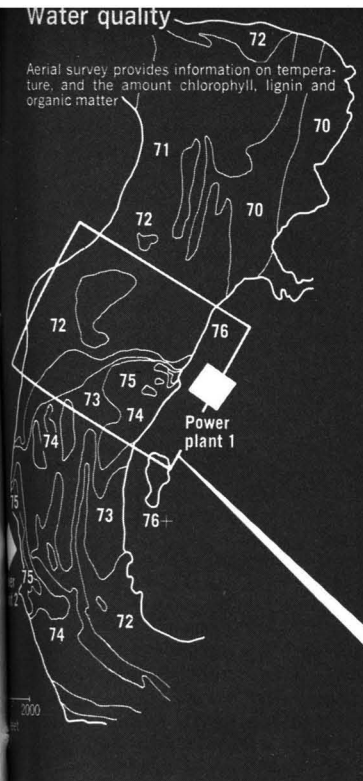


has been used successfully to produce $\pm 1^\circ\text{F}$ calibrated thermal discharge maps; water quality maps consisting of chlorophyll, gelbstoffe (organic material) and turbidity concentrations and distributions; maps of runway and highway pavement deterioration, including spalling and cracking; and is presently being used to establish criteria for a quantitative measure of forest defoliation related to insect infestation.

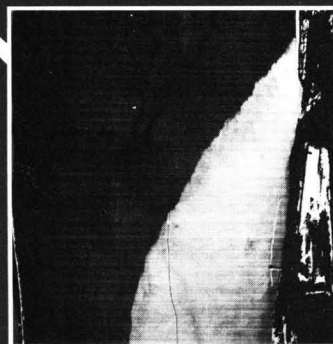
Figure 6 shows very early stages of a disease in a sugar beet field. The color-encoded stress display was generated by special processing of two of the three emulsion layers of the conventional color infrared film shown in the illustration. In Figure 6a, the photo-interpreter can readily discriminate between apparently unstressed sugar beets (light purple) and beets stressed by moisture (black areas). (Ektachrome infrared photograph—original scale 1/7000.) In Figure 6b, when a stress factor is present in a crop, energy absorption by the stressed plants decreases, causing a change in the near infrared to red exposure information. This information is encoded sequentially from essentially no stress to severe stress by the colors yellow, blue, green, red, pink, and violet. Note the striking change in stress between the sugar beets (red, pink) and the potatoes (yellow, blue). (Color encoded display of exposure information in Figure 6a.) The processing technique used has a patent pending and is accomplished by the equipment shown in Figure 5. It is expected that crop disease will be detectable by this technology long before it can be observed on the ground or by inspection of color IR film.

Water quality

Aerial survey provides information on temperature, and the amount chlorophyll, lignin and organic matter



Classic color aerial photography



Thermal scanner imagery (N.Y. State Atomic & Space Development Authority)

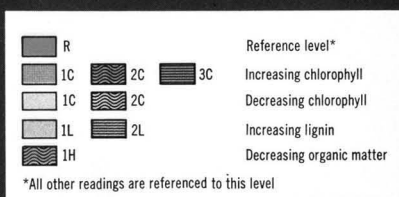
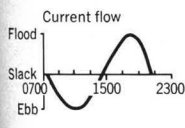
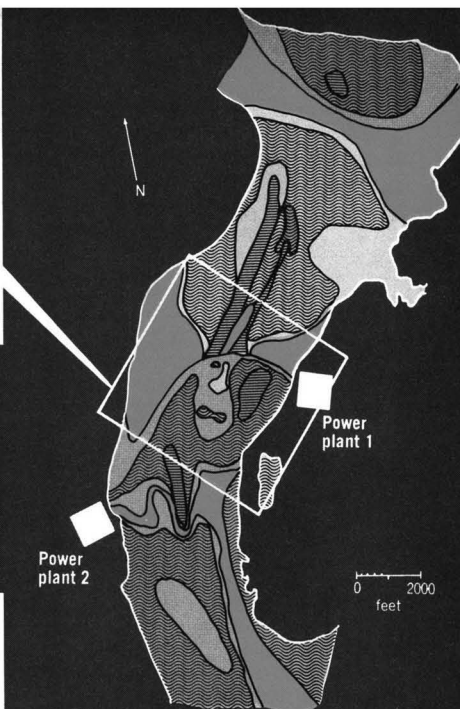


Figure 7 illustrates the types of water quality map products that are now possible by utilizing this new technology, and conventional aerial cameras and scanners together. Absolute concentrations of chlorophyll, gray matter and organic matter could have been shown on the one map by collecting a limited number of water samples that would be analyzed in the laboratory later.

On the thermal map, extensive boat surveys for calibrating the absolute water surface temperature are no longer necessary, as discussed previously.

Classic interpreters must be retrained in photometric interpretation technology, and digital data analysis. Classic environmental engineers must be trained to recognize and classify environmental stress problems in terms of effects on the photometric properties of water, vegetation, soil, pavements, and other terrains. The College of Environmental Science and Forestry, Syracuse, N.Y., has recently established photometric interpretation as part of its remote sensing curriculum.

In the future, the interpreter will first extract as much of the information as possible directly by observation and subjective judgment. Next, he will use photographic output to obtain a photometric calibration of the atmospheric and system energy attenuation effects and measure the reflectance. Finally, he will complete his analysis by measurement and manipulation of specific reflectances and, thus, acquire the accurate quantitative information he needs to generate meaningful and useful maps of environmental properties.

Additional reading

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K. R. Piech and J. E. Walker. Aerial Color Analysis of Water Quality. Journal of the Surveying and Mapping Division, ASCE. November 1971.

K. R. Piech and J. R. Schott. Atmospheric Corrections for Satellite Water Quality Studies. Society of Photo-Optical Instrumentation Engineers. Vol. 51 (1975).

K. R. Piech and J. R. Schott. Final Report NASA SKYLAB Project. Calspan Corporation (in progress).

John E. Walker is section head, Remote Sensing, Environmental Systems Department of Calspan Corp.



Douglas B. Dahm is department head, Environmental Systems Department of Calspan Corp.



Coordinated by LRE

Monitoring the environment

Conrad F. Heins
F. Douglas Johnson

University of Denver Research Institute
Denver, Colorado 80210

Edward C. Mangold

EPA
Denver, Colorado 80225

Georgia recently prepared a map which, for the first time, located all of that state's more than 35,000 lakes, reservoirs, ponds, and lagoons larger than five acres. One man constructed the map in less than a week using imagery obtained from the earth resources satellite, LANDSAT (formerly called ERTS). It was estimated that comparable work on the ground would have cost well over \$1 million and would have taken several years to complete. This example depicts one important trend in environmental measurement—the use of satellite remote sensing. It also suggests the amount of activity in the area.

At all levels of government there is an unprecedented demand for comprehensive, accurate, and timely information on the environment. As a result, new and greatly improved ways of obtaining environmental data are being developed to meet the demand. This article examines four developments that are transforming the entire field of environmental measurement:

- spectroscopy
- satellite transmission of environmental data
- remote sensing
- computerized data processing.

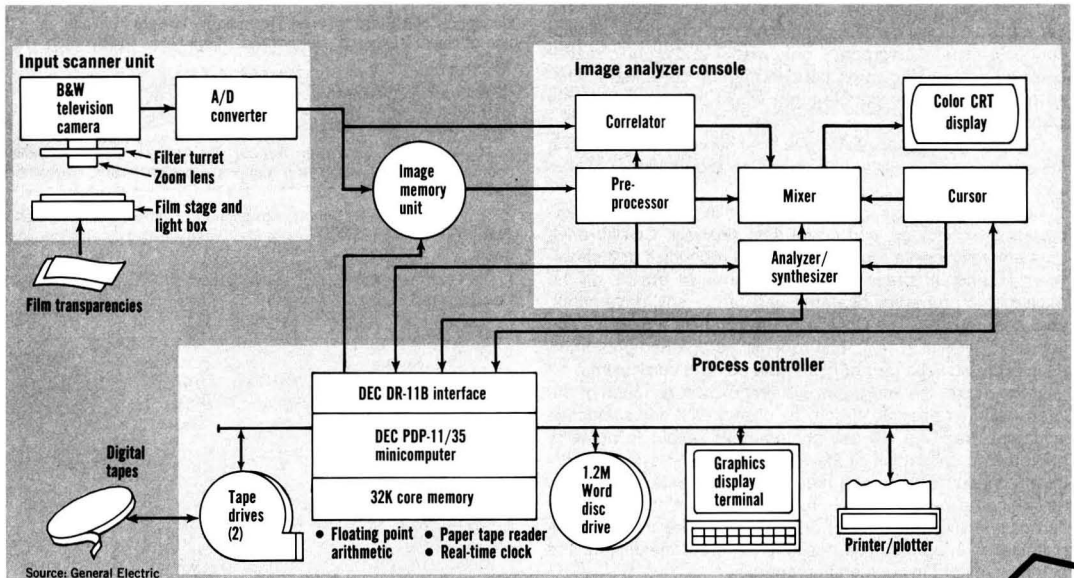
A few examples for each development have been chosen.

Reasons for change

A complex mixture of legislative, technological, and resources management factors are responsible for the trends we are observing. Legislation has generated a need for environmental data on a vastly greater scale than has hitherto been required. A brief review of this legislation reveals the extent to which environmental quality has become a key governmental concern, and that the need for environmental information is increasing rapidly for government regulators as well as industry.

The Water Quality Control Act of 1965 provided for water quality standards to be enforced by the federal and state governments. The Water Pollution Control Act Amendments of 1972, which focused on effluent limitations, set two broad national goals: to achieve by July 1, 1983, a level of water quality that protects fish, shellfish, wildlife, and recreation; and to eliminate the discharge of all pollutants into navigable waters by 1985.

Far-reaching legislation has also been enacted to deal with air pollution. The Motor Vehicle Control Act of 1965 established the authority to set emission standards for automobiles. The Clean Air Act of 1970 required uniform national air qual-





Thematic map of Philadelphia

Multispectral image data flow

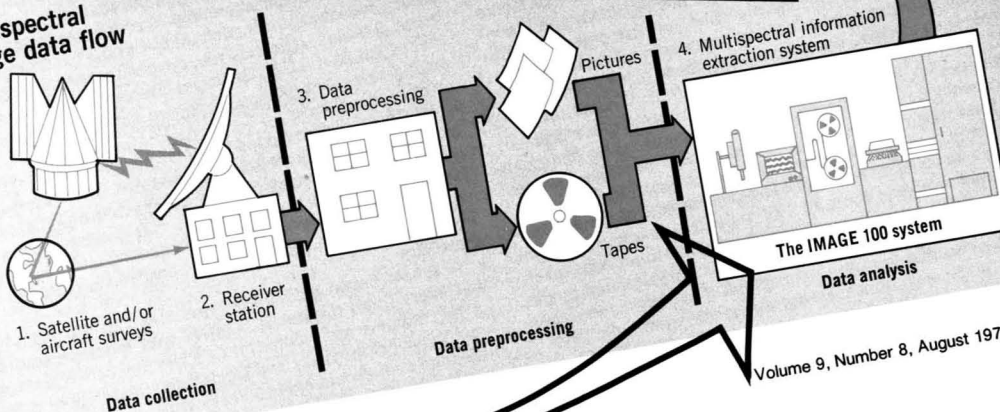
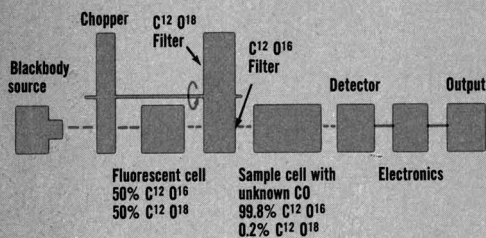


FIGURE 1

Dual isotope fluorescence carbon monoxide monitor



ty standards of two types—primary standards, which define the level of air quality necessary to preserve human health, and secondary standards, which are designed to promote the public welfare and prevent damage to animals, plant life, and property.

State and local governments have passed environmental legislation that in some cases is even more stringent than federal requirements. The California vehicle emission regulations are tighter than those for the rest of the nation. Delaware vetoed the construction of a supertanker port facility in the Delaware Bay partly on the basis of its strict water pollution control requirements.

The demand created by these laws simply could not be met by then existing instrumentation. Legally mandated environmental quality had clearly outrun the available technology. The gap was especially noticeable in measurement, the crucial parameter for legally enforced pollution standards. New techniques, instruments and apparatus were required.

Spectroscopic instruments

The Clean Air Act of 1970 generated a demand for rapid, sensitive and reliable measurements of atmospheric pollutants that provided much of the impetus for a major shift in measuring techniques. Wet chemical procedures were replaced by advanced spectroscopic methods. Spectroscopy measures pollutant concentrations by analyzing the effects of pollutant molecules on electromagnetic radiation—ultraviolet, visible, infrared and microwave. Although its potential has been recognized since the 1940's, only within the last decade have new spectroscopic techniques and advanced optical components been developed to make spectroscopy suitable for use in routine monitoring.

A key problem with spectroscopy has been one of specificity. The spectral fingerprint of a molecule consists of an array of emission or absorption lines. When two or more different kinds of molecules are present, lines can overlap and give spurious readings. This problem is particularly acute when the molecules of interest are present in very low concentrations, as is typically the case with air pollutants. The development of several new spectroscopic instruments illustrate the response to air monitoring needs.

The Akron Scientific Laboratories (now Andros, Inc.) of Berkeley, Calif., provided an ingenious solution to the problem of specificity in its development of a highly sensitive (0.1 ppm) carbon monoxide monitor for Skylab. The instrument utilizes the principle of dual isotope fluorescence (see Figure 1).

Gas samples do not have to be conditioned for the dual isotope unit because the effect of water vapor and other contaminants is eliminated by using one isotope to produce a reference beam. Similarly, performance is not degraded by dirt or condensation from the atmospheric sample—as much as 50% reduction in transmissivity can be tolerated.

In 1972, a commercial version of the Skylab monitor was

developed. A built-in zero point calibrator was added, slight design changes were made to meet EPA specifications, and the unit was marketed. In 1973, Andros sold this product line to Beckman Instruments, Inc. Beckman is selling the units as they were designed at Andros for approximately \$6,800, and is concurrently developing product design improvements.

More than 30 of the instruments have been sold to government agencies and industrial firms. The California Air Resources Board and the EPA are using the units for ambient, airborne, and automotive emissions air monitoring. For example, the EPA used the instrument on a helicopter to measure the CO profile in the Los Angeles basin: no other existing CO analyzer could have been used in this fashion.

A spectrophotometer that measures the concentration of atmospheric pollutants in vehicle exhausts was developed by Chrysler Corp. with technological expertise the company gained in designing the Hazardous Gas Detection System for the Saturn-1B stage at the Marshall Space Flight Center's Saturn Systems Development Breadboard Facility, a facility the Chrysler Huntsville Division installed and has operated since 1961. The dispersive infrared vehicle exhaust analyzer is being used by both the EPA and the State of California for vehicle emission analysis. The major advantage of this unit is that it simultaneously measures the concentrations of CO, CO₂, and hydrocarbons in a single sample.

By 1973 Chrysler had sold about 70 of these units at prices ranging from \$15,000 to \$50,000 depending on what specific instrumentation and automation components were used. The company's automobile division and General Motors, for example, are using these analyzers to test new car emissions both in their research laboratories and after production. The spectrophotometer has also been incorporated by Chrysler in a computer automated testing system for automotive emissions.

Satellite transmission

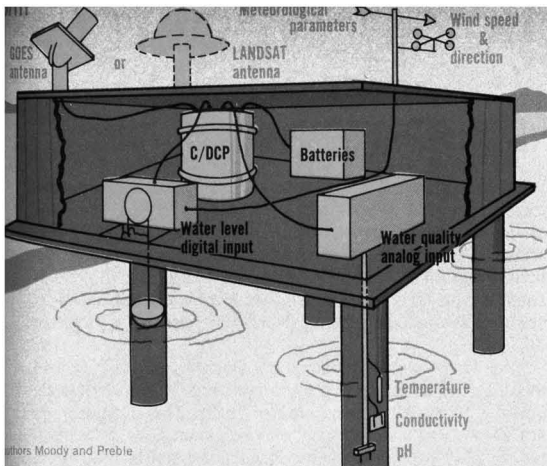
A second trend is the use of satellites to relay environmental data obtained from remotely located, automated data collection systems. Automated data collection platforms are not new. The U.S. Geological Survey uses thousands of them to monitor lake and river levels for the National Weather Service's river stage forecasts and other hydrologic applications. What is new is the use of satellites as active relay stations to permit critical information to be obtained reliably and relatively inexpensively on a near real-time basis.

The first broad scale testing of the feasibility of the satellite approach was undertaken as part of the LANDSAT program. It has proved so successful, that, with the launchings of additional satellites, agencies responsible for resources management such as the U.S. Geological Survey and the Army Corps of Engineers are gearing up to use satellite transmission on an operational basis.

NASA's Goddard Space Flight Center, the part of the agency with overall responsibility for the LANDSAT mission, funded the General Electric Co. to design and build about 220 Data Collection Platforms (DCP's) that collect and transmit data in digital form from sensors measuring up to eight different parameters. Table 1 lists the applications made by various users.

A simple timing mechanism was built into the system so that every three minutes a burst of data is transmitted. Receiving stations are located at Goddard Space Flight Center near Washington, D.C., and Goldstone, Calif. Figure 2 illustrates the overall data collection system.

In some cases the system is being used on an operational



basis. Canada's Department of the Environment, for example, is using DCP's to obtain data on water level and ice break-up from remote regions of the country. The U.S. Geological Survey in Miami, Florida, responsible for managing the highly complex water system of south Florida, has found satellite transmission to be the most practical way to obtain hydrologic data on a near real-time basis during the critical period when a storm is moving into the area, and direct ratio transmission is poor and unreliable.

A second generation of the data collection platforms is being developed to take advantage of the transmission capabilities of the Geostationary Operational Environmental Satellites (GOES), launched for the National Oceanic and Atmospheric Administration (NOAA). Unlike LANDSAT, which is primarily an experimental satellite, the NOAA satellites are part of an operational program to obtain hydrological meteorological, and oceanographic data. Two satellites are already in orbit, one over the Atlantic at about 45° W longitude and the other over the Pacific at about 120° W longitude. A total of five planned satellites will provide overlapping coverage of all but the most extreme polar regions of the globe. The data transmitting capabilities of GOES will also be available to other agencies through a memorandum of agreement with NOAA's National Environmental Satellite Service.

A number of companies are now making collection systems that utilize the GOES satellite. The Magnavox Corp. in Fort Wayne, Ind., is fabricating GOES Compatible Systems for the National Weather Service. Dorsett Electronics, in Tulsa, Okla., was recently awarded a contract by the U.S. Geological Survey to build 150 platforms that will be able to utilize either LANDSAT or GOES. Ball Brothers Aerospace in Boulder, Colo., also manufactures LANDSAT/GOES compatible systems. Now that the Department of Commerce has made the commitment to provide an operational as opposed to an experimental satellite system, other agencies and user groups are making the change over to this new technology for their own operational programs.

Table 1. Experimental applications for LANDSAT data collection platforms

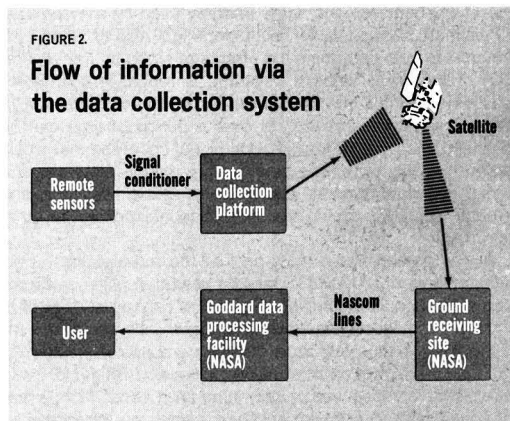
Applications	No. of users	No. of platforms assigned
Hydrology	20	75
Volcanology	2	33
Water quality	4	26
Meteorology	5	10
Oceanography	3	9
Forestry	1	3
Agriculture	1	3
Arctic environments	1	2

Remote sensing

The use of remote sensing techniques to measure pollutants and monitor environmental quality, while still in its infancy, offers great promise. The problems inherent in remote sensing as a way of obtaining quantitative information are formidable. Much progress has been made, however, in the development and practical utilization of both ground-based and aircraft- or satellite-based instruments.

Correlation spectrometry. The use of passive measuring spectrometers for qualitative measurements of gas pollution concentrations is developing on several fronts. Barringer Research, Ltd. in Ontario, markets a correlation spectrometer that uses sunlight scattered from molecules in the atmosphere to measure concentrations of SO₂, NO₂, or CO. A key feature of the selective, highly sensitive instrument is a mask containing slits corresponding to the absorption lines of the gas to be measured.

The gas concentrations in an individual smokestack plume can be determined from a distance of hundreds of yards with the correlation spectrometer. The quality of gas above a given ground point can be monitored from a moving automo-



bile by positioning the instrument to look vertically upward. The total vertical concentration of an entire metropolitan area can be estimated by driving for a few hours on the city's freeways. These vertical concentrations can then be compared to the predictions by mathematical atmospheric diffusion models for the area.

By late 1973 Barringer had sold 38 correlation spectrometers at prices between \$23,000 and \$24,000 each. Pollution control agencies in the U.S., Canada, Australia, Japan, the Netherlands, France, and Spain are using the instrument to develop pollution control strategies for major metropolitan areas.

Infrared sensors. The use of the thermal infrared emission of stack gases against a cold sky background has been made by both spectrometers and interferometers. To achieve high-spectral resolution and simplify the data reduction, a gas filter correlation spectrometer was developed by Science Applications, Inc., in La Jolla, Calif. In addition to providing high-spectral resolution for greater discrimination against interfering gas species, this design approach allows for a lightweight, portable instrument that can be easily operated as a field monitoring device by a technician.

LIDAR systems. To achieve greater accuracy and over-

come the limitations of using natural light sources, active sensors that use powerful lasers to excite and illuminate the target have been developed. The most direct use of these LIDAR (light detection and ranging) systems is to measure opacity of smoke plumes emitted from smokestacks. Smoke plume opacity is an important legally enforceable parameter that can be measured more accurately by a LIDAR than by a human observer who is subject to uncertainties because of lighting conditions.

By an analysis of the Doppler shift of the light as it scatters off the smoke particles, the velocity of gases coming from the stack can be measured to determine the total quantity of gas emitted.

LIDAR instruments in aircraft can monitor the total gas burden between the aircraft altitude and the ground for an entire metropolitan area. Such measurements are presently being made for the St. Louis Regional Air Pollution Study.

LANDSAT-1, launched by NASA less than three years ago, has demonstrated the enormous potential for using satellite-based sensors to monitor the environment. Satellite imagery is unique in a number of ways. For one, it is synoptic; one LANDSAT picture covers more than 10,000 mi². A vast amount of simultaneous data can be collected to study a variety of phenomena. The same imagery used by a hydrologist to estimate snowpack, for example, might also be used by a botanist to help determine the effects of smog on the vegetation of the area. Satellite coverage is repetitive; LANDSAT passes over the same spot at the same time of day every 18 days. Thus, comparative data over a period of time can be obtained. Finally, satellites provide global coverage that would be prohibitively expensive by any other means. However, the broad overview requires a sacrifice in spatial resolution and greater sophistication in the extraction of specific information.

It was demonstrated early-on that the multispectral scanning imagery of LANDSAT could be used to monitor phenomena such as ocean dumping. Figure 3 is an August 16, 1972, LANDSAT image of the New York Bight, a corner of the Atlantic used extensively as a dumping ground for wastes for the New York metropolitan region. Over 10,000 yd³ of sewage sludge are disposed of daily in an area about 12 mi south of Long Island. In addition, acid-iron wastes are dispersed by barge over a hairpin-shaped course in the same region.

The photograph clearly shows the acid wastes and somewhat more dimly the sewage sludge. Scientists at the Environmental Research Institute of Michigan analyzed the imagery to extract considerably more information, such as the water mass boundaries and even the relative depth of the sewage sludge. The broad-scale data from satellites can be integrated with information from laboratory analyses to improve environmental monitoring significantly.

Computerized data processing

A much greater potential for satellite sensing is beginning to be realized with the development of specialized computer programs for data interpretation. The use of computers will become increasingly important in the next few years as more agencies begin to use vast quantities of satellite data on a routine basis, and as orbiting sensors become more sophisticated. Already the accomplishments have been noteworthy.

The Johnson Space Center developed a program that identifies bodies of water 10 acres or larger by using LANDSAT data in the form of digital imagery (computer compatible tapes) and photographic images. The program prints out the information as variable scale overlays for use with conven-

tional topographical maps. It was used by four regional districts of the U.S. Army Corps of Engineers to verify their recently completed inventories of dams over 6 ft in height. These inventories were required by Congress under the National Program of Inspection of Dams (PL 92-367). The use of satellite data for this application was highly cost-effective, in some cases reducing the cost of verification by a factor of 10.

The Texas Water Development Board is planning to use the computer program to study and monitor playa lakes in six counties of the high plains area of Texas. The shallow lakes are left from rain storms and, although short-lived, they number in the tens of thousands. Repetitive satellite monitoring should permit the agency to determine the temporal and spatial distribution of lakes. The possibility exists for using them for irrigation or even for helping to replenish the underground Ogallala aquifer, the life blood of the region, which is being drawn off for irrigation faster than it is being recharged.

The Jet Propulsion Laboratory, working with EPA's National Environmental Research Center in Corvallis, Ore., has adapted software for lunar and planetary exploratory data analysis in order to characterize the water quality of inland lakes by using LANDSAT multispectral scanning data. The program provides a color printout of the lake in which each picture element (representing about one acre) is given a color ranking according to relative trophic status. LANDSAT classifications have correlated well with classifications based on lake samples obtained on or about the day of the LANDSAT overflight. The approach is particularly applicable to regions containing a great many lakes such as Florida, Minnesota, and Wisconsin. It promises to provide a rapid, inexpensive way for states under federal standards to obtain a broad scale classification of the trophic status of their lakes.

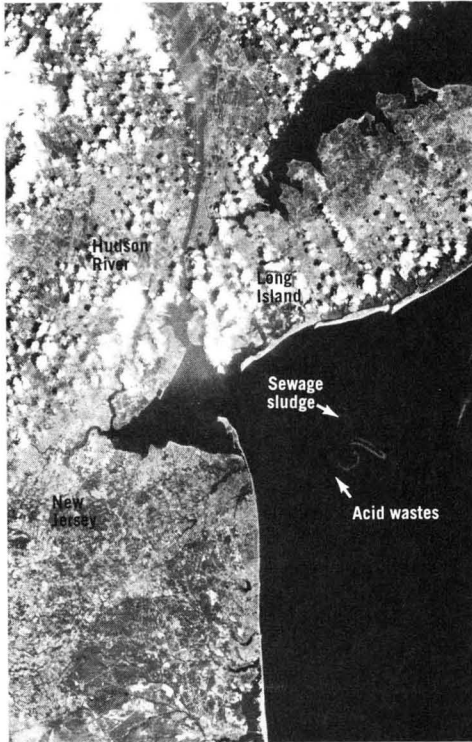
A computer program for land use classification was recently employed by EPA scientists to inventory the land usage status of strip coal mines in the Northern Great Plains. The acreages of mined area, spoils piles, regraded and revegetated land were determined by using LANDSAT digitized imagery data.

Because of the extensive computer operations required to process the vast amount of data being made available through satellite measurements (a single LANDSAT image, for example, contains 8 million picture elements), dedicated computer systems have been developed to use special purpose circuitry for extracting thematic information from multispectral scanning data. For example, General Electric, in Daytona Beach, Fla., developed its IMAGE 100 processor that accepts photographic and/or digital imagery data, and displays the output on a color video screen or records the information with a printer/plotter or color film recorder. Because it involves near real-time interaction with the user who can control or modify the analysis process using his own knowledge, the system has great flexibility and can quickly extract thematic information that matches the user's needs.

Half a dozen of the IMAGE 100 systems are in the field and others have been ordered. Customers include the Jet Propulsion Laboratory, the Johnson Space Center, the Canada Centre for Remote Sensing, and the Brazil Space Research Institute. At about \$450,000 installed, however, the units are not for everyone. General Electric also provides, at their facilities in Beltsville, Md., IMAGE 100 processing services for multispectral imagery to a growing number of customers. For example, a crop acreage inventory of 48 million acres in the San Joaquin Valley was conducted for a major agricultural firm. Using primarily LANDSAT imagery data, the General Electric scientists were able to achieve an average classifica-

FIGURE 3.

LANDSAT imagery of the New York Bight



Source: NASA

tion accuracy of about 97% and to demonstrate that crops could be inventoried at a cost of approximately a penny an acre.

The Aerospace Systems Division of the Bendix Corporation in Ann Arbor, Mich., is marketing the Multispectral Data Analysis System (M-DAS), also a user interactive system. It differs from IMAGE 100, however, in that it uses only digitized data for input. The system will handle up to 16 channels of multispectral data and, with Bendix's special purpose hardware, M-DAS can produce a series of colored thematic map overlays to be used with USGS topographical maps. Multicolored hard copy prints showing all colors of thematic interest can also be prepared.

Bendix's Earth Resources Applications Department has an active program to provide multispectral data analysis services on a contractual basis. The company's largest job to date involved using LANDSAT data to classify vegetation cover into 16 categories for a 120,000 mi² area of Alaska. The thematic maps, which were prepared in three months at a cost of \$25,000, were of sufficient detail to permit an Eskimo tribal corporation to select new lands most suitable for maintaining the tribal lifestyle of hunting and fishing. An aerial survey of the same region would have cost almost \$2 million and taken about 18 months.

The future

By the 1980's the present, limited operational use of satellite imagery will in all likelihood greatly expand. For example, this imagery may well be used on a regular basis in applications such as monitoring the sediment loadings and current patterns of lakes, estuaries, and oceans. Monitoring urban area development through the changes in spectral signatures caused by construction of new housing developments and in-

dustrial complexes will permit updating of urban area maps on a regular basis. This is not economically feasible at the present time, but should be especially useful in rapidly growing areas such as the western U.S. and Alaska where energy development is causing dramatic increases in the population.

Higher spatial resolution and additional spectral bands will increase the utility of multispectral scanner imagery from space. Beginning in 1980, the Earth Observation Satellite is expected to provide seven-band spectral coverage at 30 m resolution and four-band coverage of special targets at 10 m resolution. LANDSAT, by comparison, affords four-band spectral coverage at 80 m resolution.

Closer at hand is NASA's next research and development satellite, Nimbus G (Nimbus 7 once it is placed in orbit), scheduled for launch in the fall of 1978. The satellite has as a primary mission objective the detection, identification, mapping, and measurement of air and ocean pollution. These data will be used to establish baseline levels so that long-term trends can be determined and to provide information about location, movement, and disposition of pollutants.

In summary, the trends are toward real-time acquisition of environmental information from even the most remote parts of the globe. Using sophisticated measuring instruments, satellites and computerized data processing, we are moving into an era in which pollution and environmental quality are not treated simply as regional or even national problems, but are being understood and dealt with as global concerns.

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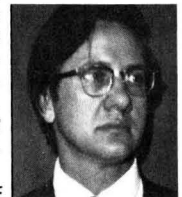
Conrad F. Heins is a research scientist with the Denver Research Institute, University of Denver. He taught courses in biochemistry and instrumental analysis at the university. For the past year and a half Dr. Heins' research interests have been in the area of technology transfer.



F. Douglas Johnson is a research technologist with the Industrial Economics Division of the Denver Research Institute. He is deputy manager of a major NASA-funded project to study the impact of aerospace technology by examining changes in industrial practice.



Edward C. Mangold is a physicist with the Environmental Protection Agency's National Enforcement Investigations Center in Denver, Colorado. He has held assignments in the design and development of instrumentation for aerospace and environmental applications. Dr. Mangold's recent work has involved environmental applications for multi-spectral scanning instruments.

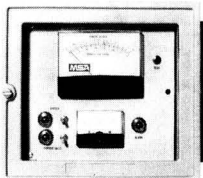


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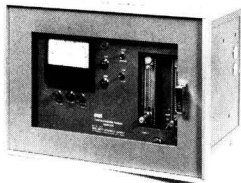
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Adsorption of Poliovirus onto Activated Carbon in Wastewater

Charles P. Gerba,* Mark D. Sobsey,¹ Craig Wallis, and Joseph L. Melnick

Department of Virology and Epidemiology, Baylor College of Medicine, Houston, Tex. 77025

■ The effect of pH and soluble organic matter on virus adsorption to activated carbon in treated sewage was determined. Poliovirus removal from wastewater effluent was greatly improved by lowering the pH to 3.5–4.5 or by reducing the amount of organics by lime coagulation. Batch studies indicated that virus adsorption to activated carbon in wastewater could be described by Freundlich isotherms. In column experiments virus removal was found to be dependent on column length as well as hydraulic loading. Virus and soluble organics adsorbed at low pH could become desorbed by a rise in pH.

The use of physicochemical and other advanced waste treatment methods will probably predominate in future years (1, 2). A group headed by Middlebrooks (cited in ref. 1) has recently reviewed the capabilities and costs of a number of advanced treatment processes and concluded that processes offering the most promise include activated carbon. In addition, several tertiary treatment plants are now in operation in the United States utilizing granular activated carbon to treat domestic wastes (3). Research has also been recently directed toward the development of powdered activated carbon for the treatment of wastewater (4). Activated carbon has been found capable of adsorbing a great variety of organic materials including viruses (2, 5).

Cookson has extensively studied the mechanism of bacteriophage T4 adsorption by activated carbon in buffered distilled water (5–8). He has postulated that the adsorption sites on the activated carbon are carboxyl or lactone groups, since adsorption can be completely blocked by esterifying these groups. He has also proposed that amino groups on the virus become associated with the negatively charged carboxyl groups on the carbon by electrostatic attraction. Adsorption was influenced by both pH and the ionic strength of the solution, with optimum adsorption at a pH of 7 and an ionic strength of 0.08.

Sproul et al. (9) have used bacteriophage T2 to evaluate virus removal by several different types of activated carbon in secondary effluent. Significant variation among individual activated carbons was found. They also demonstrated removal efficiencies of between 18 and 40% for poliovirus by sewage-fed columns of granular activated carbon operated on a continuous flow-through basis. Elution of the viruses was observed when the column runs were continued beyond the virus exhaustion point.

In comparative studies with synthetic river water and domestic sewage carried out by Watson and Drewry (10), bacteriophage f2 removals by columns of activated carbon were considerably less in those fed with wastewater. They concluded that competition for adsorption sites with the

virus by other organic matter was a major factor in the lower efficiency of activated carbon for virus removal from wastewater. These results were also confirmed by Cliver (11) using poliovirus.

This investigation was undertaken to gain additional information on virus removal from sewage effluents by activated carbon and methods by which this process could be optimized.

Materials and Methods

All virus assays were performed on BSC-1 cells which were passaged, grown, and maintained by previously described methods (12). Virus was propagated in baboon kidney cells. Kidneys obtained from immature baboons were trypsinized and grown as described (12).

A plaque-purified line of type 1 poliovirus (strain LSc) was used. Stock virus was grown in baboon kidney cells, concentrated tenfold, and partially purified by membrane chromatography (13), and stored at -70°C . Virus samples were diluted in tris(hydroxymethyl)aminomethane-buffered saline containing 2% fetal calf serum, penicillin (100 U/ml) and streptomycin (100 $\mu\text{g}/\text{ml}$). Before assay, all samples were frozen at -30°C overnight to reduce the problem of bacterial contamination in cell cultures. Virus assays were performed by the plaque-forming unit (PFU) method as used in this laboratory (14).

Chlorinated secondary effluent from a local trickling filter plant servicing a residential area of Houston, Tex., was used in this study. Samples brought to the laboratory were immediately dechlorinated by addition of sodium thiosulfate and either filtered through a series of honeycomb textile filters (Commercial Filters Division, Carborundum Co., Lebanon, Ind.) (15) with a smallest nominal porosity of 1 μ , or clarified by lime coagulation. Clarification by lime was achieved by adding calcium hydroxide until a pH of 11.5 was reached. The sewage was then mixed on a mechanical stirrer for 20 min, allowed to settle for 20 min, and the supernatant fluid was collected by decanting.

The pH of lime-treated sewage was adjusted to low pH by the addition of 1N HCl. In batch studies, sewage was buffered in some experiments by addition of either sodium acetate or glycine using concentrations of 0.05M, and pH adjustments were made by the addition of 1N HCl or 1N NaOH, before addition of the virus.

The relative removal of soluble organic matter was determined by measuring ultraviolet (uv) absorbance at 254 nm. The correlation between total organic carbon (TOC) and uv absorbance in sewage (16) and the usefulness of uv absorbance as an indicator of activated carbon performance has been previously demonstrated (17).

The activated carbon used in this study was Pittsburgh type OL (Pittsburgh Activated Carbon Division, Calgon Corp.). This granular charcoal is made from bituminous coal with a large portion of the total surface area in pores 2–50 nm in diameter. In column studies, 20 \times 50 mesh was used, while in batch studies the granular charcoal was pul-

¹ Present address; Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina, Chapel Hill, N.C. 27514.

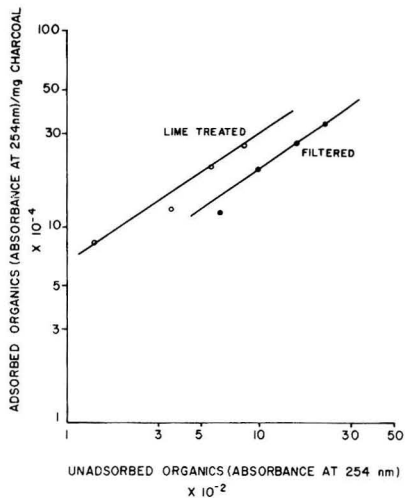


Figure 1. Freundlich isotherm plots of soluble organic carbon adsorption in wastewater effluent to activated carbon. Contact time was 90 min, the charcoal concentrations ranged from 20 to 2000 mg/l, and initial virus concentration was 6.5×10^7 PFU/l.

verized until it passed through a 325-mesh sieve.

In batch studies, virus and powdered activated carbon were placed in 500-ml amounts of wastewater and continuously mixed at room temperature (about 25°C) on a six-place mechanical paddle stirrer. After a 5-min rapid mix to wet the charcoal, the suspensions were stirred at slow speed for about 3 hr. Control wastewater samples containing virus, but without charcoal, were also studied. Charcoal was removed from suspension by passage of samples through Whatman #40 filter paper.

Virus removal from wastewater was also studied in a continuous flow system using packed columns of granular activated carbon. Columns of clear acrylic plastic with an inside diameter of 1 1/8 in. and lengths of either 18 or 36 in. were packed with the activated carbon. Wire screens at either end of the columns prevented discharge of the charcoal from the columns during operation. The columns were fitted with quick-disconnect fittings so that several columns could be placed in series if desired. Wastewater was passed through the columns at constant flow rates with the aid of a peristaltic pump. Columns were usually operated in an upflow mode, although results on virus removal did not differ when they were operated in a downflow mode.

Results

Virus Adsorption in Sewage Effluent. Adsorption studies of virus and soluble organic carbon were carried out in batch systems using both filtered and lime-treated sewage effluent (adjusted to pH 7.5). Tests were first carried out using variable charcoal concentrations and constant virus concentration. Adsorption of both soluble organic matter (Figure 1) and virus (Figure 2) conformed to a Freundlich isotherm. The Freundlich isotherm, an empirical relationship developed for adsorption phenomena, is expressed as

$$y/m = Kc^n \quad (1)$$

or

$$\log y/m = \log K + n \log c \quad (2)$$

in which y = amount of virus adsorbed at equilibrium, m = weight of charcoal, c = amount of virus remaining in solu-

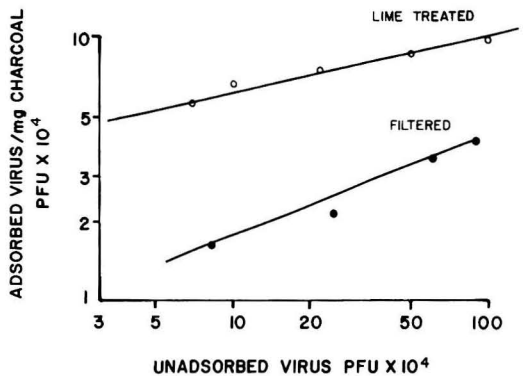


Figure 2. Freundlich isotherm plots of virus adsorption in wastewater effluent to activated carbon. Charcoal concentrations ranged from 100 to 1500 mg/l; initial virus concentration was 4.0×10^7 PFU/l.

tion at equilibrium, and n and K are experimental constants. In a plot of Equation 2, n and K are the slope and y -intercept, respectively. Since a log-log plot of y/m vs. c gave a straight line, these data conform to the Freundlich equation (Figures 1 and 2). It should be noted that at a given equilibrium virus concentration, c , the amount of virus adsorbed per unit weight of charcoal was always greater in lime-treated sewage than in filtered sewage. Experiments were also performed in which virus concentration was varied but charcoal concentration was held constant. These results could also be plotted as Freundlich isotherms (Figure 3).

The slopes and y -intercepts of linear Freundlich plots for virus adsorption varied with different batches of sewage effluent. In addition, when virus adsorption was determined periodically over several months using constant concentrations of activated carbon and virus, the extent of virus adsorption was highly variable (Table I). The amount of virus adsorbed did not appear to be related to nominal pH variations (pH 7.9–8.3), and it could not be predicted from the concentration of soluble organics as determined by uv absorbance measurements.

Effect of Concentration of Organics on Virus Adsorption. To determine if virus adsorption to charcoal was precluded by competition with wastewater organics, vari-

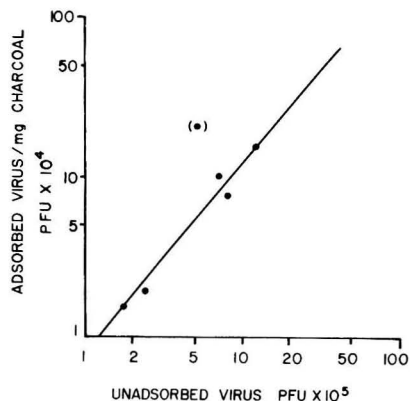


Figure 3. Freundlich isotherm plot of virus adsorption in lime-treated wastewater effluent to activated carbon. Initial virus concentrations ranged from 8.5×10^6 to 8.5×10^7 PFU/l; charcoal concentration was constant at 400 mg/l.

Table I. Summary of Poliovirus and Soluble Organic Matter Adsorption to Activated Carbon from Secondary Effluent^a

Expt. no.	No. of viruses adsorbed, PFU × 10 ⁶	Virus adsorbed, %	Initial absorbance of sewage at 254 nm	Organics removed, %	Wastewater pH ^b
1	1.6	24	0.267	62	8.3
2	0.73	11	0.229	42	8.1
3	<0.05	<1	0.234	77	8.2
4	4.6	70	0.392	33	7.9
5	<0.05	<1	0.254	63	8.0
6	1.1	16	0.475	72	8.1

^a All values represent adsorption to 200 mg of powdered charcoal in 500-ml volumes, initial virus concentration in each experiment averaged 6.5×10^6 PFU/500 ml. ^b Measured after the 3-hr contact period.

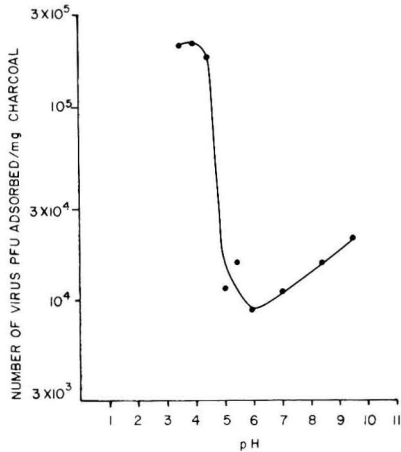


Figure 4. Effect of pH on virus adsorption to activated carbon in filtered sewage effluent. Results represent the average of two experiments with sewage effluent collected on different days. The initial virus concentration averaged 1.1×10^7 PFU/l. and the charcoal concentration was 400 mg/l.

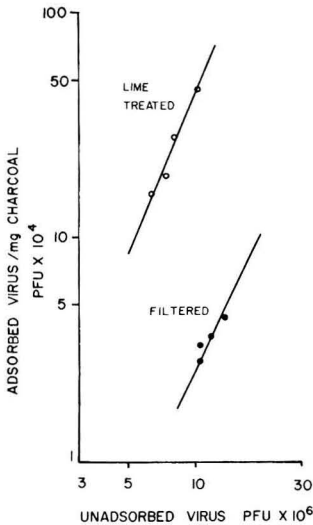


Figure 5. Freundlich isotherm plots of virus adsorption in wastewater effluent to activated carbon at pH 3.5. Charcoal concentrations ranged from 50 to 300 mg/l. and initial virus concentration was 6.4×10^7 PFU/l.

Table II. Effect of Soluble Organics Concentration on Virus Adsorption to Activated Carbon^a

Dilution of sewage effluent in tapwater	Virus adsorbed, PFU × 10 ⁵	Virus adsorbed, %	Soluble organics removed, %
Undiluted	7.3	22	58
1:2	19	57	56
1:4	24	75	50
1:10	30	92	50

^a Each solution initially contained 3.25×10^6 PFU of poliovirus/500 ml, and all samples were at pH 8.

ous dilutions of wastewater were prepared by addition of dechlorinated Houston tapwater to the filtered sewage effluent. Virus adsorption was then assessed using constant concentrations of virus and activated carbon in a batch system (Table II).

As the concentration of sewage organics was reduced by dilution, the extent of virus adsorption to charcoal increased proportionally, while the percentage of sewage organics removed remained essentially unchanged. These results indicate that soluble organics were indeed competing with virus for adsorption sites on the carbon and that a certain fraction of the organics present in the wastewater was not adsorbed to the activated carbon.

Effect of pH on Virus Adsorption. It has been shown in this laboratory that in solutions containing organic compounds, enteric viruses adsorb to cellulose ester and glass fiber filters and other adsorbent surfaces more efficiently at lower pH than at neutral levels (13, 15). This was attributed to the fact that under acidic conditions, interfering compounds had less avidity than virus for adsorbent surface sites. To determine if virus adsorption to activated carbon in wastewater was likewise enhanced, virus removal was studied at different concentrations of hydrogen ions in batch systems (Figure 4). Virus adsorption increased substantially at a pH of 4.5 or lower in filtered sewage effluent. The average amount of virus adsorbed was found to be almost 25 times greater at wastewater pH values of 3.5 to 4.5 than at the pH normally encountered in secondary effluent. Even in wastewater samples in which virus adsorption to activated carbon at a concentration of 400 mg/l. was negligible at unadjusted pH (about 8), the degree of virus adsorption at pH 3.5 was always 90% or more.

Batch tests were also carried out in both filtered and lime-treated sewage at pH 3.5 with variable charcoal concentration and constant virus concentration. The results are plotted as Freundlich isotherms in Figure 5. Although the slopes of both isotherms are similar, the isotherm for lime-treated sewage lies well above that for filtered sewage, indicating a greater efficiency of virus adsorption for the former. Virus adsorption at pH 3.5 was always found to be much more extensive than at pH 8 when using otherwise identical sewage effluent. Organic carbon removals from filtered sewage appeared to remain unchanged at pH 3.5 as compared to pH 8 as measured by uv absorbance.

Column Studies. Virus removal from wastewater effluent was also studied in a continuous flow-through system using packed columns of granular activated carbon. The effect of hydraulic loading as well as column length was studied using filtered sewage effluent without pH adjustment, and the results are summarized in Table III. Maximum adsorption occurred early in the run, with removals often exceeding 90% during the first hour. Hydraulic loading was found to influence virus removals with average virus removals of 50% at 1 gpm/ft² and 26% at 2 gpm/

Table III. Summarized Results of Column Experiments for Poliovirus Removal from Filtered Sewage Effluent^a

Test no.	Original absorbance of wastewater at 254 nm	Column length, in.	Hydraulic loading, gpm/ft ²	Bed volumes passed through columns at virus capacity	Overall % of virus removed from influent ^b	Total virus removed ^b PFU × 10 ⁶	Total virus adsorbed per gram of charcoal, PFU × 10 ⁴	Av. % reduction in absorbance at 254 nm
1	0.342	18	1	85	50	168	153	58
2	0.342	18	1	95	49	155	140	56
3	0.486	18	2	110	26	80	69	85
4	0.486	18	2	110	28	69	60	82
5	0.337	18	2	120	20	20	17	55
6	—	18	2	56	30	17	15	—
7	0.361	56	2	180	24	223	72	63

^a Initial influent virus concentration averaged 8.8×10^3 PFU/ml. ^b Based upon number of bed volumes when column capacity for virus adsorption was reached.

Table IV. Summarized Results of Column Experiment for Poliovirus Adsorption at pH 3.5^a

pH of influent	pH of effluent	Hydraulic loading, gpm/ft ²	Bed volumes passed through column at virus capacity	Overall % of virus removed from influent ^b	Total virus removed, ^c PFU × 10 ⁷	Total virus removed per gram of charcoal, PFU × 10 ⁵
3.5–4.0	8.4–9.1	2	>120	59	6.0	5.3
8.3–8.5	8.5–9.1	2	56	16	1.7	1.5

^a Initial influent virus concentration was 9.3×10^6 PFU/ml. Each column was 18 in. in length and was packed with 113 grams of granular carbon. The columns were operated in an upflow mode at the hydraulic loading indicated above. ^b Based upon processing of 120 bed volumes. ^c Based upon processing of 120 and 56 bed volumes for low pH wastewater and unadjusted wastewater, respectively.

ft². While column length did not appear to affect overall percent virus removal, the time for complete virus breakthrough in terms of bed volumes was much greater in a 56-in. column than in an 18-in. column. Contact time of the sewage with the activated carbon was about 3 min in the 18-in. column and 9 min in the 56-in. column. Virus survival in the reservoir used to feed the columns was highly variable, making it difficult at times to maintain a constant level of input virus over the time period of the column runs. Therefore, virus data were always normalized to account for virus die-off.

Because the results of batch experiments indicated that virus removal from sewage effluent was more efficient at pH 3.5 than at pH levels near neutral, a column experiment was done in which removal efficiency was determined for filtered sewage effluent at both pH 3.5 and pH 8. These results are summarized in Figure 6 and Table IV. Removal of virus from the unadjusted sewage effluent essentially ceased after passage of 56 bed volumes. Further operation resulted in a small degree of elution of infectious virus from the charcoal, which accounts for the negative percent values of virus removed in the plotted data for the unadjusted sewage effluent (Figure 6). However, the column fed with sewage effluent adjusted to pH 3.5 was still removing 25% of the influent virus after passage of 120 bed volumes. Organic carbon removals were essentially the same at both pH 3.5 and pH 8.

To determine what effect a change in pH would have on virus adsorbed to activated carbon at low pH, wastewater seeded with virus was passed through a column of activated carbon until its virus capacity was reached. A portion of the original wastewater (pH 8.4), which had been removed before adjustment to pH 3.9, was then passed through the column. The viral titer is higher in this wastewater because of a difference in viral survival at this pH, but the number of viral particles in the pH 3.9 and 8.4 wastewaters are identical. The results shown in Figures 7 and 8 indicate that both viruses and soluble organic material could become desorbed when the wastewater pH was increased.

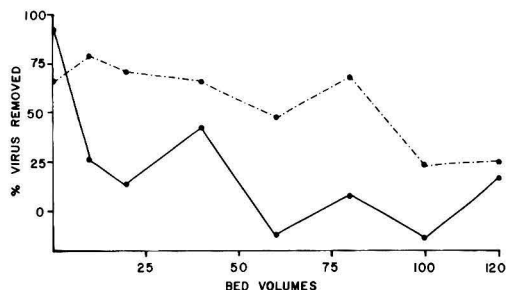


Figure 6. Effect of wastewater effluent pH on virus removal by columns of granular activated carbon
 ●—●, wastewater pH unadjusted; ---●, wastewater pH adjusted to 3.5

Glycine buffer adjusted to pH 11.5 with 1N NaOH has been used to elute viruses adsorbed to membrane filters (18). Passage of glycine buffer at this pH through the columns resulted in additional removal of viruses and organics from the activated carbon (Figures 7 and 8).

Discussion

Batch studies showed virus adsorption to activated carbon in wastewater effluent could be described by Freundlich isotherms. The isotherm tests afforded a convenient means of studying the effects of pH and wastewater quality on the efficiency of virus adsorption by activated carbon. The Freundlich plots for the adsorption data of replicate experiments conducted with different batches of sewage effluent, even with the same uv absorbance, had different slopes and y-intercepts. These differences were attributed to differences in the amount and/or the type of organic matter present which competes with the virus for adsorption sites on the activated carbon. This was borne out with batch studies which indicated that the amount of virus adsorbed to a given amount of charcoal was reciprocally relat-

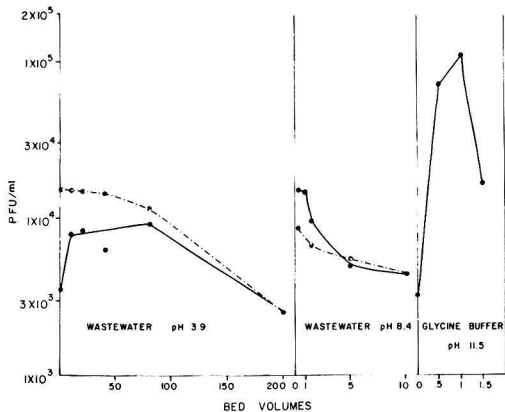


Figure 7. Effect of pH on virus retention by activated carbon
The column was 18 in. in length and was packed with 113 grams of activated carbon. Hydraulic loading was maintained at 2 gpm/ft²
● - - - ●, column influent; ● - - - ●, column effluent

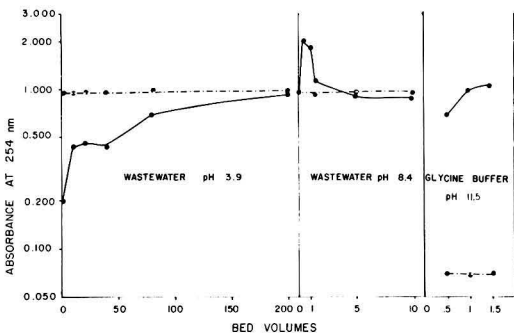


Figure 8. Effect of pH on soluble organic retention by activated carbon. Same methods as Figure 7
● - - - ●, column influent; ● - - - ●, column effluent

ed to the concentration of sewage organics. This conclusion was also supported by the greater degree of virus adsorption in lime-treated sewage than in filtered sewage. Lime clarification of secondary effluent resulted in 25–50% reductions in absorbance values, indicating appreciable reductions in the amount of organics.

In column studies, viral removal efficiency was dependent on hydraulic loading, with greater removals achieved at a lower loading. No apparent overall increase in virus removal efficiency was achieved by an increase in column length, but the time for the virus exhaustion point to be reached in terms of bed volumes was greater. The 56-in. column could be operated over a period of three days as compared with 12–24 hr for the 18-in. columns.

The adsorption of virus was dependent on pH with the greatest removals being achieved at pH 4.5 or lower. The natural pH of the sewage used in this study was found to vary from 7.5–8.5, and in this pH range viral adsorption was minimal. It was also shown that at least some of the virus and organic material adsorbed to activated carbon in columns at low pH could be eluted when the pH of the column influent was increased.

Poliovirus has two isoelectric points at about pH 7 and 4.5, with the virus becoming positively charged and exhibiting positive mobilities below 4.5 (19). Activated carbon particles have negative mobilities above pH 2.4 (8). A posi-

tive charge on the poliovirus particle below pH 4.5 may act to enhance its electrostatic attraction onto the negatively charged groups of the activated carbon. Because other enteroviruses are also known to adsorb more readily to surfaces at low pH levels in the presence of organic matter (13), their enhanced adsorption onto activated carbon would also be expected at a low pH.

In summary, the results of our studies suggest that virus removal from wastewater effluent by activated carbon is greatly improved by lowering pH to 3.5–4.5 or by reducing the concentration of wastewater organics by lime coagulation. In our studies, activated carbon adsorption of organic pollutants from wastewater at pH 4.5, or below, was comparable to that at pH 8. In addition, Weber (2) has shown that activated carbon adsorption of certain organic water pollutants may actually be enhanced at acidic pH levels. Therefore, pH adjustments to below 4.5 could be applied to a final polishing column of activated carbon to ensure maximum virus removal as well as removal of other organic pollutants. Additional studies would be required to determine if carbon column operation under acidic conditions is both practical and economically feasible.

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Hydrocarbon Consumption and Synergistic Effects in Photooxidation of Olefins

Columba K. K. Yeung¹ and Colin R. Phillips*

Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto M5S 1A4, Ont., Canada

■ Single, binary, and tertiary mixtures of ethylene, propylene, and *cis*-2-butene are irradiated in the presence of nitrogen oxides in air. The experimental data clearly demonstrate the existence of excess rates and synergistic effects in the photooxidation of olefins. An inductive analysis of the hydrocarbon consumption rates provides conclusive evidence that olefins react readily with reactive intermediates generated by hydrocarbon reactions. The kinetics of the photooxidation of ethylene is briefly discussed. The observations provide information and insights for kinetic modeling in smog formation, and emphasize the value of selective hydrocarbon control in preventing smog formation.

Careful studies on the kinetics of photochemical smog formation have indicated that the rate of hydrocarbon consumption cannot be accounted for by the oxygen atom + hydrocarbon and ozone + hydrocarbon reactions (1). Glasston and Tuesday (2) found that the reactivities of hydrocarbons in mixed hydrocarbon systems are not simply additive, and Bufalini and Altschuller (3) observed that the changes in hydrocarbon consumption rates in mixtures (compared with single hydrocarbon systems) could not be explained by the shift in oxygen atom and ozone concentrations. There is, therefore, an excess rate of reaction not accounted for.

This study has been undertaken to investigate this excess rate and the synergistic effects. Single, binary, and tertiary mixtures of ethylene, propylene, and *cis*-2-butene are irradiated in the presence of nitrogen oxides. For brevity, ethylene is used as the reference for detailed discussions, though the analysis and the comments are generally applicable to other olefins. Ethylene is important because it is the most abundant hydrocarbon component besides methane (on a mole basis) in auto exhaust and is the major contributor to the exhaust reactivity (4). Furthermore, its reactivity is very useful in the estimation of reactivities of terminal olefins (5).

Experimental

The smog chamber was, in essence, a collapsible container made of 0.0005 in. "Melinex" film (ICI) with a volume of approximately 1000 liters. Irradiation was supplied by blacklight fluorescent lamps. The light intensity expressed as the first-order rate constant for NO₂ photolysis, k_1 , was 0.30 min⁻¹. (The experimental deviation was ±0.02 min⁻¹. However, due to uncertainties in the rate constants used in calculating k_1 , an uncertainty bound of ±0.05 min⁻¹ is more appropriate.)

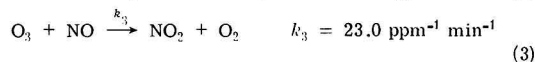
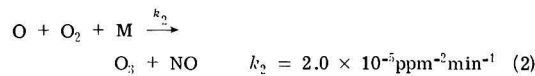
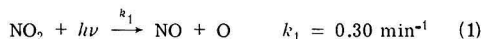
Hydrocarbons were separated by an *N*-octane/Parasil column and analyzed with a flame ionization detector. Nitrogen dioxide was measured by the Saltzman method (6). Nitric oxide was detected as nitrogen dioxide after being oxidized by acid potassium permanganate solution (7, 8). Total aliphatic aldehydes were analyzed by a modified MBTH method (9). Ozone was measured as oxidants, cor-

rected for NO₂ response, by the neutral potassium iodide method (10), and was also specifically analyzed by the DPE method (11).

For each of the above species, except hydrocarbons, a sampling train of several absorbers was used to ensure quantitative detection.

Results and Discussions

A. Single Component System: When nitrogen oxides are irradiated in pure air with ultraviolet light, the following reactions predominate:



Nitrogen dioxide is photodissociated (12) and the system rapidly approaches equilibrium,

$$\frac{[\text{NO}][\text{O}_3]}{[\text{NO}_2]} = \frac{k_1}{k_3} \quad (4)$$

with low-equilibrium ozone concentrations. With initial concentrations of [NO]₀ ≈ 0.8 ppm and [NO₂]₀ ≈ 0.2 ppm, the equilibrium concentration of ozone would be approximately 0.003 ppm and the concentrations of the nitrogen oxides would remain essentially unchanged.

When reactive hydrocarbons are introduced, the chemical changes characteristic of smog formation occur, with rapid conversion of NO to NO₂ and resultant buildup of ozone, as shown in Figure 1. It is obvious that NO must be converted to NO₂ by additional reaction paths involving hydrocarbons. In Figure 2, the calculated ozone concentrations, [O₃]_{cal}, computed on assumption of equilibrium of the NO - NO₂ - O₃ cycle—i.e.,

$$[\text{O}_3]_{\text{cal}} = \frac{k_1}{k_3} = \frac{[\text{NO}_2]}{[\text{NO}]} \quad (5)$$

are compared with the measured ozone concentrations. (To avoid uncertainties in the calculated values arising from large percentage experimental errors at low nitric oxide concentrations, only data for the first 300 min are used for analysis.) The measured concentrations are, in general, slightly lower than the calculated values, and the deviation increases with ozone concentration. Experimental errors are of course partly responsible for the differences. However, deviations are expected for the following reasons:

1. Part of the ozone would be consumed by reaction with NO in the sampling line. This discrepancy can be eliminated by correcting for the reaction during the residence time in the sampling line ($\theta \approx 2$ sec). For example, at $t = 300$ min, [O₃] = 7.5 pphm [O₃]_{cal} = 8.65 pphm, and the expected concentration, [O₃]_{cal}, after correction for the dark reaction (assuming [NO] approximately constant) would be,

¹ Present address, Shell Research Center, Oakville, Ont., Canada.

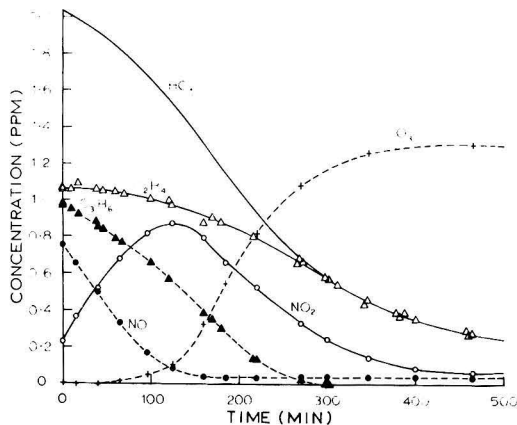


Figure 1. Concentration changes on irradiation of mixture of NO + NO₂ + C₂H₄

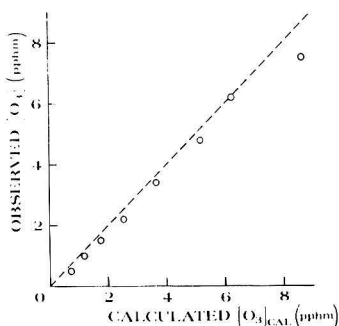


Figure 2. Comparison of computed and observed ozone concentrations

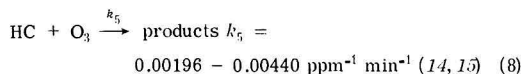
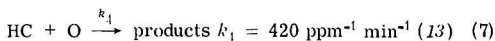
$$[O_3]_{\text{cal}}' = [O_3]_{\text{cal}} \exp \left\{ -\frac{k_5}{60} [NO] \theta \right\} \quad (6)$$

$$\approx 7.9 \text{ pphm}$$

which is in close agreement with the measured ozone concentration within experimental errors.

2. At high ozone and low nitric oxide concentrations, "side" reactions removing ozone would become increasingly important, and the assumed predominance of the O₃ + NO reaction would no longer be true.

Within experimental accuracy, then, the NO-NO₂-O₃ cycle would predominate in the photooxidation of ethylene, at relatively high NO and low O₃ concentrations. From reactions 1 to 3, the most prominent candidates for reaction with ethylene (or other olefins) are atomic oxygen and ozone, i.e.



in which HC stands for hydrocarbon (ethylene in this case). These reactions may then be conveniently considered as the initiation reactions for hydrocarbon consumption. Assuming pseudosteady state of atomic oxygen, the theoretical rate of hydrocarbon consumption (r_{th}) is given by the equation

$$r_{th} = k_1 \left\{ \frac{k_1 [NO_2]}{k_2 + k_1 [HC]} \right\} [HC] + k_5 [O_3] [HC] \quad (9)$$

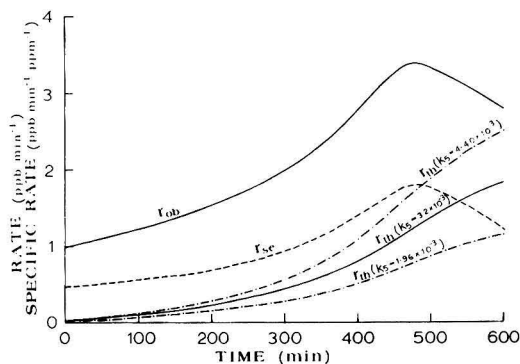


Figure 3. Observed, theoretical, and specific excess rates of ethylene consumption of for system: NO + NO₂ + C₂H₄

The computed theoretical rates (r_{th}) and measured rates (r_{ob}) of hydrocarbon consumption for the system of ethylene and nitrogen oxides are presented in Figure 3 for the extreme values and the mean value of k_5 as defined by Equation 8. The measured rates were obtained from the gradient of the concentration-time curve in Figure 1. It is immediately obvious that the ozone reaction is mainly responsible for the consumption of ethylene at the later stages of the reaction, and that the theoretical rate curve depends heavily on the value of k_5 used. Thus, accurately determined rate constants for ozone + olefins reactions are essential for any realistic kinetics modelling of photochemical smog. The average value of k_5 is used in the remaining discussion.

Comparison of the observed and theoretical rates reveals that the observed rate is much greater than the theoretical rate, especially in the early stages. It can be readily shown that any possible underestimation of the rate constants, even if true, could not fully explain the profile of the observed rate curve and excess rate (r_{ex}), defined as,

$$r_{ex} = r_{ob} - r_{th} \quad (10)$$

Some hydrocarbon must be removed by other active species by additional process(es).

If there were additional active species, the excess rate would become,

$$r_{ex} = \{\sum k_i [A_i]\} [HC] \quad (11)$$

If higher order reactions were involved, the concentration terms would have to be raised to the appropriate orders. In any case, assuming the reactions are first order with respect to hydrocarbon (which is most likely by analogy with O + HC and O₃ + HC reactions), the excess rate can be expressed in the general form,

$$r_{ex} = r_{se} [HC] \quad (12)$$

where the specific excess rate, r_{se} , includes all rate constants and concentration terms other than [HC]. By examining the specific excess rates, clues as to the nature and variation of the unknown active species may be deduced.

The specific excess rates for ethylene consumption are given in Figure 3. There is a striking resemblance between the specific excess rates and the observed rate curves. An attempt to correlate these rates gives a sample correlation coefficient greater than +0.99. This provides direct evidence that active species (other than O and O₃) are being formed by the hydrocarbon decomposition reaction. Hence, the higher the observed rate, the higher will be the concentration(s) of the active intermediate(s) and, therefore, the

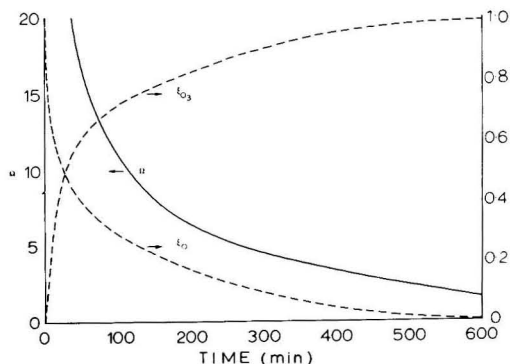


Figure 4. Temporal profiles of Ω , ϵ_0 and ϵ_{03} for system: $\text{NO} + \text{NO}_2 + \text{C}_2\text{H}_4$

higher will be the specific excess rate. The intermediates must be reactive and short-lived, otherwise there would be a buildup of these species even after the peak rate of hydrocarbon consumption, and the specific excess rate would peak much later than r_{ob} , which has not been observed. Since free radicals are formed by $\text{O} + \text{HC}$ and $\text{O}_3 + \text{HC}$ reactions, a free radical chain is an outstanding possibility.

For such a chain mechanism, propagated by active carriers (possible free radical) from either or both of the reactions $\text{O} + \text{HC}$ and $\text{O}_3 + \text{HC}$, it is possible to study the overall "chain length" of the mechanism, Ω defined as the ratio of the observed rate of hydrocarbon consumption to the theoretical rate, i.e.

$$\Omega = \frac{r_{ob}}{r_{th}} \quad (13)$$

The chain length is an indication of the number of propagation steps (effective in hydrocarbon consumption, in this case) from a single original carrier. The variations of the chain length with time for the ethylene system are given in Figure 4, together with the temporal profiles of the contributions of the $\text{O} + \text{HC}$ reaction (ϵ_0) and $\text{O}_3 + \text{HC}$ reaction (ϵ_{03}) to the total theoretical rate, i.e.

$$\epsilon_0 = \frac{k_4[\text{O}][\text{HC}]}{k_4[\text{O}][\text{HC}] + k_5[\text{O}_3][\text{HC}]} \quad (14)$$

$$\epsilon_{03} = \frac{k_5[\text{O}_3][\text{HC}]}{k_4[\text{O}][\text{HC}] + k_5[\text{O}_3][\text{HC}]} = 1 - \epsilon_0 \quad (15)$$

The chain length is much larger in the early part of the reaction when the $\text{O} + \text{HC}$ reaction plays a significant role, and levels off to 1 at the later part of the reaction when $\text{O}_3 + \text{HC}$ reaction predominates. A linear correlation of Ω with ϵ_0 gives a significant sample correlation coefficient of +0.96. This is consistent with a chain mechanism in which free radicals are the main chain carriers, effectively initiated by the $\text{O} + \text{HC}$ reaction. It is useful to compare such a hypothesis with existing knowledge in the chemistry of ethylene.

By far the most complete investigations on the reactions of oxygen atoms with olefins are those of Cvetanovic and his collaborators (13). Their work indicates that the initial product is a triplet biradical which may either stabilize or decompose. For ethylene, the activated complex undergoes almost exclusive fragmentation with methyl and formyl radicals as the prominent products (16, 17). The major reaction paths of the $\text{O} + \text{C}_2\text{H}_4$ chain, in the presence of NO , are shown schematically in Figure 5. (Much of the in-

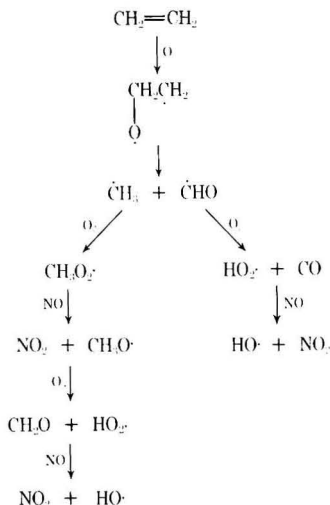


Figure 5. Schematic diagram of major reaction paths of $\text{O} + \text{C}_2\text{H}_4$ chain

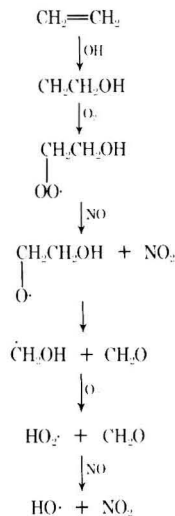
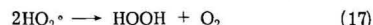
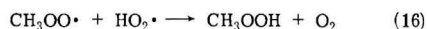


Figure 6. Schematic diagram of major reaction paths of $\text{HO} + \text{C}_2\text{H}_4$ chain

formation on the reactions of the free radicals are drawn from the sophisticated kinetic models on propylene by Niki et al. (1) and Demerjian et al. (12). The most prominent features are the conversion of NO to NO_2 , which partly explains the observed NO_2 formation as noted before, and the generation of HO . Hydroxyl radicals are efficient chain carriers and react rapidly with ethylene with regeneration of free radicals [(1) and the references therein], as shown in Figure 6. Thus, once produced, hydroperoxy and hydroxyl radicals can successfully sustain themselves by chain reactions, and account for the rapid conversion of NO to NO_2 and the fast consumption of ethylene. At later stages, due to the depletion of NO and the buildup of the radicals, termination reactions—e.g.,



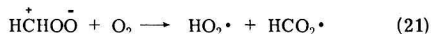
become increasingly important, and the radicals become less effective in propagating the chains, in agreement with the observed decrease in chain length, Ω , with time.

The primary step of olefin ozonolysis has been fairly well established, through the work of Criegee and others (13), to be the formation of aldehydes and zwitterions—e.g.,

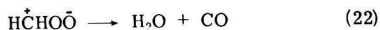


Wei and Cvetanovic (18) have shown that 1 to 1 stoichiometry occurs when ozone and olefins are reacted, which indicates that zwitterion + olefin reactions cannot be very important.

It is possible that the zwitterion may react with oxygen to form free radicals—i.e.,



The radicals would react as shown before and contribute to the excess rate of hydrocarbon consumption and NO_2 formation. However, Scott et al. (19) have shown that the major products in ozonolysis of ethylene in air are H_2O , CO , CH_2O , CO_2 , and HCOOH ; this would be consistent with the following major degradation reactions for the zwitterion:



Thus it appears that the $\text{O}_3 + \text{C}_2\text{H}_4$ reaction is less effective than the $\text{O} + \text{C}_2\text{H}_2$ reaction in initiating free radical chains, which explains why the chain length Ω approaches unity when ozonolysis predominates at later stages of the reaction.

It is also interesting to note that for both the atomic oxygen and ozone chains, the stoichiometric ratio for CH_2O produced and C_2H_4 consumed is 1:1 approximately, while that for the HO chain is 2:1. A comparison of the observed aldehyde concentration and ethylene consumed from Figure 1 shows that the ratio is approximately 2:1 in the early stages (2–3 hr), in support of the hypothesis that free radical chains (mainly $\text{HO}\cdot$ in this case), initiated mainly by the $\text{O} + \text{C}_2\text{H}_4$ reaction, are mainly responsible for the hydrocarbon consumption in this period. The ratio decreases to less than 1:1 as ozonolysis predominates and formaldehyde is removed by reactions and photolysis.

Thus, the observed results can be readily interpreted by the proposed chain mechanism, which is compatible with the present state of knowledge of the chemistry of ethylene. The kinetic model is, of course, neither unique nor complete. The lack of analytical data, particularly of the free radicals, precludes any rigorous proof of a detailed kinetic model.

A similar analytical approach can be applied to other, single-olefin systems.

B. Mixed Hydrocarbon System. In systems of mixtures of hydrocarbons, various compounds compete in the production and consumption of reactive intermediates, such as oxygen atoms, ozone, and free radicals. Since the free radicals may be produced by, or react with, any hydrocarbon in the mixture, synergistic effects would be expected on irradiation hydrocarbon mixtures. To study these effects, three single component systems, three binary mixtures, and one tertiary mixture of ethylene, propylene, and *cis*-2-butene are investigated. Figure 7 gives the temporal concentration profiles for the system of ethylene and propylene.

The observed rates of hydrocarbon consumption are again much higher than the theoretical rates. To avoid unwarranted conclusions on the synergistic effects in mixtures as a result of accumulated uncertainties in the rate constants of different components, an analytical approach, based entirely on observed data, is used. As mentioned before, it is reasonable to assume that the primary hydrocarbon reactions are first order with respect to hydrocarbon concentration. Hence, the observed rate of consumption of hydrocarbon i , r_{ob}^i , can be expressed as,

$$r_{ob}^i = r_{sp}^i [\text{HC}^i] \quad (25)$$

where the specific rate of hydrocarbon i , r_{sp}^i , includes the concentrations of all the active species reacting with i , raised to the appropriate orders, and the corresponding rate constants. By comparing the specific rates of hydrocarbons in single and mixed hydrocarbon systems, it is possible to deduce the existence of synergistic effects in the photooxidation of mixed hydrocarbons, other than the variations caused by changes in individual hydrocarbon concentrations. The specific rates of consumption of ethylene, propylene, and *cis*-2-butene when irradiated alone or with other olefins are given in Figures 8, 9 and 10, respectively. (To avoid large uncertainties caused by large percentage errors at low concentrations, the specific rates of the fast reacting hydrocarbons are obtained only for the period up to 80% hydrocarbon consumption.)

Figure 8 demonstrates that the specific rate of ethylene is markedly increased when irradiated with more reactive olefins (propylene or/and *cis*-2-butene), at least during the period when the more reactive hydrocarbon still exists at appreciable concentrations. Moreover, the more reactive the other component is, the more prominent this accelerating effect seems to be. Furthermore, this positive synergistic effect is not limited to ethylene. When propylene is irradiated with *cis*-2-butene, its specific rate is also significantly increased, compared with irradiation of propylene alone. On the other hand, the specific rate of the fast-reacting hydrocarbon in the mixture (i.e., *cis*-2-butene in its mixtures with propylene or/and ethylene, and propylene in its mixture with ethylene) is significantly reduced, as shown in Figures 9 and 10.

A seemingly puzzling feature is that the specific rate of the slow-reacting hydrocarbon in a mixture always peaks at a time much later than the time of maximum NO_2 concentration, as shown in Table I, and then drops off rapidly in

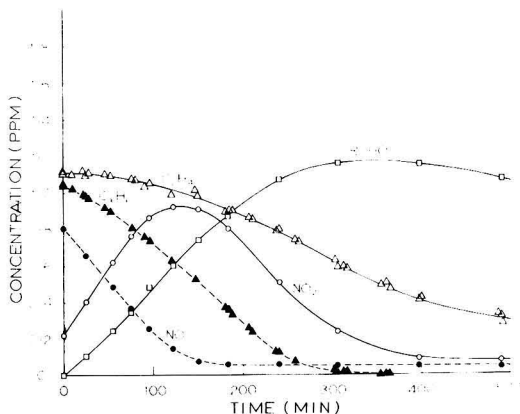


Figure 7. Concentration changes on irradiation of a mixture of $\text{NO} + \text{NO}_2 + \text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$

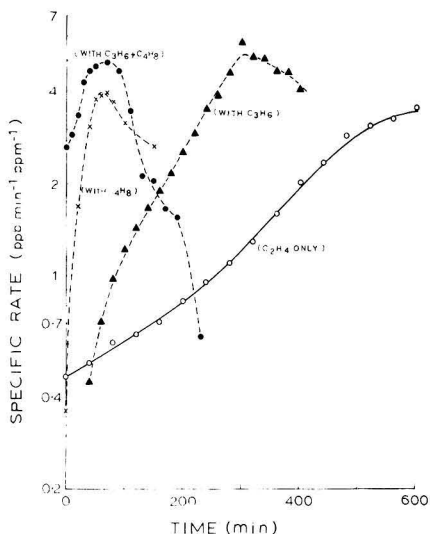


Figure 8. Specific rate of ethylene consumption

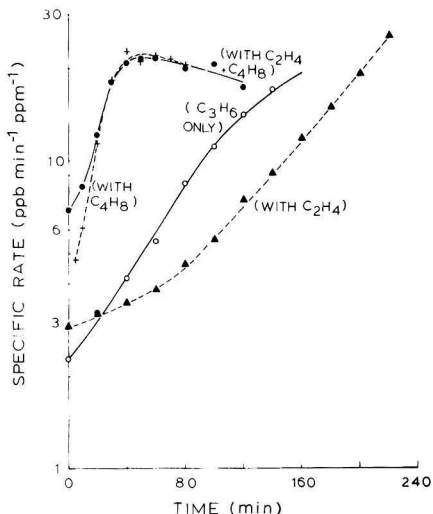


Figure 9. Specific rate of propylene consumption

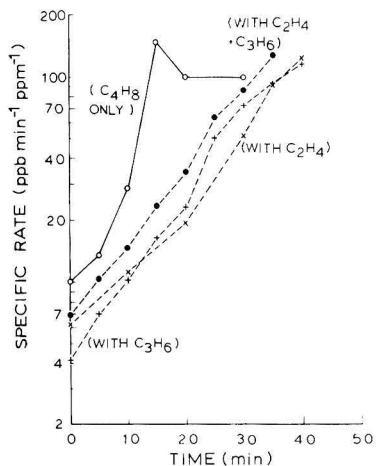


Figure 10. Specific rate of *cis*-2-butene consumption.

Table 1.^a Comparison of the Times for Peak NO₂ Concentration, Peak Specific Rate of Hydrocarbon Consumption (Slow-Reacting Component) and Complete Hydrocarbon Consumption (Fast-Reacting Components)

System, conc in ppm	Time for		
	No ₂ peak, min	Peak specific rate, min	Complete consumption, min
Ethylene (1.06) + propylene (0.97)	125	302 (C ₂ H ₄)	300 (C ₃ H ₆)
Ethylene (1.14) + <i>cis</i> -2-butene (1.06)	29	60 (C ₂ H ₄)	46–70 (C ₄ H ₈) ^b
Propylene (1.02) + <i>cis</i> -2-butene (1.09)	25.5	52 (C ₃ H ₆)	51 (C ₄ H ₈)
Ethylene (0.497) + propylene (0.485) + <i>cis</i> -2-butene (1.00)	26	68 (C ₂ H ₄) 48 (C ₃ H ₆)	46 (C ₄ H ₈)

^aFor all experiments, [NO]₀ ≈ 0.8 ppm, [NO₂]₀ ≈ 0.2 ppm. ^bNo sampling over this period.

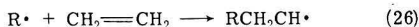
spite of increasing ozone concentration. A comparison of the specific rate curves with the concentration profiles reveals that these peak specific rates always occur when the fast-reacting hydrocarbon in the mixture is substantially depleted, as shown in Table I. Thus, for the mixture of ethylene and propylene, the specific rate of ethylene peaks at $t \approx 302$ min, while propylene is practically completely consumed at $t \approx 300$ min; and for the system of propylene and *cis*-2-butene, the specific rate of propylene peaks at $t \approx 52$ min, while *cis*-2-butene is completely consumed at $t \approx 51$ min. For the ethylene and *cis*-2-butene system, the corresponding peak occurs at $t \approx 60$ min. Regrettably, there was no sampling of hydrocarbons over the period $t = 46$ –70 min. The actual moment of complete consumption of *cis*-2-butene could have occurred at any time within this period. Within experimental accuracy, however, it may be concluded that this abrupt change in the specific rate of the slow-reacting hydrocarbon, when the more reactive component is depleted, is general in mixed hydrocarbon systems.

From the kinetic point of view, these observations indicate that olefins (particularly ethylene) react readily with reactive intermediates (besides O and O₃), probably oxygen-rich radicals, which are most copiously produced by initial reactions involving more reactive olefins. As discussed before, ethylene reacts very readily with reactive intermediates (mainly HO·) initiated by its reactions with O and possibly O₃. Recent kinetic studies in propylene (1, 12) have provided evidences that hydroxyl radicals and other free radicals are copiously generated in the photooxidation of propylene. Thus, in the system of ethylene and propylene, ethylene faces a much higher free radical concentration than it would have faced if it existed alone (even at the same total hydrocarbon concentration), owing to the large free radical-producing capacity of propylene. This increases the rate of consumption of ethylene by increasing the number of free radical chains. Each chain might conceivably have a shorter chain length due to increased rate of termination reactions as a result of increased free radical and NO₂ concentrations. In general, then, the reactivity of the slow-reacting hydrocarbon in a mixture is increased because it encounters a higher concentration of reactive intermediates due to the higher reactivity of the fast-reacting hydrocarbon. Moreover, since this acceleration effect de-

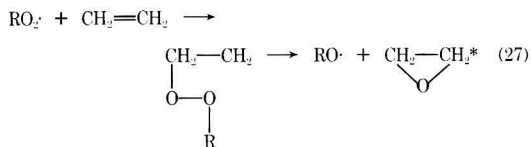
pends on the free radical contribution of the fast-reacting hydrocarbon, the specific rate is expected to decrease rapidly when the free radical concentration from the fast reacting hydrocarbon drops sharply. If the reactivities of the hydrocarbons are greatly different, then the drop would be expected to occur when the fast-reacting hydrocarbon is substantially depleted, as observed in this work.

On the other hand, since the reactive free radicals produced by the fast-reacting olefins are being scavenged and the slow-reacting hydrocarbon has a lower free radical producing potential, the fast-reacting hydrocarbon faces a lower free radical concentration than it would if it were to exist alone. The excess rate caused by free radical chains would be reduced. This negative synergistic effect, together with the reduced NO₂ formation rate, (and therefore atomic oxygen concentration) explains the significant drop in the specific rate of hydrocarbon consumption of the fast-reacting hydrocarbon.

For the tertiary mixture, (Figures 8 and 9) it is observed that when *cis*-2-butene is depleted ($t \approx 46$ min), the specific rate of propylene peaks and starts dropping at $t \approx 48$ min. However, it is not clear why the specific rate of ethylene stays relatively constant until $t \approx 80$ min, although this could be due either to the relative constancy in the specific rate of propylene over the same period, or to the aldehyde product from the *cis*-2-butene. When propylene is also depleted ($t \approx 180$ min), on the other hand, there is again a rapid drop in the specific rate of ethylene consumption. This implies that ethylene is partly consumed by certain reactions which are more effective in removing ethylene, than other olefins. A possible reaction is free radical polymerization (13, 20) which occurs more readily with ethylene—i.e.,



where R \cdot represents any free radical including oxygen-rich radicals. Another possibility, though speculative, is oxygen transfer from peroxyradicals, RO₂ \cdot (3)—i.e.,



These reactions are relatively less effective in generating efficient chain carriers (e.g., HO \cdot) and explain the more rapid drop in the specific rate of ethylene (compared with propylene) after its peak.

Conclusions

When nitrogen oxides are irradiated in air in the presence of olefins, the NO—NO₂—O₃ cycle still predominates, and provides the atomic oxygen and ozone which initiate hydrocarbon reactions. A thorough analysis of the hydrocarbon consumption rates of the ethylene system indicates that ethylene reacts readily with reactive intermediates, which are more effectively produced by the O + C₂H₄ reaction than by the O₃ + C₂H₄ reaction. The observations can

be readily interpreted by a chain mechanism involving free radicals (with HO \cdot and HO₂ \cdot as the major chain carriers). The analysis also reveals the dominance of ozonolysis in the later stages of the reaction, and, therefore, the importance of an accurately determined rate constant for this reaction in kinetic modeling. It should be emphasized, however, that it is the rapid conversion of NO to NO₂ by chain reactions in the early stages which makes possible the high ozone concentration responsible for the rapid ozonolysis.

Analysis of the specific rates of hydrocarbon consumption of mixed olefin systems demonstrates the existence of synergistic effects and provides evidence that olefins react readily with reactive intermediates produced by initial reactions involving more reactive olefins. Thus, the reactivity of an olefin is increased when mixed with more reactive olefins and decreased when mixed with less reactive olefins. This emphasizes the value of selective control of the more reactive hydrocarbons in air quality control as a means of reducing the absolute reactivity of the reactive hydrocarbons and minimizing the reactivities of other less reactive components.

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Accumulation and Elimination Studies of Four Detergent Fluorescent Whitening Agents in Bluegill (*Lepomis macrochirus*)

Charles R. Ganz,* Janos Schulze, and Per S. Stensby

Dyestuffs and Chemicals Division, CIBA-GEIGY Corp., Greensboro, N.C. 27409

Frank L. Lyman

Department of Industrial Medicine, CIBA-GEIGY Corp., Ardsley, N.Y. 10502

Kenneth Macek

Bionomics, EG and G, Inc., Wareham, Mass. 02571

Bluegill were exposed in dynamic flowthrough tank water systems to each of four sulfonated stilbene fluorescent whitening agents (FWA's) to determine to what degree these products accumulate in portions of the fish which may be consumed by humans. FWA test concentrations were DASC-3, 1 mg/l.; DASC-4, 0.1 and 0.01 mg/l.; BSB, 0.1 mg/l.; NTS-1, 0.1, 0.01, and 0.001 mg/l. Exposure periods ranged from 35–70 days after which the fish were transferred to water free of the test chemical. During the tests, fish and water were periodically sampled and analyzed. Of the four compounds tested, only NTS-1 yielded tissue levels above those present in the tank water. The 5–10 fold accumulation of NTS-1, however, is not considered significant biomagnification by EPA pesticide registration guidelines (20). FWA was completely eliminated from exposed fish within 14 days of their transfer to clean water. Accumulation studies using ^{14}C -labeled DASC-4 both confirm the lack of accumulation found in the studies with nonlabeled material and afford evidence that no metabolites of the FWA's are being accumulated. Evidence is also presented that the accumulation behavior of the *cis* photoisomers of the stilbene FWA's is similar to that of the parent *trans* stilbene compounds. It is concluded that the compounds tested are likely to present little risk of accumulating and persisting in natural fish populations.

Fluorescent whitening agents (FWA's), particularly those of the sulfonated stilbene class, are used in home laundry detergent formulations to impart a visual whitening effect to laundered fabrics. A number of papers have reviewed both the chemical properties and applications of FWA's (1–6). FWA's usually comprise less than 1% by weight of a detergent formulation. Published estimates (7) place the annual U.S. consumption in the 15–20-million-pound range. The anticipated development of more effective FWA's may reduce this quantity in the near future (8).

Although much of the FWA is adsorbed onto fabric substrates during washing (3), it is likely that small amounts of these compounds will be present in laundry wastewater. The fraction of these residual FWA's which eventually reaches effluent receiving waters is dependent upon the degree of removal during waste treatment and upon natural elimination processes. Ganz et al. (9) have carried out investigations of FWA removal in six waste treatment plants of varying design. The results indicate that waste treatment effects a substantial reduction (56–99+%) in the concentration of FWA's initially present in raw wastewater. The extent of removal is dependent upon the treatment process but in all cases adsorption to the sewage sludge appears to be the dominant removal mechanism. Additional investigations (10, 11) indicate that, except in isolated instances, the concentration of FWA's in natural waters is below 1 ppb. Thus, both the quantity of FWA's reaching

receiving waters and the concentration of FWA's in such waterways appear to be very small.

The acute toxicity of FWA's to a number of species of fish has been investigated. Sturm, Williams, and Macek (12) examined the acute toxicity of DASC-3, DASC-4, and NTS-1 (see Table I for structures) in bluegill (*Lepomis macrochirus*) using ethylene glycol to completely solubilize the FWA's. The 96-hr TL_{50} values found are shown in Table II. Keplinger et al. (13) have reported on the acute fish toxicity of BSB as well as those FWA's mentioned above (see Table II). The test species used were rainbow trout (*Salmo gairdneri*) and channel catfish (*Ictalurus punctatus*). No cosolvent was used for solubilization so that, with the exception of DASC-4, the solubility limits of the test compounds had to be exceeded to obtain a toxic response. It can be speculated that some of the mortalities may have been due to suffocation caused by suspended solid material lodging in the gills of the fish rather than to the systemic toxicity of the FWA. From the data in Table II it can be seen that the TL_{50} values of some typical detergent FWA's in a warm water species (bluegill), a cold water species (trout), and a bottom feeder (catfish) are far in ex-

Table I. Test Materials

DESIGNATION ^a	STRUCTURE
DASC-3	
DASC-4	
^{14}C -DASC-4	
BSB	
NTS-1	

^a DASC-3, DASC-4 and NTS-1 are official FWA designations which have been adopted by the ASTM. An official designation for BSB has not yet been proposed.

Table II. Acute Toxicity of FWA's in Various Species of Fish

FWA	96-Hr TL ₅₀ in mg/l. (95% confidence interval)		
	in Bluegill ^a (<i>Lepomis macrochirus</i>)	in Rainbow trout ^b (<i>Salmo gairdneri</i>)	in Channel catfish ^b (<i>Ictalurus punctatus</i>)
DASC-3	32 (24-43)	750 (500-1000)	1060 (736-1530)
DASC-4	26 (21-31)	108 (61-190)	86 (68-109)
BSB	—	130 (116-145)	126 (113-140)
NTS-1	474 (387-581)	1780 (1150-2750)	943 (706-1260)

^aData taken from Sturm et al. (12). ^bData taken from Keplinger et al. (13).

cess of expected concentrations in natural waters.

Jensen (14) reported finding detectable quantities of a nonionic textile FWA in sludge from a sewage plant in Sweden treating textile mill wastes. He later found the same FWA in the fatty tissue of fish caught in a river, downstream from the outfall of this plant. Subsequent chronic exposure of goldfish to this FWA under controlled laboratory conditions indicated that it accumulated in goldfish to at least 1000 times above the corresponding concentration in the water. The accumulated FWA was rapidly eliminated upon transfer of the fish to water free of the FWA.

U.S. detergent-FWA's are generally ionic sulfonated compounds and thus would be expected to have a significantly lower affinity for fatty tissue than the nonionic FWA studied by Jensen. Sturm et al. in the work cited above (12) found that this was indeed the case. These investigators combined the three anionic FWA's for which acute toxicity had been tested, with the nonionic FWA studied by Jensen and tested the mixture for long-term accumulation in both bluegills and channel catfish. The exposures were carried out over a period of 90-105 days at FWA concentrations of 12.5, 1.25, or 0.125 mg/l. for each FWA (total FWA concentrations of 50, 5, and 0.5 mg/l.). The fish tanks were protected from light during the study to prevent photochemical conversions from occurring. The results showed that only occasional fish samples contained concentrations of the three anionic FWA's above the 0.01-mg/kg quantitation limit. Most of the samples assayed contained only traces of these FWA's which could not be quantitated. The nonionic FWA, on the other hand, was accumulated in substantial quantities although it was subsequently eliminated upon transfer of the fish to water free of the test chemical. The results with the nonionic FWA were in good agreement with those obtained by Jensen.

The present paper describes accumulation studies designed to provide additional useful data regarding the impact of detergent fluorescent whitening agents on the aquatic environment. The three anionic FWA's investigated by Sturm et al. as well as one additional anionic FWA were studied in separate accumulation tests rather than in combination. The concentrations used included levels 10-100 times higher than those used by Sturm et al. In addition, the tests described here were carried out without protection from fluorescent light or natural daylight. This permitted information to be obtained about the accumulation of both the parent trans FWA's as well as their cis photoisomers. The latter are readily formed from the trans isomers, in solution, by absorption of incident radiation of approximately 360 nm (15). Analytical procedures were designed in all cases to take into account both the trans and the cis isomers. Finally, a study was conducted in which fish were exposed to ¹⁴C-labeled DASC-4. The aim of this study was to obtain some information about the presence or absence of metabolites of anionic FWA and also to confirm some of the results found in the studies with nonlabeled material.

Experimental

Test Materials. Four of the most widely used U.S. detergent FWA's, designated DASC-3, DASC-4, NTS-1, and BSB, supplied by CIBA-GEIGY Corp., were investigated. In addition, DASC-4 was prepared by CIBA-GEIGY Corp. with a radioactive carbon-14 label randomly distributed in the triazine rings. The specific activity of ¹⁴C-DASC-4 was 10.5 μCi/mg. The structures of the above materials are shown in Table I. The assay of the materials used is as follows: DASC-3, 94% active, 6% water; DASC-4, 76% active, 15% sodium chloride, 5% sodium carbonate, 4% water; ¹⁴C-DASC-4, 97% active, 3% water; BSB, 88% active, 4% sodium chloride, 8% water; NTS-1, 93% active, 7% water.

Test Conditions. Bluegills (*Lepomis macrochirus*) were chosen as the test fish because of their wide distribution in U.S. waters and their extensive usage as test fish in standard bioassays (16). The exposures were carried out in dynamic systems using FWA concentrations ranging from 0.001-1 mg/l. Fish and water samples were taken from the test tanks periodically and analyzed for the respective FWA. The edible portion—i.e., the entire carcass of the fish with the exception of the organs contained in the visceral cavity—was analyzed. The exposures were continued until no significant increase was noted in the concentration of FWA in the fish at three successive sampling periods. The minimum exposure period was 30 days. Following the exposure phase, the remaining fish were transferred to water free of the FWA. Fish and water were again periodically sampled and analyzed. This elimination phase was continued until no significant amounts of FWA were found in the fish.

The duration of the exposure and elimination phases, as well as the concentrations of the various FWA to which the fish were exposed, are shown in Table III. The tests included in all cases one concentration considered to be at least 100 times greater than the maximum expected environmental levels.

Fish Exposures. All fish, for each exposure, were held in

Table III. Parameters Used in the Various Fish Exposures

Test material	Mean wt of fish, g	Nominal tank water concn, mg/l.	Duration of test, days	
			Exposure phase	Elimination phase
DASC-3	50.0	1	70	14
DASC-4	57.0	0.1	35	7
	4.5	0.01	30	14
¹⁴ C-DASC-4	4.5	0.01	30	14
	4.5	0.001	30	14
BSB	51.0	0.1	49	14
NTS-1	55.0	0.1	49	14
	50.0	0.01	35	21
	50.0	0.001	35	21

the laboratory for at least 30 days prior to introduction into the test system. During that period, mortality in various test populations never exceeded 2% and fish were judged to be in excellent physical condition. All exposures were conducted using a modification of a continuous flow proportional dilution apparatus (17) which provides for the automatic intermittent introduction of test material and diluent into the test system. Aerated well water (pH 7.1–7.3; total hardness 40 mg/L as CaCO₃; dissolved oxygen 7.5 mg/L, temperature 18°C ± 0.5) was provided at a rate such that each tank received the equivalent of six water changes per 24 hr. Fish were fed a dry pelleted ration ad libitum each day.

Exposures of all fish to nonradioactive FWA's were conducted in 500-liter fiber glass tanks. Two different sizes of fish were used as indicated in Table II. For larger fish (about 50 grams) 60–80 specimens were introduced into each unit. For smaller fish (about 4.5 grams), 1050 specimens were introduced per unit. In all cases the ratio of biomass to volume ranged from 6–10 g/l. In all cases stock solutions were made fresh daily and shielded from exposure to light by wrapping with aluminum foil. All stock solutions were made in distilled water except for those used in the 0.1 mg/L NTS-1 test. Stock solutions for this exposure were made in 90% acetone solution. Exposure of fish to ¹⁴C-DASC-4 was conducted in 30-liter glass aquaria each containing 100 of the smaller fish.

Fish samples were taken from each experimental unit at various preset intervals during both the exposure and the elimination phases (e.g., day 1, 3, 7, 14, 21, etc.), rinsed with water, rinsed with acetone, eviscerated, and frozen for storage prior to analysis. Duplicate water samples for chemical analysis were removed periodically from each experimental unit, placed in amber glass bottles, and, with the exception of radioactive samples, preserved by addition of NH₄OH. Parallel control units were maintained for each exposure.

Analysis of FWA in Fish Tissue. All workup procedures were carried out in laboratories equipped with yellow lights (no uv components) to prevent photoisomerization of the FWA during analysis. The fish were analyzed for FWA by extraction and thin layer chromatography as described below. All reported tissue concentrations are on a wet weight basis.

Sample Preparation. Fish were maintained frozen during shipment and were stored in a freezer upon receipt. Fish were periodically removed from the freezer and their outer surface was washed with distilled water and acetone. Each fish (or, in the case of some of the DASC-4 studies, a composite of 80 small fish) was cut into approximately 1/4-in. pieces with serrated scissors and frozen solid either by mixing with Dry Ice or by sandwiching the pieces between sheets of aluminum foil surrounded by beds of Dry Ice. The frozen pieces were ground, in portions, into a fine powder using a Waring Blender fitted with a 250-ml stainless steel cup and a vented cap (18). The blender cup was cooled with Dry Ice prior to introduction of the sample. If necessary, a jacket of Dry Ice in a plastic bag was placed around the blender cup to ensure that the cup was kept cold throughout the blending operation. Warming of the blender cup caused the fish tissue to adhere to the blender walls resulting in poor grinding and difficulties in recovering the sample from the blender. Following grinding, each sample was transferred to a loosely capped jar and returned to the freezer until analyses could be performed. Ground samples were stored at least overnight before analyzing to allow any residual Dry Ice to sublime. Duplicate ground samples of each fish were analyzed for the respective FWA as described below.

Analysis of DASC-3. Twenty-gram samples of the ex-

posed fish and an untreated control fish were twice extracted with 20-ml portions of acetone–water–concd ammonium hydroxide (90–10–5). To increase extraction efficiency, the mixture was sonicated with a Sonifier ultrasonic cell disruptor (Heat Systems Ultrasonics, Inc.) fitted with a Microtip accessory. After centrifugation, the extracts were combined, washed with 15 ml chloroform and the upper phase was removed and concentrated to 2 ml under a stream of nitrogen. If necessary, a small amount of water was added to bring the volume to 2 ml. Aliquots of the control and unknown concentrates were applied to alternating lanes of a silica gel TLC plate (Q-4, Quantum Industries, Inc.). Varying quantities of DASC-3 standards, superimposed on spots of control extract, were applied in the open lanes. Prior to development, the TLC plate was irradiated for 20 min, at a distance of 15 cm, with a 254-nm uv lamp (C-81, Ultraviolet Products, Inc.). This served to establish an equilibrium between the parent trans isomer and its primary photoproduct, the cis isomer, both in the spotted standards and in the samples. In this way, total DASC-3, present in the fish as both the trans and cis isomers, could be determined by analyzing only the trans isomer. The latter, as opposed to the corresponding cis isomer, was readily separated from interfering background substances. The equilibrated plate was developed to a distance of 10 cm in a presaturated tank containing acetone–water–concd ammonium hydroxide–tetrabutylammonium iodide (90–4–10–2 grams). DASC-3 concentration was estimated by visually comparing the fluorescence intensity of the trans DASC-3 bands ($R_f = 0.70$) in the samples with those in the standards while exposing the developed plate to a 366-nm uv light (XX-15C, Ultraviolet Products, Inc.). Recovery of DASC-3 from “spiked” fish samples was 70 ± 10% using this method. The quantitation limit was somewhat dependent on the nature of the sample, but was usually about 0.02 mg/kg.

Analysis of DASC-4. Ten-gram ground samples of fish tissue (including an untreated control) were extracted with a 20-ml portion of acetone–water–concd ammonium hydroxide (90–10–5). To increase extraction efficiency and help remove interfering substances, 5 grams of sodium chloride were added to each sample and the resultant mixture was sonicated in a 40-ml tapered bottom centrifuge tube. Following centrifugation, the upper liquid phase was removed and concentrated under a stream of nitrogen. The residues were reconstituted in 4 ml of acetone–water (90–10) and 0.4 ml of the resultant solutions was finally diluted with 0.1 ml of acetone–water (90–10). Standard solutions of DASC-4 were prepared in a mixture of 1 part acetone–water (90–10) and 4 parts reconstituted “control” extract to simulate the matrix in which the sample was contained.

The standards and samples were applied to alternating lanes of a silica gel TLC plate (EM Laboratories #5763) and the plate was treated as described for DASC-3 above. DASC-4 concentration (R_f trans isomer = 0.55) was determined in the same manner as the DASC-3 concentration. Recovery was 80 ± 10%. The quantitation limit was 0.01 mg/kg.

Analysis of BSB and NTS-1. In the case of these two compounds both the trans and the cis isomers could be separately analyzed. The BSB and NTS-1 were extracted from the fish tissue in the manner described for DASC-4 except that BSB required two extractions to obtain adequate recovery. The solutions resulting from reconstitution and subsequent dilution of the extract residues were each applied to two TLC plates (EM Laboratories #5763). To one of the plates was applied trans isomer standards. This plate was used to determine the trans isomer content of the samples. On the second plate was spotted cis isomer standards.

The latter were prepared by irradiating acetone/water stock solutions of trans NTS-1 for 30 min, at a distance of 15 cm, with a 366-nm source or trans BSB for 2 hr with a fluorescent desk lamp (containing two 15-W cool white bulbs) in order to establish a photoequilibrium between the cis and trans isomers. The cis isomer content of the irradiated solutions was then determined by difference after determining the fraction of trans isomer remaining. The resultant mixed isomer solutions of known composition were then used to make dilutions for cis isomer standards based on their respective cis isomer contents. Irradiated NTS-1 solutions usually contained isomer ratios of 40 cis/60 trans while irradiated BSB solutions contained isomer ratios of 10 cis/90 trans. The cis isomers from BSB probably included both the cis, cis form as well as the cis-trans form. The TLC plates prepared for BSB analysis were developed in the same solvent system as DASC-3. The BSB isomers were separately estimated under 366-nm uv irradiation. The plates containing NTS-1 were developed to a distance of 10 cm in a presaturated chamber containing dioxane-benzene-methanol-concd ammonium hydroxide 40-50-20-5. The NTS-1 isomers were estimated in the same manner as the BSB. The separate amounts of trans and cis isomers were added together to obtain total BSB or NTS-1. The R_f values of the four compounds were as follows: trans BSB, 0.45; cis BSB, 0.40; trans NTS-1, 0.30; cis NTS-1, 0.25. Recoveries using this method were typically in the range of $80 \pm 10\%$. Quantitation limits were 0.01 mg/kg. Traces below this concentration were sometimes discernible, but could not be quantitated.

Analysis of ^{14}C -DASC-4 in Fish. The fish used in this study were smaller than those used in the above studies. Samples for analysis were, therefore, obtained by grinding the four fish taken at each sampling interval and removing duplicate representative 0.5-gram samples from the pooled mixture. The samples were combusted in a Biological Material Oxidizer (Beckman Instruments, Inc.) and the $^{14}\text{CO}_2$ trapped in 15 ml of a liquid scintillation cocktail consisting of 50 grams of 2,5-diphenyloxazole, 0.5 gram of 2,2'-phenylene-bis(4-methyl-5-phenyl)oxazole, 430 ml of toluene, 300 ml of methanol, and 270 ml of phenethylamine. The radioactivity in the resultant solutions was measured in a liquid scintillation counter equipped with an automatic external standard accessory (Nuclear Chicago Mark II, or its equivalent). The detection limit using ^{14}C -DASC-4 with a specific activity of $10.5\mu\text{Ci}/\text{mg}$ was $0.0006\text{ mg}/\text{kg}$ fish tissue.

Analysis of FWA in Water. All water samples, with the exception of those containing ^{14}C -DASC-4 were treated, upon sampling, with concentrated ammonium hydroxide (1 ml to 1 l. of water) to help prevent precipitation of FWA during shipping. All samples were taken in amber bottles to prevent further photochemical isomerization of the FWA after sampling. All analytical work was carried out under yellow lights as an added precaution against photoisomerization. Duplicate samples were analyzed by either fluorimetry, colorimetry, or TLC as described below.

Analysis of DASC-3, DASC-4, and BSB. Water samples containing these FWA were analyzed by fluorescence spectroscopy following photoequilibration of the fluorescent trans isomer and the nonfluorescent cis isomer. Equilibration was necessary because the test tanks were exposed to light during the tests, and water samples taken from these tanks contained varying ratios of cis and trans isomers. Equilibration permitted the determination of total FWA content from the quantity of only the fluorescent trans isomer. DASC-3 and DASC-4 solutions required irradiation with 254-nm uv light for 30 min to establish the photoequilibrium. BSB solutions required 2-hr irradiation under a fluorescent desk lamp containing two 15-W cool

white bulbs for equilibration. In each case suitable standards were photolyzed along with the unknown samples. The total FWA content of each irradiated unknown solution was determined from the standard curve obtained from the irradiated standard solutions. Fluorescence measurements were obtained with a Hitachi/Perkin-Elmer MPF-2A Spectrofluorometer. This assay was usable over the range of 0.001-1 mg/l.

Analysis of NTS-1. Samples having concentrations in the 0.1-mg/l. range were analyzed by a modified methyl green colorimetric method (19). The methyl green reagent was prepared by dissolving 10 mg of methyl green (CI #42585, J. T. Baker, Inc.) in 500 ml of distilled water and washing the resultant solution with chloroform before use. A 200-ml portion of each water sample was analyzed by first adjusting the pH to 7 and transferring to a separatory funnel. Five milliliters of the methyl green reagent, 5 ml of 2N HCl, and 5 ml of chloroform were added and the mixture was shaken vigorously. The blue-green chloroform extract was drawn off and its absorbance measured at 636 nm. A second 200-ml portion of the same solution was analyzed after the addition of 0.1 ml of an acetone-water (90-10) solution containing $20\mu\text{g}$ of NTS-1. The added NTS-1 was used as an internal standard to monitor the amount of complex extracted since this proved to be a significant variable between samples. The absorbance due to the known, added amount of NTS-1 was calculated by subtracting the absorbance of the "unspiked" sample from that of the "spiked" sample. The amount of FWA in the original sample was then calculated from the absorbance of the known amount of FWA added.

Samples containing NTS-1 in the range of 0.01 or 0.001 mg/l. were analyzed by extraction and TLC. Aliquots of 50 ml (for the 0.01 mg/l. range) or 500 ml (for the 0.001 mg/l. range) of water were mixed with 10 and 50 ml, respectively, of methyl ethyl ketone and then saturated with sodium chloride. The upper phase was removed and concentrated to dryness. The residue was taken up in 1 ml of acetone and cis and trans NTS-1 were determined by quantitative TLC in a manner similar to that described for the fish analyses except that standards used were pure acetone-water (90-10) solutions rather than dilutions in "control" extract.

Analysis of ^{14}C -DASC-4 in Water. Two 5-ml aliquots of each water sample were transferred to scintillation vials containing 15 ml of Insta-Gel emulsifier (Packard Instruments, Inc.). The mixtures were shaken well and counted on a liquid scintillation counter.

Results and Discussion

The results of the accumulation studies with DASC-3 and DASC-4 are summarized in Table IV. It can be seen that only sporadic trace concentrations (less than 0.05 mg/kg) of DASC-3 and DASC-4 were present in the fish at exposure levels of 1 mg/l. and 0.1 mg/l., respectively. In most instances, no detectable FWA was found. The data indicate that there is no tendency for DASC-3 and DASC-4 to be taken up and stored in the fish.

Since DASC-3 and DASC-4 are among the most widely used detergent FWA's in the U.S., it was felt that the foregoing conclusions should be confirmed by an accumulation study employing radiolabeled FWA. Such a study would not only substantiate the lack of accumulation of parent compound, but would also afford data regarding the possible formation and accumulation of FWA metabolites. The latter, if present, may not have been detected by the analytical methods employed in the accumulation studies with unlabeled material.

Due to the strong structural similarity between DASC-3

Table IV. Mean Concentrations of DASC-3 and DASC-4 in Tank Water and Fish Tissue Samples Taken During Accumulation Studies

Day-phase	DASC-3 concn, 1 mg/l. exposure tank		DASC-4 concn, ^a 0.1 mg/l. exposure tank	
	in Tank water, ^b mg/l.	in Fish tissue, ^c mg/kg	in Tank water, ^b mg/l.	in Fish tissue, ^a mg/kg
1-Exposure	0.85	NS	0.09	ND
3	0.93	NS	0.09	Tr ^d
7	0.95	Tr ^e	0.11	ND
14	1.10	0.04	0.10	<0.03 ^f
21	NS	NS	0.09	Tr ^d
28	0.87	Tr ^e	0.09	ND
35	NS	NS	0.10	ND
56	0.80	Tr ^e	g	g
70	0.93	Tr ^e	g	g
1-Elimination	NS	Tr ^e	0.00	ND
3	NS	Tr ^e	0.00	ND
7	NS	Tr ^e	0.00	ND
14	NS	NS	0.00	ND

^a Average of duplicate analyses on two individual fish. ^b Average of duplicate analyses. ^c Average of duplicate analyses on three individual fish. NS = Not sampled. ND = None detected (<0.01 mg/kg). ^d Trace detected (<0.01 mg/kg). ^e Trace detected (<0.03 mg/kg). ^f One of the fish analyzed showed only trace quantities while the second contained 0.03 mg/kg. ^g Duration of exposure phase was 35 days.

and DASC-4 the latter was labeled with carbon-14 (see Table I) and tested as a model compound for both. Test concentrations of 0.01 and 0.001 mg/l. were chosen, since these were considered to be above the anticipated environmental levels and since higher concentrations would have presented difficulties in disposing of the spent tank water. A test tank containing unlabeled DASC-4 at a concentration of 0.01 mg/l. was run concurrently for comparison purposes. The results of the studies with ¹⁴C-DASC-4 are shown graphically in Figures 1 and 2. It is readily seen that at both of the concentrations tested, the levels of radioactivity in the fish were approximately equal to those in the tank water throughout the study. Any radioactivity found in the fish was rapidly dissipated upon transfer of the fish to water free of the test material. The reason for the unusually high radioactivity in the 18th-day water samples could not be readily determined but was probably the result of inadvertent contamination. In any event this result does not appear to have had any serious influence on the conclusions of the study. Fish removed during the concurrent study with unlabeled material contained no detectable DASC-4 (<0.01 mg/kg). These results confirm that no significant quantities of either DASC-4 or possible DASC-4 metabolites are accumulated in the fish.

Detectable concentrations of BSB were found in the fish tissue, but, as shown in Figure 3, these concentrations remained below the corresponding levels in the water throughout the exposure phase of the study. Any BSB found in the fish tissue was rapidly eliminated upon transfer of the fish to water free of the test chemical.

As shown in Table V and in Figures 4 and 5, fish exposed to NTS-1 at concentrations ranging from 0.001-0.1 mg/l. had tissue levels about five- to tenfold greater than the corresponding concentration in the water. This is not considered significant accumulation according to the proposed EPA guidelines for registering pesticides (20). Again, the test chemical rapidly disappeared from the fish tissue when the fish were transferred to water containing no NTS-1.

The tests described above were all carried out under lighting conditions which allowed photoisomerization to occur. In the case of NTS-1, it was possible to obtain some information about the relative extent to which the trans and cis isomers were taken up by the fish. In the studies at 0.001- and 0.01-mg/l. levels, both the tank water and the fish were separately analyzed for cis and trans NTS-1. The samples from the 0.01-mg/l. tank (see Table V) yielded percentages of cis NTS-1 which were approximately the same both in the water and in the fish. In the samples from the 0.001-mg/l. study it was not possible to compare cis/trans

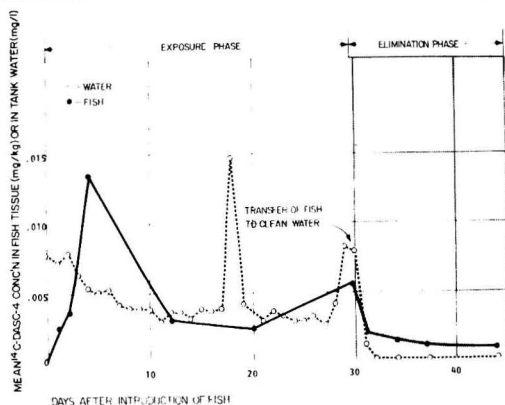


Figure 1. Concentration of ¹⁴C-DASC-4 in bluegill and in tankwater during accumulation study
Nominal tankwater concentration, 0.01 mg/l.

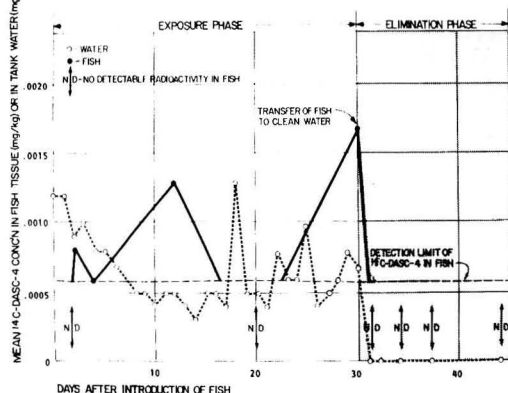


Figure 2. Concentration of ¹⁴C-DASC-4 in bluegill and in tankwater during accumulation study
Nominal tankwater concentration, 0.001 mg/l.

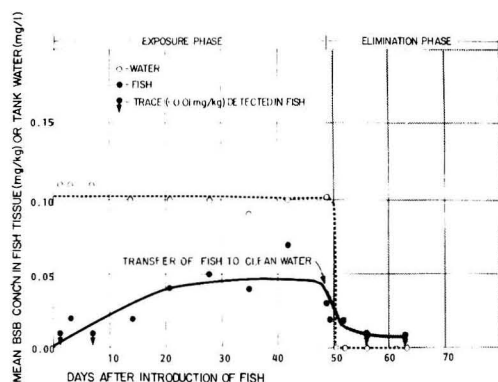


Figure 3. Concentration of BSB in bluegill and in tankwater during accumulation study
Nominal tankwater concentration, 0.1 mg/l.

Table V. Concentration of NTS-1 and Percentage of *cis*-NTS-1 in Fish and Tank Water Samples Taken During NTS-1 Accumulation Studies^a

Day-phase	Mean NTS-1 Concentration											
	0.1 Mg/l. exposure tank				0.01 Mg/l. exposure tank				0.001 Mg/l. exposure tank			
	in Water, mg/l.	Cis in water, %	in Fish, mg/kg	Cis in fish, %	in Water, mg/l.	Cis in water, %	in Fish, mg/kg	Cis in fish, %	in Water, mg/l.	Cis in water, %	in Fish, mg/kg	Cis in fish, %
1-Exposure	0.10	NA	0.17	31	0.017	30	0.02	50	0.0016	32	Tr	—
3	0.08	NA	0.34	49	0.017	27	0.05	38	0.0016	32	Tr	—
7	0.09	NA	0.37	28	0.017	27	0.08	25	0.0015	30	Tr	—
14	0.09	NA	0.32	25	0.015	33	0.15	40	0.0014	32	0.02	50
21	0.10	NA	0.22	46	0.015	33	0.06	33	0.0017	40	0.01	—
28	0.10	NA	0.73	27	0.013	31	0.11	37	0.0016	38	0.01	—
35	0.08	NA	0.41	29	0.014	22	0.13	38	0.0018	38	0.02	50
42	0.11	NA	0.44	32	—	—	—	—	—	—	—	—
49	0.11	NA	0.39	18	—	—	—	—	—	—	—	—
1-Elimination	ND	NA	0.16	24	ND	—	0.17	—	ND	—	0.02	50
3	ND	NA	0.14	23	ND	—	0.04	—	ND	—	0.01	—
7	ND	NA	0.07	<15	ND	—	0.05	—	ND	—	Tr	—
14	ND	NA	<0.04	—	ND	—	Tr	—	ND	—	ND	—
21	—	—	—	—	ND	—	ND	—	ND	—	ND	—

^a Each reported value is an average of the results from at least two independent fish or water samples, each analyzed in duplicate. NA = Not analyzed. ND = None detected (<0.01 mg/kg for fish; <0.01 mg/l. for water from the 0.1 mg/l. tank; <0.001 mg/l. for water from the 0.01 mg/l. tank; <0.0001 mg/l. for water from the 0.001-mg/l. tank; Tr = Trace detected, but not quantifiable (<0.01 mg/kg).

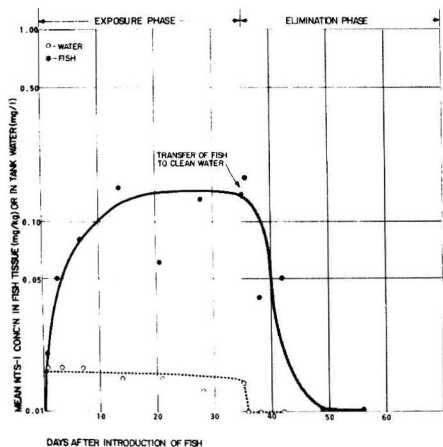


Figure 4. Concentration of NTS-1 in bluegill and in tankwater during accumulation study
Nominal tankwater concentration, 0.01 mg/l.

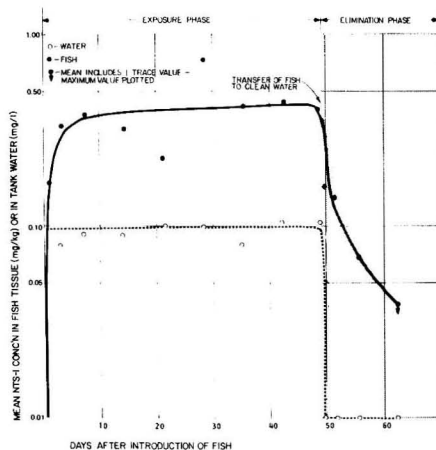


Figure 5. Concentration of NTS-1 in bluegill and in tankwater during accumulation study
Nominal tankwater concentration, 0.1 mg/l.

isomer ratios since only a few of the fish analyzed from this tank contained quantifiable NTS-1 levels. The isomer ratios in the water, however, were in good agreement with those in the 0.01-mg/l. tank water samples. Similarly, *cis/trans* isomer ratios were not determined in the water samples from the NTS-1 study conducted at 0.1 mg/l. Isomer ratios in the fish, however, were in good accord with those found in the fish from the 0.01-mg/l. study. From the above results, it would appear that there is little difference in the rate and extent to which the *cis* and *trans* isomers were accumulated.

Attempts were made also to analyze for *cis* and *trans* isomers in fish and water samples from the BSB study. It was possible to determine that the water samples generally contained about 90% *trans* isomer and 10% *cis* isomer. Thus, the *cis* isomer concentration throughout the exposure phase of the study was about one tenth of the 0.1-mg/l. total BSB concentration or about 0.01 mg/l. Since no *cis* isomer (<0.01 mg/kg) was detected in any of the fish sam-

ples, it would appear that *cis* BSB behaves similarly to *trans* BSB in that it does not show any significant accumulation above the concentration in the water.

The question of metabolism and buildup of metabolites in the fish was partially treated in the investigation with ¹⁴C-DASC-4. The absence of accumulated radioactivity demonstrated that neither parent compound nor possible metabolites of this FWA are accumulated in fish. Although this result cannot be directly extrapolated to the other FWA's investigated in this study, it can be inferred, both from structural similarities and from the ionic nature of the compounds involved, that ingested FWA would be eliminated rapidly by the fish and that a buildup of metabolites would not be likely to occur.

Conclusion

The results of the investigations described here demonstrate that, under controlled conditions, there is very little tendency for the detergent FWA's studied to accumulate in

fish tissue when present at concentrations far in excess of those expected in natural waters. Although extrapolation to the real-life situation in a lake or stream is difficult, it would appear that these studies have provided for a sufficient margin of safety to conclude that these FWA's are likely to present little risk in terms of accumulation and persistence in natural fish populations.

Acknowledgment

The aid of W. F. Holman and J. R. Duthie of the Environmental Water Quality Research Department of the Procter and Gamble Co. in planning and supporting the ¹⁴C-labeled DASC-4 portion of this work is appreciated. We also wish to thank Daniel Ryskiewich for the preparation of the radiolabeled materials. In addition, we would like to acknowledge the technical assistance of Richard Court.

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Removal of Dissolved Molybdenum from Wastewaters by Precipitates of Ferric Iron

Gary R. LeGendre and Donald D. Runnells*

Department of Geological Sciences, University of Colorado, Boulder, Colo. 80302

■ Molybdenum is an important industrial element. It is also an essential metallic cofactor in several enzymes. At high concentrations in forage it can be toxic to ruminant animals. High concentrations of Mo are in the aqueous, solid, and airborne effluents from many industrial operations. In the laboratory it can be removed from aqueous effluent by adsorption or coprecipitation with solid ferric hydroxide at low pH. A field example is given, taking place today in a stream in Colorado that receives dissolved molybdenum from a mining and milling operation. The precipitate in the stream is a mixture of iron compounds, including natrojarosite, $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, goethite, $\text{FeO}(\text{OH})$, and amorphous material enriched in molybdenum.

Molybdenum is an important element in the metallurgical, chemical, and agricultural industries. Molybdenum is also an important micronutrient in plants and animals. At present, molybdenum is known to be present as a metallic cofactor in seven enzymes (1). In plants, molybdenum plays an essential role in fixation of nitrogen and reduction of nitrate.

As with most nutrients, an excess of molybdenum can be detrimental. Molybdenum toxicity, variously termed teart disease, peat scours, and molybdenosis, has been reported in ruminant animals (cud-chewers) from many parts of the world (2). The primary toxic effect in animals seems to be an interference with copper metabolism, causing an induced copper deficiency (3). The digestive system in rumi-

nants seems to make these animals much more susceptible to molybdenosis than nonruminants. As far as we know, there have been no demonstrated cases of molybdenum toxicity in man. Molybdenosis in ruminants is characterized by diarrhea (scouring), loss of appetite, discoloration of hair, joint abnormalities, osteoporosis, lack of sexual interest, degeneration of testes, and in severe cases, death (3, 4). The disorder is treated by adding copper salts to the diet of the animal or by direct injection of solutions of copper.

The concentration of molybdenum in soils varies greatly, with many containing from 0.6-3.5 mg/kg of Mo (5). Plants also vary widely in their content of molybdenum. Concentrations of Mo in plants range from deficiency levels of less than 0.10 mg/kg to values as high as 300-400 mg/kg (6). Legumes tend to concentrate molybdenum, probably due to its role in nitrogen fixation. High levels of molybdenum do not seem to harm plants, but deficiencies can lead to such conditions as "whiptail" in cauliflower and "yellow-spot" in citrus (2).

Cattle and sheep which develop molybdenosis usually do so as a result of grazing on vegetation which is enriched in molybdenum (7). Concentrations of molybdenum in plants of 5-15 mg/kg can cause toxic effects (3). The copper status of the animal tends to determine the critical concentration of Mo at which symptoms of toxicity first appear. Miltimore and Mason (8) suggest that a ratio of Cu-Mo of less than 2-1 in forage plants represents a value at which molybdenosis can be expected, but there is disagreement on this point. Chappell (9) has presented an excellent summa-

ry of much of the available information on the transport and biological effects of molybdenum.

Because of the toxicity induced in ruminants by ingestion of molybdenum-rich vegetation, the Federal Water Quality Committee in 1968 (10) suggested a standard of 5 $\mu\text{g}/\text{l}$. in irrigation water for continuous use on all soils and 50 $\mu\text{g}/\text{l}$. for intermittent use on fine-textured soils. Chappell (9) has pointed out that many streams in the U.S. contain molybdenum in concentrations above 50 $\mu\text{g}/\text{l}$., and many of these are associated with industrial sources of the metal. In addition, problems of molybdenum toxicity associated with airborne material from industrial operations have been reported from the U.S., The Netherlands, and England (9).

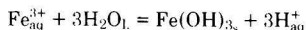
We have found that molybdenum is the principal dissolved metal in the aqueous effluent from many copper, molybdenum, and uranium flotation mills in southwestern U.S. This probably occurs because molybdenum is highly soluble as anionic MoO_4^{2-} at the high values of pH used in flotation circuits, whereas most of the other metals are precipitated as the hydroxides. In waters we have collected and analyzed from several tailings ponds associated with large open-pit copper mines in Arizona, dissolved Mo ranges from about 1 mg/l. up to about 30 mg/l. In the tailings water from a uranium mill in southern Colorado, the concentration of dissolved Mo is as high as 900 mg/l. And in the aqueous discharge from large molybdenum mills in Colorado, the dissolved Mo occurs in concentrations up to about 25 mg/l.

Methods and Results

Analytical Determinations. Dissolved molybdenum was determined in our laboratory by Robert Meglen using a modified colorimetric thiocyanate procedure (11). Iron was done by atomic absorption. Other dissolved components were determined by a commercial laboratory following the procedures of Standard Methods, 13th Ed. (12). The estimated analytical errors for dissolved molybdenum and iron are indicated in Tables I and II. The blank membrane filters were analyzed by X-ray fluorescence, using a solid state detector, with a lower limit of detection of approximately 1.5 ppm.

Previous Studies. It is well known that molybdenum can be removed from aqueous solution by sorption or coprecipitation with flocculent hydroxides of iron and aluminum (13-22). By varying the Fe/Mo ratio and the pH, nearly total removal of dissolved molybdenum can be achieved in laboratory studies.

Laboratory Experiments. We have used ferric oxyhydroxide to remove dissolved molybdenum from samples of actual mill waters taken from three different tailings ponds associated with copper mills. As shown in Figure 1, removal of more than 95% of total dissolved molybdenum was achieved for each of the three mill waters tested when the ratio of dissolved ferric iron added to total dissolved molybdenum exceeded about 10/1. The other chief dissolved components in these mill waters were calcium and sulfate, with a TDS of about 2500. The initial pH values were 7.7, 7.0, and 8.1. The ferric iron was added as dissolved ferric chloride, without additional base. Hydrolysis of added Fe^{3+} produced a flocculent precipitate and caused a drop in pH to about 3 in each case, according to the following reaction:



No buffers were added to the test solutions in Figure 1.

In experiments using buffered mill waters, it was found that optimal removal of molybdenum occurred in the presence of flocculent ferric hydroxide at values of pH from about 3 to 4. The results were somewhat erratic, probably

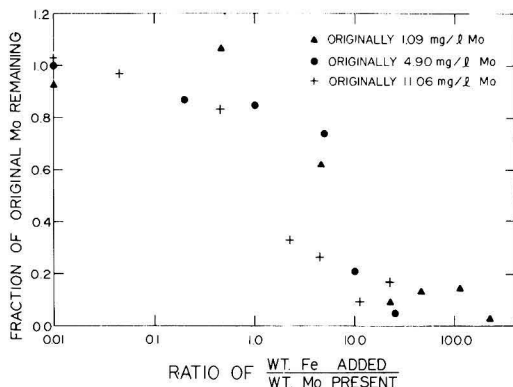


Figure 1. Removal of dissolved Mo by added ferric chloride solution

due either to interactions between the components of the buffers and the dissolved molybdenum or to differences in the chemical character of the precipitate of ferric hydroxide.

Significant removal of molybdenum was also achieved by precipitation of aluminum hydroxide in the mill waters, but the quantity of dissolved aluminum required was much greater than iron. We found the optimum pH for removal of molybdenum by aluminum hydroxide to be about 4.5. Jones (14) found that dissolved molybdenum was scavenged most effectively by hydrous aluminum oxides at a pH of about 5.2.

We were not able to remove dissolved molybdenum using manganese because we could not form a precipitate of manganese hydroxide at the appropriate low pH values without using extreme concentrations of dissolved manganese.

Field Experiments. Figure 2 shows the area of central Colorado where a general study of molybdenum is being conducted. Detailed studies of transport and removal of molybdenum, reported in this paper, were conducted on Tenmile Creek and the Blue River, both downstream from the Climax molybdenum mine, and on Clear Creek, downstream from the Urad molybdenum mine. Figure 3 shows the details of the sampling sites on these two drainages. Tenmile Creek, the Blue River, and Clear Creek are all en-

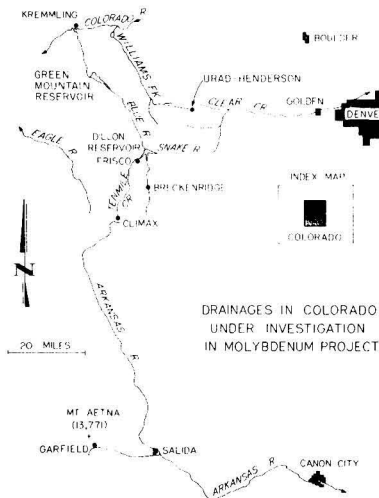


Figure 2. Location and index maps of study sites

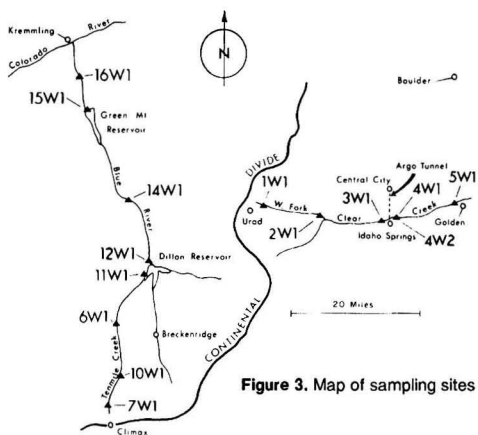


Figure 3. Map of sampling sites

riched in molybdenum due to the mining and milling operations upstream.

The concentration of dissolved molybdenum in the streams in question varies with the time of year, the stage of runoff, and the extent of release of water from the tailings ponds. At the time and under the conditions of this study (summer and fall low water, 1972), the five sample sites along Clear Creek (Figure 3) showed from 110–1500 $\mu\text{g/l}$. total molybdenum, and the eight sites along Tenmile Creek and the Blue River showed 140–430 $\mu\text{g/l}$. Samples taken at site 10W1 on Tenmile Creek (Figure 3) during spring high water, 1973, showed 13,400 $\mu\text{g/l}$. total molybdenum. In comparison, the median concentration of molybdenum in streams in the U.S. has been reported to be 0.35 $\mu\text{g/l}$. (23), and from numerous samples we have collected in Colorado we tend to view any value over about 10 $\mu\text{g/l}$. as anomalous. The concentrations of molybdenum in the streams investigated are therefore anomalous compared to other streams in the state not associated with mining operations. The highest concentrations of total molybdenum observed in Tenmile Creek, the Blue River, and Clear Creek are clearly related to releases of waters from the mills upstream.

To establish what proportion of the total molybdenum in the study streams was suspended or dissolved, we performed a series of filtrations through membrane filters. A portable filtration cell was designed and constructed of nylon and Plexiglas (22). The sample waters were passed through 0.45 and 0.01 μ membrane filters under 30 lb./in.² of nitrogen pressure, with continuous magnetic stirring. One to two liters of water were filtered in just a few minutes using this apparatus. Between successive filtrations the apparatus was rinsed with 10% (v/v) HCl and distilled water to remove impurities. Filtered and nonfiltered samples were collected in clean polyethylene bottles and immediately acidified to pH 1.5 with ultrapure HNO₃. Analyses of three blank filters showed negligible molybdenum (less than about 1.5 ppm).

Because of the possible important role of iron in removing or transporting molybdenum in natural waters, all samples were analyzed for both iron and molybdenum before and after filtration. The results of filtration through a 0.01- μ filter are shown in Tables I and II for Clear Creek, Tenmile Creek, and the Blue River.

The data shown in Tables I and II show that most of the iron in the water can be removed by filtration (our lower limit of detection was approximately 4 $\mu\text{g/l}$), but no detectable removal of molybdenum occurred in 15 of the 16 experiments. Only in the case of sample 4W1 (Table I) was

Table I. Data from Water Samples Collected from Clear Creek, Clear Creek County, Colo.

F denotes filtered samples (0.01 μ). U denotes unfiltered. Total range of error is approximately two standard deviations.

Sample	pH ± 0.05	Mo, $\mu\text{g/l}$, ± 17	Fe, $\mu\text{g/l}$. ± 30	% Removal, Fe	% Removal, Mo
1W1-F	7.8	1500 \pm 70	0	~100	0
1W1-U		1530 \pm 70	130		
2W1-F	8.0	340	0	~100	0
2W1-U		370	240		
3W1-F	7.8	210	0	~100	0
3W1-U		220	300		
4W1-F	6.8	110	280	99	37
4W1-U		180	38,200 \pm 600		
4W2-F	8.0	245	50	83	0
4W2-U		215	290		
5W1-F	7.8	510	20	98	0
5W1-U		510	1,250		

Table II. Data from Water Samples Collected from Tenmile Creek–Blue River Drainage System, Summit and Grand Counties, Colo.

F denotes filtered sample (0.01 μ). U denotes unfiltered. Total range of error is approximately two standard deviations.

Sample	pH ± 0.05	Mo, $\mu\text{g/l}$. ± 17	Fe, $\mu\text{g/l}$. ± 30	% Removal, Fe	% Removal, Mo
6W1-F		160	0	~100	0
6W1-U	8.3	140	90		
7W1-F		140	0	~100	0
7W1-U	8.3	150	800		
10W1-F		190	30	94	0
10W1-U	8.3	200	480		
11W1-F		400	10	90	0
11W1-U	8.3	390	100		
12W1-F		430	0	~100	0
12W1-U	8.2	430	40		
14W1-F		290	20	86	0
14W1-U	8.3	310	140		
15W1-F		220	0	~100	0
15W1-U	8.3	210	40		
16W1-F		210	0	~100	0
16W1-U	8.3	210	60		

significant molybdenum removed by filtration. This sample was immediately downstream from an inlet of acid mine water, and the resulting mixed water had the lowest pH (6.8) and highest Fe/Mo weight ratio (220) of any sample. Only in this sample did the lower pH and high iron content allow significant removal of molybdenum in solid form, as was demonstrated in our laboratory studies of mill waters (Figure 1). Results of filtration through 0.45- μ filters are not given here, but they show an average removal of iron approximately 70% that found with the 0.01- μ filters.

The results in Tables I and II were obtained on relatively clear stream waters during the summer and fall of 1972. A separate filtration experiment on turbid water taken from Tenmile Creek during spring high water in 1973 showed similar removal of iron (3600 $\mu\text{g/l}$. reduced to 190 $\mu\text{g/l}$), with no detectable removal of molybdenum (constant at 13,400 $\mu\text{g/l}$). The results of our work thus seem applicable to waters which are either clear or turbid, indicating that essentially all of the molybdenum in the stream waters is dissolved (or smaller than 0.01 μ).

It is apparent from previous work (14, 21) that pH exerts a major influence on removal of dissolved molybdenum by

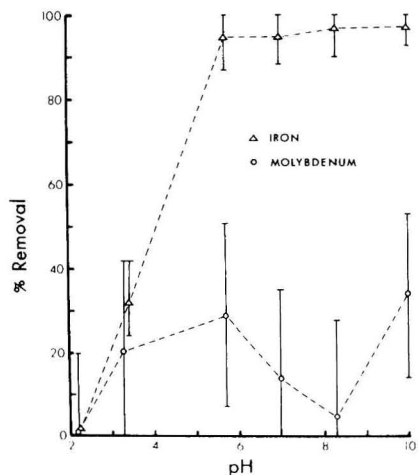


Figure 4. Removal by filtration of Fe and Mo from water sample 3W1, as a function of pH. 0.01- μ membrane filter. Error is ± 1 std dev

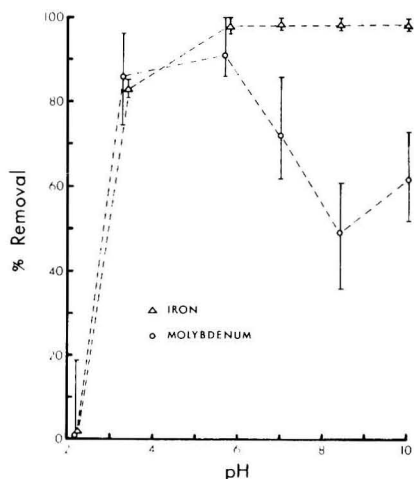


Figure 5. Removal by filtration of Fe and Mo from water sample 4W1, as a function of pH; 0.01- μ membrane filter. Error is ± 1 std dev

ferric oxyhydroxides. To test further this effect on natural samples, samples of water four liters in volume were collected from Clear Creek at sites 3W1 and 4W1 (Figure 3). As shown in Figure 3, site 3W1 is immediately upstream from the point of entry of a small flow of acid mine water from the Argo drainage tunnel into Clear Creek, and site 4W1 is just below the point of entry of the acid mine water on the same side of the creek. Chemical analyses for molybdenum and iron on the two samples of nonfiltered creek water showed the following:

3W1	4W1
Mo = 121 μ g/l.	Mo = 174 μ g/l.
Fe = 1200 μ g/l.	Fe = 44,800 μ g/l.
Fe:Mo = 9.9	Fe:Mo = 259

A single analysis of water from the Argo tunnel yielded a pH of 2.5 and a total iron of 215,000 μ g/l.

The large samples of stream water taken upstream and

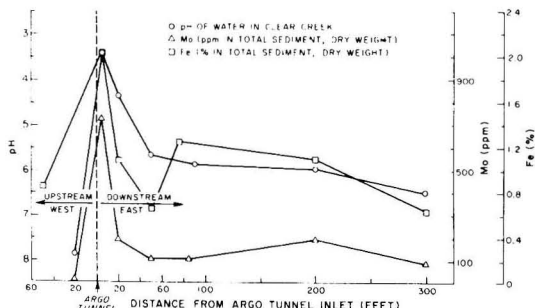


Figure 6. Concentration of Fe and Mo in bottom sediment of Clear Creek above and below inlet of acid mine water from Argo Tunnel. Note inverted scale of pH of stream water

downstream from the Argo Tunnel were acidified in the field to pH 1.5 with nitric acid, then taken to the laboratory. In the laboratory several aliquots of each of the two bulk samples were taken and made more basic by adding 1N NH_4OH , over a pH range of 2–10. Each aliquot was then filtered through a 0.01- μ membrane filter and the filtrate was analyzed for Fe and Mo. Figures 4 and 5 show the extent of removal of Fe and Mo by filtration as a function of pH. In samples 3W1, with a Fe–Mo ratio of 9.9 (Figure 4), a maximum of 7–50% of the Mo was removed, with best removal over a pH range of 4–6. All of the iron (detection limit 4 μ g/l.) was filtered out above a pH of 5; this undoubtedly reflects the decreasing solubility of iron hydroxide as a function of increasing pH. In contrast, in sample 4W1, with a Fe/Mo ratio of 259, nearly 100% of the Mo was filtered out over a pH range of 3.5–5.5. Again, Fe was totally removed above pH 5. These experiments show the important role of both Fe–Mo ratio and pH in scavenging of Mo by ferric oxyhydroxides. They also give a clue as to possible processes for control and removal of molybdenum in contaminated waters.

Removal Processes in Clear Creek

The point of entry of the acid mine water from the Argo Tunnel into Clear Creek offers a possible site of scavenging and removal of the dissolved molybdenum from the creek. A heavy orange precipitate forms on the bottom sediments of Clear Creek as the acid, iron-rich water from the tunnel enters and is oxidized and neutralized by Clear Creek water. The flow of water from the tunnel is only a small fraction of the flow of Clear Creek, so the iron-stained sediment forms a well-defined band a few feet wide down the north side of the creek. Figure 6 shows the content of total iron and molybdenum in the affected sediment along the north side of Clear Creek upstream and downstream from the point of entry of water from the Argo Tunnel. After removing particles larger than about $\frac{1}{2}$ in in diameter, the stream sediment was pulverized for the analyses in Figure 6.

Although some of the iron and molybdenum occur as natural components within the grains of silicates in the sediment, most of these two metals are present in the heavy orange precipitate resulting from oxidation and neutralization of the acid drainage. The pH of the creek water is also illustrated in Figure 6, with the scale inverted to facilitate comparison with the data for Fe and Mo. The pH drops about three units immediately below the tunnel, with a concomitant rise in molybdenum in the sediment from 38 mg/kg directly above the tunnel to about 625 mg/kg just below the point of entry of the acid mine water. The content of total iron changes from 0.7% above the tunnel to

about 2.03% below the tunnel. This is in accord with our laboratory experiments (Figure 1 and discussion) in which the precipitation of ferric oxyhydroxide at a low pH results in scavenging and removal of the dissolved molybdenum from the stream water.

Interpretation

From the literature and our experiments, it is clear that molybdenum can be removed almost quantitatively from various waters by precipitation of ferric oxyhydroxide at low pH. However, the exact mechanism of this removal is unknown. At least three mechanisms are possible: (1) mechanical coprecipitation of molybdenum ions or solid molybdenum oxide with ferric oxyhydroxides, (2) adsorption of bimolybdate ions on the surface of the ferric oxyhydroxide, or (3) precipitation of an iron-molybdenum compound. An investigation of the mechanism of removal was not within the bounds of our study, but information in the literature suggests that all three mechanisms are plausible.

Concerning mechanical mixtures of molybdenum and iron oxides or hydroxides, experimental studies of the solubility of natural iron-molybdenum oxides led Bhappu et al. (17) to conclude that mechanical mixtures of iron hydroxide and a ferric molybdate compound do occur in nature. Mikhailov (24) also concluded that mechanical mixtures of iron hydroxide and pentavalent molybdenum oxyhydroxide form in the oxidized zone of ore deposits. And Jenne (25) has emphasized the importance of processes of solid state diffusion, coprecipitation, and surface sorption of heavy metals by hydrous oxides of iron and manganese.

With regard to possible sorption reactions, at pH values below about 5.2, colloidal particles of hydrous ferric oxide in pure water possess a surface charge which is positive (26). Dissolved molybdenum occurs in natural water chiefly as molybdate (MoO_4^{2-}) and bimolybdate (HMoO_4^-) ions (27), but the dissociation constant for bimolybdate ion to molybdate ion is not known accurately. Values from 4-6 are reported in the literature for this constant (28-30). Polymeric anionic forms are probably also important at high concentrations of molybdenum and low pH (31, 32). The possibility therefore exists for adsorption or incorporation of anionic molybdenum into positively charged iron oxyhydroxides at low values of pH. Jones (14) in fact concluded that removal of molybdenum from solution by iron oxides was the result of exchange of molybdenum anions for hydroxyl ions on the surfaces of the particles.

A mixed compound of molybdenum and ferric iron is the third possible type of precipitate. Several workers have examined the chemical and crystallographic nature of one of the principal weathering products of molybdenum, ferrimolybdate (33). Its composition has generally been given as $\text{Fe}_2(\text{MoO}_4)_3 \cdot n\text{H}_2\text{O}$, but it now seems probable that ferrimolybdate consists of a mixture of certain oxides and hydroxides of ferric iron and hexavalent molybdenum (34, 17). Ferrimolybdate forms where sulfides of molybdenum and iron are exposed to weathering. It seems possible that it could be one of the phases present in the orange precipitate forming today in the sediments of Clear Creek due to neutralization of the iron-rich acid water from the Argo Tunnel, but this possibility could not be confirmed in our study. Lack of thermodynamic data and adequate field measurements prevented us from calculating a meaningful state of saturation of the mixed water with respect to either ferrimolybdate or ferric hydroxide. However, two analyses of the precipitate, dissolved from the sediment by acid leaching, showed weight ratios of iron to molybdenum ranging from about 25-1000. In comparison, the weight ratio of Fe to Mo in ideal ferrimolybdate is 0.39. It thus seems clear that the orange precipitate below the Argo

Tunnel is mainly one or more compounds of iron, enriched in molybdenum in an unknown form.

Two samples of precipitate-rich sediment were selected for X-ray diffraction analysis. Heavy liquids and the Frantz electromagnetic separator were used to concentrate the iron-rich fraction. By comparison to the Powder Diffraction Index (35), five principal peaks of natrojarosite, $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, and one principal peak of goethite, $\text{FeO}(\text{OH})$, were identified in one sample, showing that the precipitate is a mixture of at least two iron compounds. No characteristic peaks for ferrimolybdate were found, and of course, amorphous precipitates of iron would not be detected by X-ray diffraction. The second sample was completely amorphous by X-ray diffraction. The presence of the natrojarosite and goethite were verified by treating the sediment with a solution of concentrated hydrochloric acid and stannous chloride to dissolve the iron oxides and hydroxides. After this treatment, only the characteristic peaks for the natrojarosite and goethite had disappeared from the diffraction pattern.

Conclusion and Applications

From this study we conclude that removal of dissolved molybdenum by precipitates of ferric iron is an effective process in the laboratory and in at least one field situation. Under the proper conditions of low pH and high iron content, it appears that essentially all dissolved molybdenum can be removed.

In the stream waters which we studied, with the exception of one sample, the molybdenum was not removed by filtration through a 0.01- μ filter. We conclude that molybdenum in natural waters is essentially all dissolved and that only under extraordinary conditions of low pH and high iron can simple filtration be used for removal. However, at least some molybdenum-rich waters can be effectively purified by removal of precipitated ferric compounds at low pH. This promising procedure is now being bench tested by two of our associates in engineering, Bruce Zander and Roger Jorden, as a possibly economic method to purify certain industrial effluents and to recover the molybdenum values.

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Formation and Emission of Nitric Oxide in Fluidized Bed Combustion

Donald J. Parks¹ and Edward A. Fletcher*

Department of Mechanical Engineering, University of Minnesota, Minneapolis, Minn. 55455

■ Propane-air mixtures alone and with added nitric oxide, ammonia, or dimethylamine were burned in a fluidized bed. Bed temperature, flow rate, fuel-air ratio, particle size, bed depth, and the amount of fuel bound nitrogen were varied. Much less nitric oxide is formed from atmospheric nitrogen than is formed in conventional combustion processes. The amounts formed are higher than equi-

librium amounts at each bed temperature with stoichiometric and rich mixtures and lower with lean mixtures. In lean flames, when nitrogen is chemically bound to fuel, virtually all of the fuel-bound nitrogen is converted to nitric oxide. Powdered nickel almost completely eliminated nitric oxide from the products of rich mixtures.

Conventional uncontrolled combustion emits 300-1500 ppm of nitric oxide (1). With temperature and available oxygen controlled, emissions can be reduced to 100 ppm (1, 2) or less (3). Fuel fixed nitrogen may be exhausted as nitric oxide (4).

Fluidized bed combustion promises to reduce sulfur dioxide emission, simplify design, and reduce capital costs (5). Boiler development is taking place in the United States (6-9) and in Europe (5, 10, 11).

It is often held that, because of their low operating temperatures, fluidized beds would produce little nitric oxide (5, 6, 12, 13). But some previous studies (7, 14-20) have suggested that local temperatures may be much higher than the average bed temperature, and that nitric oxide may be produced from fuel-bound nitrogen as well as from atmospheric nitrogen. Jonke et al. (17-19) especially have stressed the latter, but Bishop (7) concluded that the nitrogen content of coal had no effect. We felt that a study of nitric oxide formation and emission from beds burning pre-mixed hydrocarbon-air would be instructive. Accordingly,

¹ Present address, Boise State University, Boise, Idaho 83707.

we studied the combustion of propane-air mixtures. Nitric oxide emission was studied first as the bed parameters were varied. Then, nitric oxide was added to the reactants, and its fate was observed. Finally, ammonia and dimethylamine were added, in small amounts, to the reactants, so that their roles in the formation of nitric oxide could be observed. The stability of the bed and the formation of other pollutants are dealt with elsewhere (21).

Experimental

Apparatus. The apparatus consisted of a combustor with its gas-handling system, a temperature measurement and control system, and sampling probes and analytical instrumentation.

The combustor consisted of a plenum, a distributor, a test section, and a disengaging section.

The plenum was made from standard 5-in. steel pipe, flanged at the top for mating with the distributor and test section, and capped at the bottom. Its inside diameter was 126 mm; it was 152 mm high. Two flame-arresting screens in the plenum evited flashback.

The distributor should cause a pressure drop at least one-tenth that of the bed (22) to ensure uniform fluidization. Our most successful distributor was a 12.5-mm thick sandwich of a Johns-Mansville ceramic fiber insulation, Cerafelt, between an 80 × 80 mesh nickel upper screen and a rigid lower screen. It was held in place between flanges on the plenum and test section by appropriate rings and copper and Cerafelt gaskets.

The test section was also made of 5-in. pipe, 260 mm high. It could be equipped with a 203-mm high extension to accommodate deep beds. It had a 152 × 76-mm quartz window and was lined with a 1.6-mm sheet of type 309 stainless steel. Ten holes evenly spaced up the side of the test section could be either plugged or fitted with thermocouple probes. A spark plug near the top of the section served as an ignition source.

The disengaging section above the test section was wider (203 mm) and constricted at the top to increase the outflow velocity. It prevented loss of splashing sand, and backflow of room air.

Fuel, air, and added gases were mixed in a common manifold that communicated with the plenum.

Temperature measurement and control were achieved by the use of thermocouples and a water cooled stainless steel coil submerged in the bed. Chromel-Alumel thermocouples, encased, except for their junctions, in magnesium oxide and sheathed in 1/8-in. Inconel 600, were used. No radiation correction was applied to the thermocouple readings. The thermocouples immersed in the bed were assumed to be in radiative equilibrium with their surroundings.

If there were no heat losses, the bed temperature would be the adiabatic flame temperature. We regulated the bed temperature by controlling the heat loss. Gross control was achieved by variation of the insulation thickness; fine control was achieved by variation of the immersion depth of the coil. The bed temperature could be controlled in this way to within five degrees.

England et al. (23) suggest that probe and line materials affect nitric oxide measurements. Tygon tubing, filters, and solid type dryers can remove NO₂ from test samples. We used a quartz probe and Pyrex and Teflon sample lines. Our 6-mm diameter probe's tip was flared and filled with quartz wool, and the sampling rate was low so that sand was not held to the tip by suction. A Pyrex, ice-cooled moisture trap was included in the sample line close to the probe. This arrangement was inert and did not remove NO₂ from samples.

Nitric oxide analyses were made with a Thermo-Electron

Model 10A Chemiluminescent NO-NO_x Gas Analyzer. The instrument was calibrated with a standard Scott Research Laboratories mixture and with mixtures that we made from nitric oxide and air in our laboratory.

Procedure. Combustion was established first in a low-flow-rate stoichiometric mixture, which burned quietly above the surface of the bed. The flow rate was then increased to fluidize the bed and produce a splash zone. Soon after, the reaction zone descended into the bed (provided the steady state temperature was high enough) and the fuel burned stably within the bed. The fuel-oxidant ratio and the temperature could then be adjusted to the desired test condition. We usually use a single temperature to characterize the bed, although detailed probing showed there was some spatial variation.

Nitric oxide concentrations were uniform in a given cross section of the reactor. Longitudinal nitric oxide profiles were, therefore, measured with axial probes. Some of the nitric oxide had been oxidized to NO₂ by the time the sample had reached the instrument. All of the NO_x measured by the instrument is referred to here as nitric oxide.

Bed temperature, gas flow rate, fuel-air ratio, and bed depth were varied independently above and below a mid-range reference set of operating conditions. The midrange reference used for the 0.65-mm particles was: 5-cm bed depth, 0.258 m/sec gas velocity (based on cold flow), stoichiometric mixture, and a bed temperature range from 867-1256K. A typical procedure involved varying one of the three parameters, bed depth, gas flow rate, or fuel-air ratio above and below its midrange value with the other two fixed at their midrange values. With each variation, a full range of bed temperatures was tested. The entire procedure was then replicated, within operating limits, for three other particle sizes: 0.46, 0.92, and 1.55 mm. With very rich mixtures (fuel-air equivalence ratio, $\phi = 1.2$ or more) the Thermo Electron Instrument did not measure properly in its NO_x operating mode, apparently because of catalytic destruction of NO in its stainless steel converter.

Added nitric oxide was used to study the effect of combustion and passage through a bed on nitric oxide already formed. A 5-cm deep bed of 0.65-mm sand was used at a gas flow rate of 0.258 m/sec. The variables in these experiments were fuel-air ratio ($\phi = 0.8; 1.0; 1.1; \text{ and } 1.2$), bed temperature (950K, 1144K, and 1256K), and amount of added nitric oxide (0, 50, 200, and 1000 ppm).

Ammonia and dimethylamine were added, in small amounts, to the cold reactants to learn what effect fuel-bonded nonatmospheric nitrogen would have. Bed parameters were made as nearly like those of the added nitric oxide experiments as possible. The chemiluminescent analyzer could apparently convert the amines to nitric oxide. To assure ourselves that we were indeed measuring only nitric oxide from combustion, we ascertained that any amine that somehow might have survived passage through the reactor was removed in the cold trap.

Results

The present study involved many variables. Figures 1-3 show variations of nitric oxide concentration and temperature within and above the fluidized bed for the midrange experiment using 0.65-mm particles. We shall describe trends observed with systematic variations of gas flow rate, fuel-air ratio, bed depth, particle size, and amount of fuel-bound nitrogen with reference to this midrange experiment. The reactor could be made to operate in one of two stable modes depending on the temperature. Although the transition temperature varied, the existence of two modes was apparent in all tests. At low bed temperature most of the combustion took place above the bed; at high bed tem-

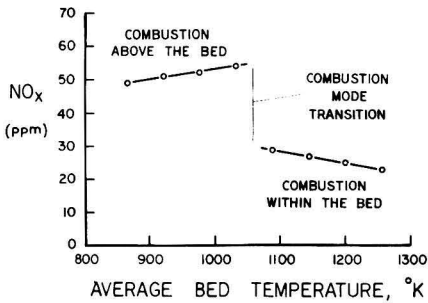


Figure 1. Variation of NO emission with average bed temperature at the midrange reference operating condition, 0.65-mm particles in a 50-mm deep bed with a stoichiometric mixture flowing at a nominal velocity of 0.258 m/sec

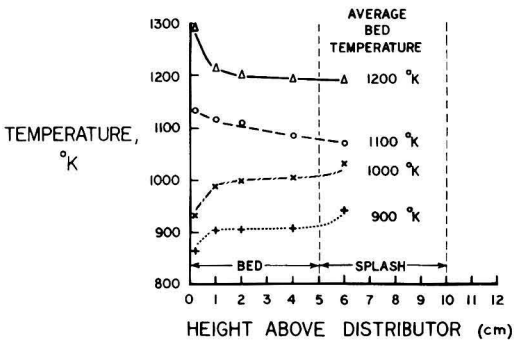


Figure 2. Steady state temperature profiles with a stoichiometric mixture at the midrange reference operating condition

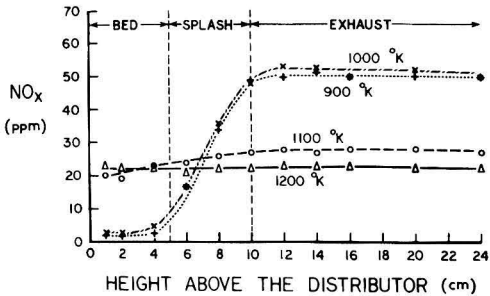


Figure 3. NO profiles with a stoichiometric mixture at the midrange reference operating condition

peratures combustion took place within the bed. The latter mode is of greater interest.

Nitric Oxide from Atmospheric Nitrogen. Bed Temperature. Nitric oxide production varied with temperature primarily because the temperature was related to the operating mode. As the average bed temperature went up, the amount of nitric oxide emitted increased slowly at first. When transition occurred, the nitric oxide concentration suddenly dropped, and the temperature profile inverted. Figure 2 shows temperature profiles, at four average bed temperatures, of the reference operating condition. Below the transition temperature, the temperature increased going up the bed. Most of the reaction was taking place above the bed. Above the transition temperature, the temperature decreased through the bed. Most of the reaction was apparently taking place near the distributor. Nitric oxide profiles also depended strongly on the operating

mode. Figure 3 shows this. When average bed temperatures were 900 and 1000K there was very little nitric oxide below the surface of the bed. At 1100 and 1200K, there was nearly as much nitric oxide in the gas down in the bed as there was above it, and the nitric oxide concentration didn't change much after its initial formation. At low bed temperatures, the characteristic propane flame could be seen above the surface. The bed made a low, gurgling sound. During transition, light blue flashes accompanied by loud pops were observed in the bubbles. After transition the sand glowed uniformly. At bed temperatures above 1200K the combustor was nearly silent. There was less combustion in bubbles and more in the zone just above the distributor.

Gas Flow Rate. Variation of the flow rate displaces nitric oxide profiles but does not change their form. Figure 4 shows that increasing the flow rate decreases the transition temperature. Nitric oxide production is lower at lower flow rates when burning is taking place in the bed. This trend is shown even more strongly in Figure 5, which combines data for the complete range of gas flow rates with all four particles sizes in beds at 1256K. The continuity shown indicates that the increase of nitric oxide formation with gas flow rate does not depend appreciably on particle size or bed depth.

The results obtained with various sand particle sizes are essentially the same (21), suggesting that the reaction is not a sand catalyzed one.

Fuel Air Ratio. The variation of nitric oxide emission at several bed temperatures with fuel air ratio is shown in Figure 6. It may be surprising that less nitric oxide was produced by lean mixtures. The nitric oxide concentration of

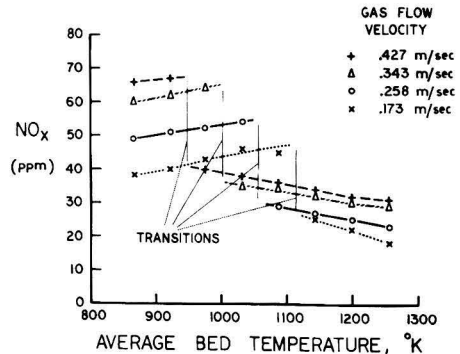


Figure 4. Variation of NO emission with temperature at various gas flow velocities

Particle size and bed depth are midrange. The mixture ratio is stoichiometric

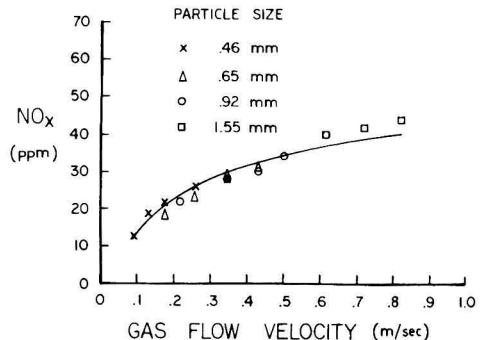


Figure 5. Variation of NO emission with gas flow velocity from beds of variously sized particles

Bed temperatures was 1256K. The mixture was stoichiometric. The 150-mm bed was made of 1.55-mm particles. The other sizes were in a 50-mm bed

the $\phi = 0.6$ products was only about one-fourth that of the stoichiometric mixture. The maximum nitric oxide concentration occurred in rich mixtures. The products of rich mixtures interfered with nitric oxide measurement, so there is some uncertainty about the position of the maximum. Other particle sizes gave similar results (21).

Bed Depth. The variations with temperature of nitric oxide emissions from various bed depths are shown in Figure 7. When burning occurred down in the bed there was little effect; deeper beds emitted somewhat less nitric oxide. However, when combustion took place mostly in bubbles or above the bed, deep beds produced much more nitric oxide. The bubbles breaking the surface from deep beds were larger than those from shallow beds.

Particle Size. The most notable effect of particle size on nitric oxide emissions stemmed from its indirect effect on the gas-flow rate operating range. Larger particles require higher flow rates to be fluidized. If the bed is not fluidized, burning occurs above the bed. Figure 8 shows nitric oxide emissions observed when gas flow rates were below those required to fluidize. The bed itself remained cold. More nitric oxide was emitted from this type of operation than from any operation in which the bed was fluidized.

Nonatmospheric Nitrogen. Nitric Oxide. Nitric oxide added to stoichiometric and lean mixtures was apparently little affected by passage through the bed. The amount of nitric oxide found in the products (Figure 9) was the sum of that added with that which would have been formed under the otherwise similar operating condition. The throughflow ratio is defined as the nitric oxide found minus the nitric oxide measured in a similar situation with none added, divided by the amount added. For lean and stoichiometric mixtures it was close to one at all the bed temperatures.

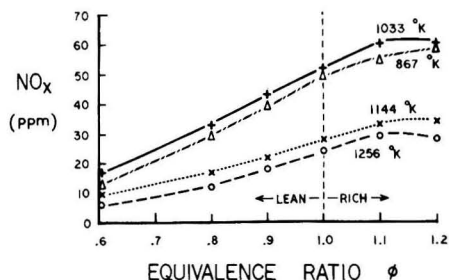


Figure 6. Variation of NO emission with fuel-air ratio at the reference condition, at various bed temperatures

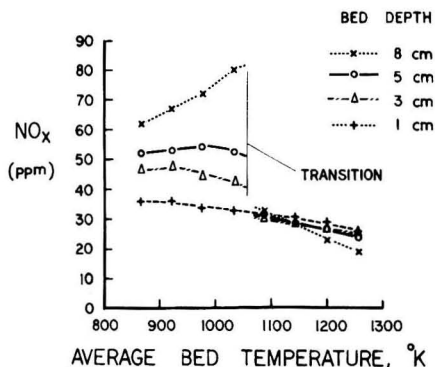


Figure 7. Variation of NO emission with bed temperature, of a stoichiometric mixture flowing at 0.258 m/sec through 0.65-mm particles in various depths

With rich mixtures, there was some reduction of nitric oxide (Figure 10). The extent of the reduction depended on the amount of nitric oxide added, suggesting that the order of the reaction with respect to nitric oxide may be greater than one. Most of the reduction occurred in the hotter zone near the bottom of the bed as is evidenced by the concentration profiles shown in Figure 11.

Amines. It is convenient to define a conversion ratio for fuel contained nitrogen. It is the measured nitric oxide concentration in the products minus the concentration that would have been produced without the addition of the amine divided by the maximum amount that could have been produced from the amine added. A conversion ratio of one implies that all of the amine nitrogen ended up as nitric oxide. Figure 12 shows the results of adding various amounts of ammonia over a range of fuel-air ratios and bed temperatures. Figure 13 shows the results obtained with dimethylamine.

With the lean mixture, the conversion ratio for 320 ppm

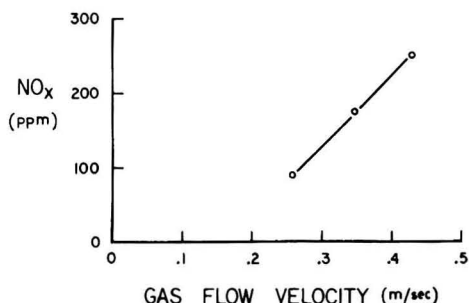


Figure 8. Variation of NO emissions with gas velocity from combustion of a stoichiometric mixture above an unfluidized 50-mm deep bed of 1.55-mm particles

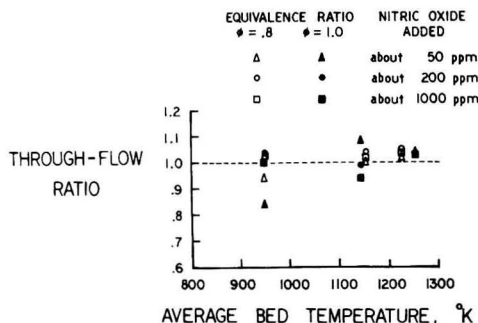


Figure 9. Throughflow of added nitric oxide in lean and stoichiometric mixtures

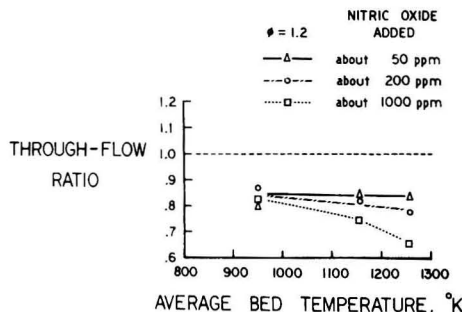


Figure 10. Throughflow of added nitric oxide in rich mixtures

of added ammonia was essentially one. With stoichiometric mixtures it was somewhat less. Higher ammonia concentrations gave lower conversion ratios. The dip in the curve coincided with a peak in carbon monoxide and hydrocarbon production just above the transition temperature. The conversion ratio was as low as 0.66 for 320 ppm added ammonia and 0.42 for 1100 ppm added ammonia with rich mixtures.

With dimethylamine, lean mixtures gave conversion ratios somewhat greater than one, but, in view of the possible uncertainties involved in metering dimethylamine, no strong conclusion should be made from this result. With rich mixtures, the conversion ratio was about 20% lower—the same relative reduction that was observed with ammonia.

Nitric oxide profiles for rich and stoichiometric mixtures at bed temperatures above and below the transition temperature (Figure 14) indicated that the conversion differences noted between these two fuel-air mixtures occurred in the zone where the combustion was taking place. Comparison of the $\phi = 1.0$ and the $\phi = 1.2$ profiles at 1200K showed that the production of nitric oxide in the first 2 cm of the bed determined the emission of nitric oxide from the

combustor. There was only a slight reduction of nitric oxide as the products traveled through the remainder of the bed and in the exhaust stream above it.

Catalytic Reduction of Nitric Oxide. Our observations with rich mixtures, of the reduction of nitric oxide, both in the bed and in the stainless steel converter in the gas analyzer, led us to do a single experiment in which we added a fine nickel powder to the bed. The results are of interest, not only for fluidized beds but in processes involving nitric oxide in general.

The bed temperature was 1256K, ϕ was 1.4. With 1000 ppm of nitric oxide being added to the fuel-air stream, the nitric oxide concentration 12 cm above the distributor was 460 ppm. Nickel powder was then slowly added. After about 5 ml of powder had been added the nitric oxide concentration dropped to about 1 or 2 ppm. With $\phi = 1.2$, the nitric oxide concentration in the exhaust was still near zero. The nitric oxide concentration gradually increased with time, however, indicating that the effect was decreasing. Examination of the bed afterward showed that the nickel powder had sintered into lumps.

Discussion

Very little nitric oxide is formed from the nitrogen of the air, in fluidized beds burning propane. When combustion occurs above the bed or explosively in bubbles more nitric oxide is formed than when combustion is taking place quietly down in the bed, because much higher than average bed temperatures would obtain in such bubbles. But even with deep quiet combustion nitric oxide emissions often exceed the average bed temperature equilibrium concentrations.

In fluidized beds, there may be small-scale high-temperature regions. In the combustion of propane-air such a region low in the bed is suggested by the temperature profiles of Figure 2.

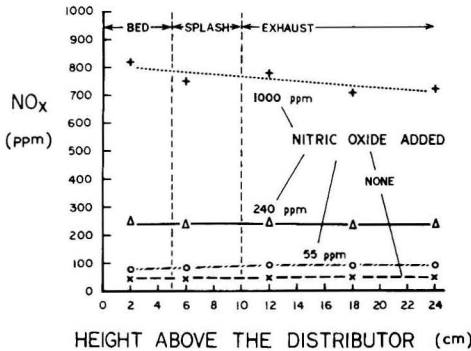


Figure 11. Nitric oxide concentration profiles under fuel-rich operating conditions, ($\phi = 1.2$)
Flow velocity through the 50-mm bed of 0.65-mm particles was 0.26 m/sec, and the temperature was 1156K

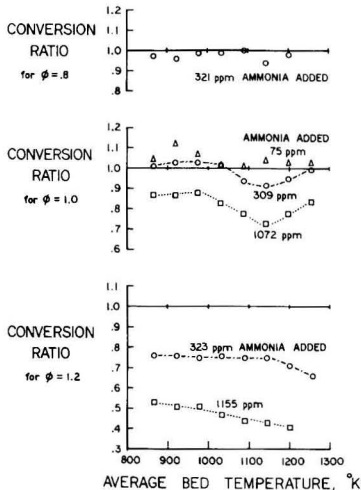


Figure 12. Conversion of added ammonia to nitric oxide under midrange operating conditions

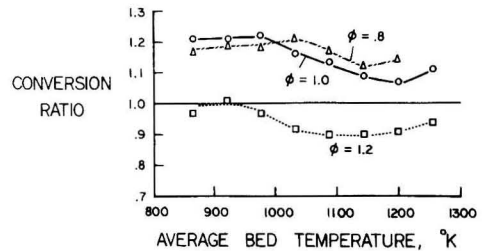


Figure 13. Conversion of added dimethylamine to nitric oxide under midrange operating conditions

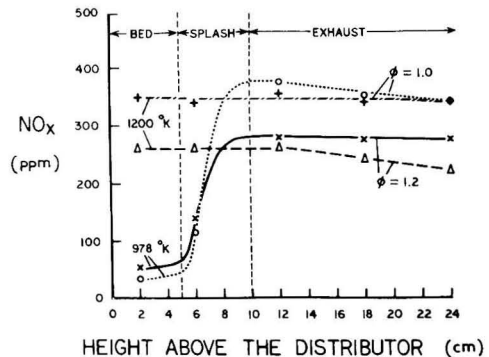


Figure 14. Nitric oxide profiles with added ammonia for the midrange operating condition

Indeed, such a region seems to be an essential feature of deep combustion and accounts for the observed nitric oxide concentrations and their variations with flow velocity shown in Figure 5, where the bed temperature was 1256K and there was virtually no reaction in bubbles.

We can rationalize these observations with a model that assumes the existence of a thin, high-temperature region near the distributor, in which all chemical reactions to produce nitric oxide occur. Our concentration profiles suggest that nitric oxide is neither produced nor destroyed in the main bulk of the reactor. We assume that the thickness of this reaction zone increases with flow velocity in such a way as to make the residence time of gas in the reaction zone independent of flow velocity. To simplify the numerical calculations, we assume that the heat of combustion is independent of the temperature and that the specific heats of reactants and products are equal and constant. Pure reactants enter the zone from below at the reaction zone temperature, T_r , having been heated by conduction from it, and pure products leave from the top at temperature T_r to mix quickly with the material in the main bulk of the reactor. Because the region is thin, lateral heat losses are negligible. Heat flows, however, from the reaction zone to the bulk zone and to the preheat zone. The temperature of the bulk zone is maintained constant by the abstraction of the proper amount of heat from it by cooling coils. The temperature of the reaction zone is thus constant and uniform. Our objective is to calculate T_r , relating it to the bed temperature, T_o , and the superficial flow velocity, V_o , and thus to calculate the nitric oxide concentration, C_{NO} . Since the residence time in the reaction zone is independent of the flow velocity, the nitric oxide concentration is proportional to its rate of formation. Hence,

$$C_{NO} = W e^{-E/T_r} \quad (1)$$

where W is a constant which includes constant reactant concentrations and an Arrhenius term to give it the dimension, ppm, and E is the activation energy divided by R . To evaluate T_r , we write an energy equation about the reaction zone.

$$\frac{dU}{dt} = \dot{m}_{in} h_{in} - \dot{m}_{out} h_{out} + \dot{Q}_p + \dot{Q}_b \quad (2)$$

where \dot{m} 's are mass flow rates, h 's are specific enthalpies, U is internal energy and the \dot{Q} 's are the rates of heat flux from the preheat zone and the bulk zone. If flow is steady, $dU/dt = 0$ and $\dot{m}_{in} = \dot{m}_{out} = \dot{m}$. Thus

$$h_{out} - h_{in} = q_p + q_b \quad (3)$$

where the q 's are heat flows per unit mass of gas flow. Since reactants and products are at the same temperature, $(h_{out} - h_{in})$ is the heat of the chemical reaction per unit mass, Δh , which is in turn equal to $C_p (T_o - T_a)$, where C_p is the specific heat, T_o is the initial temperature, and T_a is the adiabatic flame temperature. Furthermore, q_p is the heat which flows into the preheat zone from the reaction zone to preheat the incoming gas. Thus, $q_p = C_p (T_o - T_r)$ from which

$$C_p (T_o - T_a) = C_p (T_o - T_r) + q_b$$

$$\text{and} \quad C_p (T_r - T_a) = q_b \quad (4)$$

The physical interpretation of Equation 4 is that the bulk zone, which is cooled, is a heat sink for the reaction zone, and extracts from it exactly the proper amount of heat to reduce the temperature from its adiabatic value, T_a , to its nonadiabatic value, T_r .

To evaluate q_b we make use of the heat transfer coefficient in the bulk of the bed.

$$\dot{Q}_b = kA(T_b - T_r) \quad (5)$$

where k is the heat transfer coefficient and A is the cross-sectional area of the reaction zone.

Also

$$\dot{m} = \rho_o V_o A \quad (6)$$

where ρ_o is the cold gas density.

Thus

$$q_b = \frac{\dot{Q}_b}{\dot{m}} = \frac{k(T_b - T_r)}{\rho_o V_o} \quad (7)$$

If the gas is assumed to be ideal $\rho_o = pM/RT_o$, and

$$q_b = \frac{k(T_b - T_r)RT_o}{pMV_o} \quad (8)$$

Equations 4 and 8 can be combined to give

$$T_r = \frac{(kRT_o/pMC_p) T_b + V_o T_a}{(kRT_o/pMC_p) + V_o} \quad (9)$$

To evaluate T_r , we assumed that the gases had the physical properties of N_2 . The adiabatic equilibrium flame temperatures were calculated exactly, and a heat transfer coefficient of 3.82×10^{-3} cal/cm²-sec-K was estimated from data on page 73 of reference 5. Equation 9 becomes

$$T_r = \frac{0.1079 T_b + V_o T_a}{0.1079 + V_o} \quad (10)$$

where V_o is expressed in m/sec.

Table I shows the T_r 's calculated from the flow velocities for each of the points in Figure 5.

These values of T_r can be used with the corresponding nitric oxide concentrations to make a least squares fit of Equation 1. The result is

$$C_{NO} = 3876 \exp \left(\frac{-9849(0.1079 + V_o)}{0.1079 T_b + T_a V_o} \right) \quad (11)$$

The line in Figure 5 is constructed from Equation 11. The agreement with the experimental points is quite good.

The physical picture suggested by the foregoing analysis, then, is the following: In silent combustion at high bed temperatures, the incoming gas burns in a thin reaction

Table I. Reaction Zone Temperatures and Nitric Oxide Concentrations from Quiet Beds^a

V_o , m/sec	T_r , K	C_{NO} , ppm, ex	C_{NO} , ppm, calcd ^b
0.087	1708	13	12
0.131	1811	19	17
0.173	1879	22	21
0.173	1879	18	21
0.217	1932	22	24
0.258	1970	23	26
0.259	1970	26	26
0.342	2025	28	30
0.343	2026	29	30
0.343	2026	28	30
0.427	2064	32	33
0.427	2064	31	33
0.498	2088	34	35
0.613	2117	40	37
0.613	2117	40	37
0.718	2136	42	39
0.817	2150	44	40

^aBed temperature is 1256K, adiabatic flame temperature is 2268K. ^bCalculated from Equation 11.

zone near the distributor. Heat is transferred to the rest of the reactor from this zone at the same rate that heat is lost from the bulk zone to maintain its temperature constant. The reaction zone temperature is thus lower than the adiabatic flame temperature, but higher than the bulk temperature. As the gas flow rate is increased at a given bed temperature, the reaction zone temperature goes up, because a smaller fraction of the available energy is abstracted from it to maintain the bed temperature. With increasing reaction zone temperature, the rate of formation of nitric oxide increases. This accounts for the effect of gas flow rate on nitric oxide emission.

As the bed temperature is reduced, bubbles of unreacted gas pass through the reaction zone to react later, explosively, in or above the bed, after having been preheated (overheated?). The flame temperatures in these bubbles may be even higher than the adiabatic flame temperature, T_a . Higher concentrations of NO are produced in these pockets of gas. This accounts for the increasing noise, accompanied by increasing nitric oxide emission which results from reducing the bed temperature at a given equivalence ratio and flow rate (Figures 1 and 4).

In lean flames, virtually all fuel bound nitrogen was converted to nitric oxide (Figures 12 and 13). In lean and stoichiometric mixtures virtually all of the added ammonia emerged as nitric oxide except when very large amounts, 1072 ppm, were added. With dimethylamine, the result was similar.

In the reaction zone, reactive nitrogen is more likely to find an (more plentiful) oxygen atom for a partner than another nitrogen atom, and nitrogen, except in N_2 and nitric oxide, is quite reactive. N_2 and nitric oxide are relatively inert at the bed temperatures. Thus, nitric oxide, once formed is extremely stable (Figures 9, 10, and 11). Kinetics thus seems to favor the formation of nitric oxide from fuel bound nitrogen.

Rich mixtures containing fuel nitrogen evolve less nitric oxide than do lean mixtures. Figure 14 shows that at 1200K in similar runs, a stoichiometric mixture evolves 350 ppm while a mixture that is 20% rich ($\phi = 1.2$) evolves about 250 ppm. At low bed temperatures, where the equilibrium concentration of nitric oxide is low because N_2 is very stable, the nitrogen in nitric oxide is also relatively firmly bound, albeit not so firmly as in N_2 . Thus low bed temperatures, although they favor low equilibrium nitric oxide concentrations, stabilize nitric oxide if it does happen to be formed from a source other than atmospheric nitrogen. Fortunately, it may be possible to hasten its decomposition with catalysts such as nickel.

Since most of the interesting chemistry takes place in the localized hot region (usually near the distributor), very little additional chemical change takes place in the greatest portion of the bed, where there are effectively no inhomogeneities. Thus, changes in operating variables such as fuel-air ratio (Figure 6), which affect what happens in the hot zone, most strongly affect nitric oxide concentrations. High combustion intensities and flow rates increase nitric oxide concentration at a given set of "average" bed operating conditions (Figure 4). This is shown in Figure 5, in which data obtained with 4 particle sizes ranging from 0.46 mm to 1.55 mm are superimposed. Over a ninefold variation of gas velocity, with changing particle sizes, nitric oxide formation increased regularly with gas velocity. Operating variables which affect only the "average" bed conditions, bed temperatures, particle size, and bed depth do not affect nitric oxide evolution very much.

The combustion of carbon would be somewhat different. Carbon particles burn in diffusion flames. Burning is diffusion limited rather than reaction-rate limited. Combustion

takes place in a region near the surface of the carbon in which temperature and fuel-air ratio are related in a way that is totally different from what they are in premixed flames. Carbon particles are scattered throughout the bed. Macroscopically, the bed is homogeneous, but microscopically, around each carbon particle there are very large gradients in temperature and composition. As we have seen, both of these factors affect thermal nitric oxide production.

In any case, when the fuel contains bound nitrogen, nitric oxide emissions may possibly be reduced by operation of the bed at somewhat elevated temperatures. Figure 10 suggests that with 1000 ppm in a fuel-rich bed, higher temperature operation will reduce concentrations, probably by increasing the rate of destruction of nitric oxide. (This concentration is far above the equilibrium value.) Raising the temperature to reduce nitric oxide emissions is contrary to our intuitive ideas, and it may be undesirable from the standpoint of sulfur scavenging and avoiding slag formation. The optimum operating conditions will, of course, have to be chosen from a consideration of the effects of many variables.

In conclusion, then, it seems that the prospect of reducing nitric oxide emissions from combustion by using a fluidized bed process appears to be good. When fuel contains no bound nitrogen, nitric oxide emissions are low, even with lean mixtures. When the fuel contains bound nitrogen it may be desirable to burn rich mixtures in beds, relying on catalysts to keep nitric oxide levels near their low equilibrium values, and then to complete combustion in a later stage.

Acknowledgment

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Fate of Trace Metals in Los Angeles County Wastewater Discharge

Francois M. M. Morel,* John C. Westall,¹ Charles R. O'Melia,² James J. Morgan³

Ralph M. Parsons Laboratory for Water Resources and Hydrodynamics, Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge, Mass. 02139

■ A chemical equilibrium model of the Los Angeles County sewage is presented which accounts for the chemical speciation of trace metals. Many metals are found in very insoluble sulfide (Zn, Hg, Ag, Cu, Cd, Pb) or oxide (Cr, Fe) forms, while some (Ni, Co, Mn) are relatively soluble. A study of the oxidation and dilution of the sewage by seawater demonstrates that most metals tend to be solubilized upon disposal in the ocean and that unmeasurable increments in the natural metal concentrations should result in the farfield. It is argued that the sewage particulate is not mobilized in the vicinity of the outfall and that the nearby sediments are a mixture of naturally occurring sediments and sewage particulate. About 0.5% of the sewage particulate—and its metal content—can be accounted for in the reduced area.

The possible short- and long-range effects of the disposal of trace metals in the coastal environment are a matter of growing concern. Rational management of such practices is made difficult by lack of understanding of the factors that regulate the fate of metals in the ocean. This report represents an effort to confront our understanding of the chemistry of wastewaters discharged into seawater with experimental data on the concentrations of various metals in sediments adjacent to a major outfall system. The first section of this report outlines some background information on the Joint Water Pollution Control Project (JWPCP) of the Los Angeles County Sanitation District chosen for this study. In the second section, chemical equilibrium models of sewage and sewage-seawater mixtures are employed to examine the possible speciation of trace metals that are discharged. The fate of metals deposited in the area adjacent to the outfalls is discussed in the third section.

¹ Present address, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

² Present address, Department of Environmental Science and Engineering, School of Public Health, University of North Carolina, Chapel Hill, N.C.

³ Present address, W. M. Keck Laboratory, California Institute of Technology, Pasadena, Calif.

JWPCP Outfall System

The JWPCP outfall system is well suited for a study on the fate of metallic pollutants for several reasons:

1. The quantities of wastewater are very large (~370 mgd) and they consist of both domestic and industrial sewage containing high metal concentrations, so that the effects are most dramatic and easily measured. Table I gives the average concentrations in the treated effluent of 11 metals selected for this study. These concentrations are compared to the concentrations in the Southern California coastal waters and the ratios are indicative of possible magnitudes of effects. Chromium and lead are comparatively the most concentrated metals in the sewage with ratios $C_{\text{sewage}}/C_{\text{seawater}}$ of about 4000 and 6000, respectively. The last three columns of Table I give mass emission rates for the metals studied: JWPCP outfalls are major contributors of metals to the Bight. For several metals they account for more than a quarter of the total input estimated as the sum of sewers, rivers, rainfall, aerial fallout, vessel dumping, and various discrete sources.

2. The JWPCP sewage treatment is fairly typical of commonly used primary treatment techniques. The sedimented sludge is digested anaerobically, centrifuged, and the centrate is re-mixed with the primary effluent, contributing much of its particulate—and metal—load.

3. The two main JWPCP submarine outfalls—a 90-in. "Y" outfall and a 120-in. "dog leg" outfall, both discharging at a depth of 60 meters at the edge of the continental shelf—have been designed for specific hydraulic performance; the rise of the plume as well as the dilution of sewage by seawater have been especially well studied (1).

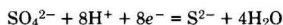
4. Monitoring programs of the sewage composition have been carried out at the JWPCP plant (2), and a study of the metal concentrations in the nearby sediments has been completed (3) so that an experimental data base is available.

Equilibrium Models

To discuss the behavior of sewage upon dilution and oxidation, it is first necessary to understand the redox level and speciation of metals in the sewage itself. For this pur-

pose, a chemical equilibrium model (4, 5) of the inorganic species in sewage has been used; to this basic inorganic model a set of representative organic ligands and an adsorbing surface have been added, and the effects of both on metal speciation will be seen.

The input to the inorganic model includes the analytical concentrations of trace metals found in sewage, the analytical concentrations of major metals and ligands, and the measured pH of 7.7 (Table II, column 1). Because the redox level (p_e) is not an experimentally measured quantity, we have attempted to find a range of p_e where the calculated partition of metals between the particulate and soluble phases matches the experimentally determined filterable/nonfilterable fractionation. In the JWPCP sewage, the p_e is probably best described as a function of the bacterially mediated reduction of sulfate,



coupled with the oxidation of organic carbon. The activity of SO_4^{2-} is much greater than that of S^{2-} and effectively constant: Thus, the free sulfide activity—hence the solubility of metal sulfides—is a valuable indicator of the redox level of sewage. [It could be argued here that metals are rendered insoluble by precipitation with complex organic matter; however, the paucity of data on such forms does not allow their inclusion in the model. In any case, equilibrium between metals and sulfide—with the resulting precipitation of very insoluble metal sulfides—ought to be a good approximation for sewage which has been digested (6).]

Trace metal speciation as a function of the negative logarithm of the total sulfide concentration in the sewage ($p\text{TOTS}^{2-}$) is presented in Figure 1. It is shown that over the range $p\text{TOTS}^{2-} = 3.7$ –5.5, the activity of free sulfide ion is controlled successively by the solubilities of iron, zinc, and copper sulfides; accordingly the p_e as computed from the sulfate/sulfide equilibrium varies over three plateaus at p_e -4.0, -3.47, and 2.94. (For future study it should be noted that important analytical information about sewage composition is given either by a precise measure of the free sulfide concentration or by the relative analytical concentrations of copper, zinc, iron, and sulfide. Routine analytical techniques that are now in use do not really yield either.)

Experimental data (2, 3) show the majority of trace metals to be in the nonfilterable fraction of sewage, with the exception of nickel, cobalt, and manganese found in approximately equal concentrations in the filterable and non-

filterable fractions. ("Nonfilterable" is operationally defined as the solid retained by a 0.45 μM Millipore filter. This is taken as an approximation of the total suspended matter.) In attempting to match these data to a region in Figure 1, one finds the transition range between p_e -4.0 and p_e -3.47 to be in reasonable agreement: Most metals are in an insoluble sulfide (Zn, Hg, Ag, Cu, Cd, Pb) or oxide

Table I. Trace Metals in JWPCP Sewage Outfall

	Concentrations, $\mu\text{g/l}$, estimate			Mass emission rates, T/yr, to So. Calif. Bight		
	JWPCP ^a sewage	So. Calif. ^b seawater	Sewage-seawater ratio	JWPCP ^c	Total ^d	JWPCP/total ratio
Fe	9900	10.0	1000	5300	20,000	0.27
Zn	2400	10.0	250	1300	2,400	0.54
Cr	860	0.2	4000	460	700	0.66
Cu	560	3.0	200	300	1,000	0.30
Pb	250	0.04	6000	140	550	0.25
Ni	240	6.0	40	130	400	0.33
Mn	130	2.0	70	70	350	0.20
Cd	30	0.1	300	16	65	0.25
Ag	20	0.3	70	11	20	0.55
Co	10	0.2	50	5	25	0.20
Hg	1	0.03	30	0.5	10	0.05

^a Data from SCCWRP (2) 1971 averages. ^b Selected from SCCWRP tabulation (2) of literature data. These data show great variability. This is particularly true for the less abundant metals, the estimates of which are probably too high. ^c Mass emission rates obtained by multiplying column 1 by $540 \times 10^9 \text{ l/yr}$ (1971 flow). ^d Sum of wastewater discharges, surface runoff, vessel coating, ocean dumping, rainfall, and aerial fallout as estimated by critical examination of SCCWRP data (2).

Table II. Equilibrium Models of JWPCP Sewage

- Log total Concn	Inorganic model, ^a %	Addition of organics, ^{a,b} %	Addition of adsorbing surface, ^{a,b,c} %
Fe, 3.7	$\text{Fe}_2\text{O}_3(\text{s})$, 100	$\text{Fe}_2\text{O}_3(\text{s})$, 100	$\text{Fe}_2\text{O}_3(\text{s})$, 100
Cr, 4.8	$\text{Cr}(\text{OH})_3(\text{s})$, 97 $\text{Cr}(\text{OH})_4^-$, 3	$\text{Cr}(\text{OH})_3(\text{s})$, 97 $\text{Cr}(\text{OH})_4^-$, 3	$\text{Cr}(\text{OH})_3(\text{s})$, 52 $\text{Cr}(\text{OH})_4^-$, 3 ADS, 45
Cu, 5.0	$\text{CuS}(\text{s})$, 100	$\text{CuS}(\text{s})$, 100	$\text{CuS}(\text{s})$, 100
Cd, 6.5	$\text{CdS}(\text{s})$, 100	$\text{CdS}(\text{s})$, 100	$\text{CdS}(\text{s})$, 100
Pb, 6.0	$\text{PbS}(\text{s})$, 100	$\text{PbS}(\text{s})$, 100	$\text{PbS}(\text{s})$, 100
Zn, 4.5	$\text{ZnS}(\text{s})$, 100	$\text{ZnS}(\text{s})$, 99	$\text{ZnS}(\text{s})$, 99
Ag, 6.7	$\text{Ag}_2\text{S}(\text{s})$, 100	$\text{Ag}_2\text{S}(\text{s})$, 100	$\text{Ag}_2\text{S}(\text{s})$, 100
Hg, 8.3	$\text{HgS}(\text{s})$, 100	$\text{HgS}(\text{s})$, 100	$\text{HgS}(\text{s})$, 100
Ni, 5.4	$\text{NiS}(\text{s})$, 42 Ni^{2+} , 2 $\text{Ni}(\text{CN})_4^{2-}$, 56	$\text{NiS}(\text{s})$, 22 Ni^{2+} , 2 $\text{Ni}(\text{CN})_4^{2-}$, 56 GLY, 10 GLU, 10	$\text{NiS}(\text{s})$, 14 Ni^{2+} , 2 $\text{Ni}(\text{CN})_4^{2-}$, 56 GLY, 10 GLU, 10 ADS, 8
Co, 6.8	$\text{CoS}(\text{s})$, 97 Co^{2+} , 2	$\text{CoS}(\text{s})$, 95 Co^{2+} , 2 GLU, 2	$\text{CoS}(\text{s})$, 93 Co^{2+} , 2 GLU, 2 ADS, 2
Mn, 5.6	Mn^{2+} , 50 MnHCO_3^+ , 24 MnSO_4 , 19 MnCl^+ , 6	Mn^{2+} , 50 MnHCO_3^+ , 24 MnSO_4 , 19 MnCl^+ , 6	Mn^{2+} , 45 MnHCO_3^+ , 21 MnSO_4 , 17 MnCl^+ , 6 ADS, 9

^a Other inputs to the model (2): $\text{pH} = 7.7$, $\text{pCa} = 2.75$, $\text{pMg} = 3.0$, $\text{pBa} = 5.0$, $\text{pAl} = 4.5$, $\text{pCO}_3 = 2.0$, $\text{pSO}_4 = 2.3$, $\text{pCl} = 1.8$, $\text{pF} = 4.0$, $\text{pNH}_3 = 2.2$, $\text{pPO}_4 = 3.3$, $\text{pCN} = 5.0$. Ionic strength = 0.01, $T = 25^\circ\text{C}$. ^b Organic ligands added: pAcetate = 3.3, pGlycine = 3.8, pTartrate = 3.6, pGlutamate = 3.7, pSalicylate = 3.8, pPhthalate = 3.9. ^c Adsorbing surface: $10 \text{ m}^2 \text{ l}^{-1}$, constant potential. The computation is performed according to the James and Healy model (8) which considers coulombic, solvation, and specific chemical energy interactions. The chemical energy term is essentially a fitting parameter and has been chosen arbitrarily in the model to represent high chemical affinity of the adsorbing surface for all metals (about 10 kcal/mol).

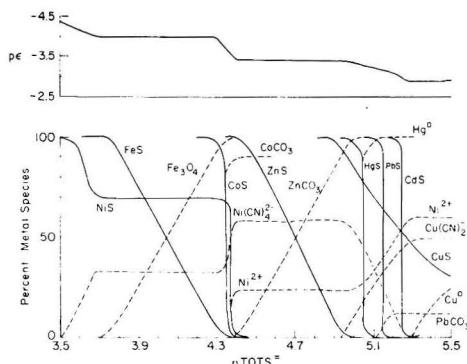


Figure 1. Metal speciation in sewage vs. total sulfide. Input is similar to that given for the inorganic model in Table II, except that the total sulfide is imposed and the p_e is calculated from the $\text{SO}_4^{2-}/\text{S}^{2-}$ equilibrium.

(Cr, Fe) form; the sulfides of cobalt and nickel dissolve in this region, cobalt being replaced by a more soluble CoCO_3 , and nickel being rendered soluble. Significant amounts of chromium, cobalt, nickel, and manganese may be adsorbed onto the particulate fraction, as will be discussed later.

A better agreement between model and data could certainly be achieved through minor variations in pH, p_e , or equilibrium constants. But in any case, this basic inorganic model allows us to choose a range of p_e from which computation of dilution and oxidation effects can begin. Table II, column 2, presents a summary of metal species in the inorganic model of JWPCP sewage, computed at an intermediate p_e in this range, $p_e = -3.6$. As stated above, most metals are in insoluble forms; the sulfides of cobalt and nickel are partially dissolved, and manganese is in various soluble forms.

To make the model more realistic, organic ligands should be included. However, since very little analytical information concerning organics in the JWPCP sewage is available, we have chosen to select a set of organics that represent various functional groups and complexing behaviors consistent with the results of Manka et al. (7) for the organic fraction of various wastewaters. Acetate, tartrate, glycine, salicylate, glutamate, and phthalate were added, each at an equivalent carbon concentration of $10^{-3}M$ ($6 \times 10^{-3}M$ carbon is an upper limit on the experimental dissolved organic carbon in JWPCP sewage). The principal results of this computation are shown in the third column of Table II. By choosing an upper limit on the dissolved organic carbon, it is hoped that the probable effects of organic ligands will be overestimated; nonetheless the addition of organics has little effect on the results of the computation. The only metals that show significant binding with the organic ligands are cobalt and nickel; the reactivity of most other metals is limited due to the extreme insolubility of the solid forms.

The last column of Table II shows the results of a model similar to that of column 3 but including an adsorbing surface in addition. The surface was made to possess characteristics similar to those of metal oxides, and the computations of adsorption were made according to the model of James and Healy (8). Only four metals were found to adsorb markedly: chromium, cobalt, nickel, and manganese. That the particulate fraction of manganese in sewage (about 20–50%) is indeed adsorbed, can be experimentally corroborated by mixing sewage with seawater and readily "solubilizing" the manganese. In contrast, no such desorption effect can be shown for chromium, nickel, or cobalt.

Overall an equilibrium model for sewage can be made to match closely the existing experimental data, but such effort is not warranted until more detailed analytical data are obtained. Since organics are likely to be less important in the plume where they start decomposing, and since the metals studied should readily desorb in seawater, the inorganic model will serve as our basic tool to investigate the chemical processes that should govern the fate of sewage metals entering the ocean.

Figure 2 presents in concise form a summary of results from a large number of computations for various mixtures of sewage and seawater at various redox potentials. The pH imposed at each dilution was calculated from the carbonate alkalinity and total carbonate of the corresponding sewage-seawater mixture. The ionic strength was approximated by the appropriate dilution of sewage ($I = 0.01$) with seawater ($I = 0.5$). The lines in Figure 2 demarcate the domain of p_e and dilution in which various insoluble forms of the trace metals are stable. A detailed description of soluble speciation has been omitted to preserve clarity in the figure.

Figure 2 shows that, in general, oxidation has a much greater effect on the solubilization of metals than dilution.

However, there are two effects of dilution which should be mentioned: (1) at low dilution and moderate oxidation the carbonates of zinc, lead, and cobalt precipitate because of the high concentration of carbonate in sewage, and the hydroxide of chromium(III) precipitates because of the relatively high concentration of chromium. (2) At high dilution, the chloride from seawater can bind significant quantities of metals, and for the well-oxidized, well-diluted system, the chloride complexes of Ag, Hg, Pb, Cd, and Mn represent the major species of these metals.

The significant effect of oxidation on most metals (Fe, Zn, Cu, Co, Ni, Pb, Cd, Hg, Ag) is the dissolution of the sulfide solid; in addition, a more complicated behavior for Cu and Hg is observed. A fraction of the cupric sulfide is oxidized first to a $\text{Cu}(\text{CN})_2^-$ (cuprous) complex, and after exhaustion of available CN^- , the formation of metallic copper is seen. Upon further oxidation, various soluble complexes of the cupric ion predominate. Mercury shows a similar pattern of oxidation from HgS to metallic liquid mercury and finally to the mercuric ion. At higher p_e levels are the oxidation of Cr(III) to Cr(VI), the transition of Fe_3O_4 to FeOOH , and the formation of insoluble manganese and cobalt oxides.

As sewage enters the ocean environment and is simultaneously diluted and oxidized, the chemical equilibrium is presented on Figure 2 by a point moving to the right and upward. No kinetic information is contained in this figure such that, unless the reactions are fast, it does not describe the composition of the system but, rather, the driving force at each point. Typically, in the JWPCP outfalls, a dilution of 50 is obtained immediately in the plume, and little or no oxidation takes place at that time. For the soluble fraction or the light particles transported far from the outfall, higher dilutions are slowly obtained at the same time that oxidation proceeds. A final situation is reached, represented by the top right-hand corner of Figure 2, where most of the metals are solubilized in the free form or various chloride, carbonate, or hydroxide complexes.

This solubilization of metals increases their retention time in the water column and ensures a very high dilution. Hence, in the farfield the concentrations of metals should not be increased measurably over the natural seawater background. The situation is drastically different in the immediate vicinity of the outfall as will now be discussed.

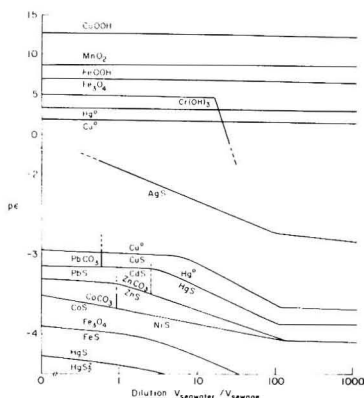


Figure 2. Metal solids as function of dilution and oxidation

Composition of diluting seawater:

$p\text{H} = 8.2$, $p\text{Ca} = 2.0$, $p\text{Mg} = 1.2$, $p\text{Ba} = 6.7$, $p\text{Fe} = 6.8$, $p\text{Zn} = 6.8$, $p\text{Cr} = 8.4$, $p\text{Cu} = 7.3$, $p\text{Pb} = 9.7$, $p\text{Ni} = 7.0$, $p\text{Mn} = 7.4$, $p\text{Cd} = 9.0$, $p\text{Ag} = 8.5$, $p\text{Co} = 8.3$, $p\text{Hg} = 9.8$, $p\text{Al} = 7.0$, $p\text{CO}_3 = 2.6$, $p\text{SO}_4 = 1.5$, $p\text{Cl} = 3.6$, $p\text{F} = 4.2$, $p\text{NH}_3 = 6.0$, $p\text{PO}_4 = 5.7$, $p\text{CN} = 9.0$. Ionic strength = 0.5

Table III. % Concentrations Relative to Zinc

	Sewage		Top 4 cm of sediments	
	Total (SCCWRP)	Particulate (Galloway)	B.21	B.20
Zn	100	100	100	100
Ag	0.83	0.78	0.89	0.93
Cr	36	41	41	41
Cu	23	27	28	29
Pb	10	14	19	20
Cd	1.2	1.6	2.7	3.1
Co	0.41	0.20	0.22	0.32
Ni	10	5.3	1.3	1.6
Mn	5.4	3.6	15	14

Nearfield Deposition: The Question of Mobilization

It is well documented (2, 9) that, in the normally oxic ocean floor off Palos Verdes, there exists an area of reduced surface sediments about 10 miles long and one mile wide on a NW-SE axis around the county outfall system. Since enough organic carbon must be brought continuously to the ocean floor to maintain anaerobic conditions in this region, a relatively high sedimentation of sewage particulates is implied. We shall examine in this section what metals are likely to be mobilized in the reduced sediments, how this is reflected in the changes of relative concentrations from sewage particulate to surface sediments, and whether metal concentrations in the reduced area are consistent with estimated sedimentation rates.

The system composed of the reduced surface sediments and the associated anoxic seawater is roughly equivalent to a very low dilution of sewage by seawater: After initial dilution in the plume, an effective reconcentration takes place for those particulates that settle near the outfall. Since, in addition, bacterial activity must maintain the redox level of these sediments at about the same p_e as that of primary effluent, the bottom left corner of Figure 2 represents the possible set of solid species to be expected in this region. Of the metals under study, only nickel, possibly cobalt, and, of course, manganese are likely to be dissolved in the reduced sediments.

Given an average current velocity of 0.1 m sec⁻¹, suspended particles will be transported outside of the area of reduced sediments within 24 hr. Our laboratory experiments have demonstrated no significant mobilization of metals, except nickel and manganese, over a day, in aerated mixtures of sewage and seawater. It seems therefore justifi-

fied to assume that no significant mobilization in the water column or in the sediments will occur for iron, zinc, silver, chromium, copper, lead, cadmium, and mercury contained in the particles that reach the reduced sediments. This will be referred to as the "no-mobilization hypothesis."

Except for iron, manganese, and, to a lesser degree, cobalt, all metals studied are found in much greater concentrations in the sewage particulate than in the local natural sediments (10). Since zinc, silver, chromium, copper, lead, and cadmium are not likely to be mobilized, and since they are comparatively scarce in natural sediments, one would expect the relative concentrations of these metals to be similar in sewage particulate and in the top layers of the sediments adjacent to the outfall. Table III shows a comparison of these concentrations normalized to that of zinc. The first column corresponds to the data published by SCCWRP for the average concentrations of metals in the total sewage for 1971. The second column is Galloway's measurement of a one-week composite of metal concentrations in sewage particulate. (The actual metal concentrations corresponding to column two are about 40% lower than those corresponding to column one—e.g., the total concentration of zinc in the sewage is reported as 2.4 mg l.⁻¹; the concentration of zinc in the particulate fraction is 4100 mg kg.⁻¹ while the average total suspended solids is 330 mg l.⁻¹—this is equivalent to 1.4 mg l.⁻¹ of zinc in sewage. However, the relative concentrations are in reasonably good agreement.) Cobalt, nickel, and manganese are seen to be twice as concentrated in the total sewage as in the particulate, in agreement with their particulate and soluble fractions as previously mentioned. The numbers given in columns three and four of Table III have been obtained from the average of concentrations reported by Galloway for the top 4 cm of box cores B20 and B21, situated right at the "Y" outfall and about one mile N-W of it, respectively.

The values for zinc (of course), silver, chromium, and copper show fairly good agreement in the four columns as expected. Lead and cadmium show unexpected relative enrichment in the sediments. For the remaining three metals—cobalt, nickel, and manganese—significant fractions of which are soluble in the sewage, only the last three columns should be compared. The numbers for cobalt show fair agreement, probably fortuitously so, given the $\pm 100\%$ error reported for the core data, the possibility of cobalt mobilization, and the high background of cobalt in sediments. Nickel is clearly mobilized while manganese is much more concentrated in the sediments than the sewage particulate, reflecting the large natural abundance of manganese in the area. The same situation is to be expected for iron.

Figure 3, obtained by normalizing the surface concentrations of metals in various Phleger and box cores to that of the surface concentration of B20, demonstrates that the relative metal concentrations are more or less conserved throughout the surface of the reduced sediments. Despite some scatter in the data, the figure suggests strongly that metal concentrations in the reduced sediments depend solely on the position of the sample. This is in agreement with the no-mobilization hypothesis.

A study of relative metal concentrations in the surface sediments thus demonstrates only one major discrepancy with the simple expected result: a relative enrichment of lead and cadmium. This difficulty can be resolved in three ways: (1) One can question the data, which leaves no possible conclusion until more data are gathered; (2) a mobilization of unknown nature can be postulated for all metals. Similar mobilization of Zn, Ag, Cr, and Cu, higher than that of Pb and Cd would explain the data; (3) the no-mobilization hypothesis can be upheld and relative enrichment of lead and cadmium has then to be explained.

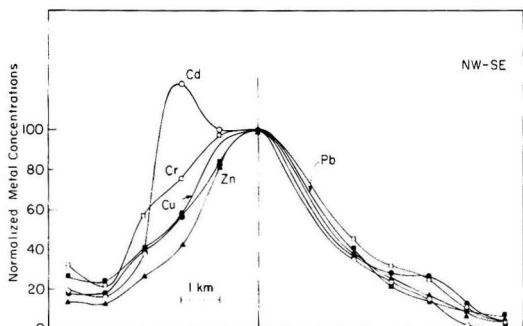


Figure 3. Total concentration in sediments vs. distance from outfall. Cobalt, nickel and manganese have been omitted as irrelevant. Data for silver are scattered while those for iron and mercury are not available.

Although the success of the no-mobilization hypothesis as shown by Figure 3 and the top four lines of Table III argues against it, mobilization (second alternative above) cannot be disproved and has in fact been postulated by Galloway (3) and Hendricks (11) to explain the data. We shall pursue the third hypothesis—no-mobilization—and demonstrate that it is consistent with estimated sedimentation rates and that plausible mechanisms for enrichment of lead and cadmium exist.

Having studied the similarities that metal concentrations in sewage particulate and in the sediments exhibit relative to one another, one has to remember that metal concentrations in the sediments are about three times smaller than those in the sewage particulate. Why? Is this consistent with what we know of the fate of the sewage? Two possible explanations can be entertained: First, and contrary to the no-mobilization hypothesis, the metals might be mobilized from the particulate during and after settling to the ocean floor. Second, an increase in the bulk mass of the particulate might be taking place either through oxidation or by mixing with natural sediments, thus apparently "diluting" the metal concentration. The second explanation would be consistent with the no-mobilization hypothesis.

To decide which of these two mechanisms is more likely, a new piece of experimental information is needed. It is provided by Myers' studies of organic carbon concentrations (12). Myers' experiments demonstrate minimal reduction of organic carbon concentration in the particulate of aerated JWPCP sewage-seawater mixtures over 24 hr. Under anaerobic conditions no significant decrease in organic carbon concentration is seen for periods up to a month, probably due to incomplete oxidation of organics by sulfate. It seems thus logical to extend the no-mobilization hypothesis to the organic fraction of sewage particulate that reaches the nearby reduced sediments. Organic carbon concentrations (12) in sewage particulate (34%), natural particulate (1%), and the top 4 cm of cores B20 and B21 (11%) would then imply a ratio of about 2 to 1 for the rates of sedimentation of natural particulate over that of sewage origin in the area of these cores. This is about the ratio that would explain the concentrations of Zn, Ag, Cr, and Cu at the surface of these cores if data consistent with that of SCCWRP are used for concentrations of metals in sewage particulate. (That is, Zn: 7200 mg kg⁻¹ in sewage particulate; 130 mg kg⁻¹ in natural particulate; 2400 mg kg⁻¹ in the top 4 cm of B20 and B21.)

By integrating the total mass of organic carbon accumulated near the outfall, Myers has estimated that only about 0.5% of the total sewage organic carbon can be accounted for in the reduced sediments. Since we are hypothesizing

that no significant mobilization of any kind is taking place in this area, it is crucial to verify that this is consistent with the aquatic transport and settling characteristics of the sewage particulate. Figure 4 presents typical results obtained in the laboratory with a sedimentation column. First it should be noted that within the scatter of the data, the metals seem to settle at the same rate as the bulk of the sewage particulate. This was implicitly assumed in the preceding discussion.

Second, the dramatic differences between the sedimentation velocities observed in undiluted sewage and in sewage-seawater mixtures can be shown to be primarily an effect of the dilution: Through serial dilutions and multi-level sampling of the sedimentation column, interactions—flocculation, coagulation—between particles can be demonstrated to take place, increasing apparent sedimentation velocities of the suspensions more concentrated in sewage. [Sedimentation velocities can be greatly overestimated in sedimentation column experiments. There is no easy way to measure what actual sedimentation velocities are for the high dilution of sewage in the plume, since even for the maximum sewage-seawater dilutions practicable in the laboratory (1:30), particle interaction can be shown to take place. It should also be noted that comparison of various sedimentation column experiments is rendered difficult by the critical importance of the positioning of the sampler.] By use of an average plume height of 20 meters and maximum settling time of 24 hr it is estimated that only these particles with sedimentation velocities in excess of 10⁻² cm sec⁻¹ will reach the reduced sediments. For experiments at 1:10 dilutions, 3 ± 2% of the total sewage particulate is found to settle faster than 10⁻² cm sec⁻¹. This can be said to be consistent with an estimate of 0.5% of the total sewage particulate settling in the reduced sediments adjacent to the outfall.

Estimating that half a percent of the total suspended solid mass discharged through the outfall in 1971 (330 mg l.⁻¹ × 5.4 10¹¹ l.) settles over an area of about 15 km², one obtains an average sedimentation rate of about 6 mg year⁻¹ cm⁻² for the sewage particulate over the reduced area. This is to be compared with 9 mg year⁻¹ cm⁻² reported by Emery (13) as the natural sedimentation rate in this region. However, in the immediate vicinity of the outfall, the sedimentation rate of sewage particulate is likely to be much higher than the computed average value so that some explanation has to be found for the expected 2 to 1 ratio of natural sewage sedimentation rates over cores B20 and B21. In this respect, it should be noted that the interactions observed among particles in sedimentation column experiments are likely to take place in the plume as well, and that the sedimentation rate of natural particulate is probably increased significantly by the presence of the sewage particulate. This point has been made by Myers as has the probable increase in productivity and thus in "natural particulate"—near the outfall. Further study is indicated for these phenomena. The relative sedimentation rates of natural and sewage particulate implied by the no-mobilization hypothesis do not seem unlikely in any case.

It remains to explain the relative enrichment of lead and cadmium. A possible explanation is that lead and cadmium are much more abundant than expected in the "natural" particulate near the outfall. This could be mediated by preferential uptake of these metals by microorganisms. Another explanation is that lead and cadmium particles settle faster than the bulk sewage particulate. Data such as presented in Figure 4 do not confirm or contradict this possibility, but the consistency of lead and cadmium with other metals in Figure 3 argues against it. Also it is intriguing to note that lead and cadmium are the only two metals for

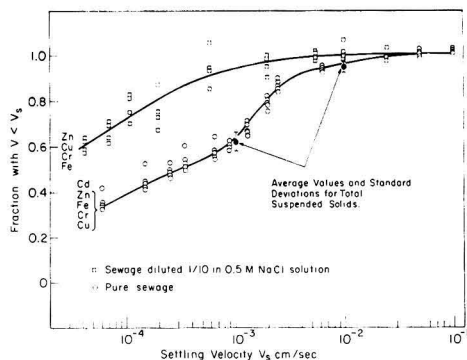


Figure 4. Settling velocity distribution of 24-hr sewage composite

which settling of airborne particles could contribute significantly to the deposition in the sediments (10). Flocculation of these particles with sewage particulate in the water column could lead to the relative enrichment of lead and cadmium in the sediment.

Whatever the mechanism of enrichment, it should be noted that since only 0.5% of the total sewage particulate is postulated to settle in the reduced area, even a small supplementary source or differential settling behavior of lead and cadmium would explain the relative enrichment in the sediments adjacent to the outfall. Elucidation of the actual mechanisms involved in differentiating the fate of lead and cadmium from that of other metals is clearly an important area for further research. So far we are merely speculating.

Conclusion

In the particular case of the Los Angeles County sewage outfall system, it seems that much insight can be gained into the factors that govern the fate of trace metals by using chemical equilibrium models. It is argued that metals transported in the farfield tend to be solubilized by dilution and oxidation and that the objective—not necessarily desirable—of effective waste dispersion is well met in their case. An extremely simple interpretation of existing data on the metal content of the reduced sediments near the outfall is proposed, where the only significant phenomenon is a mixing of “natural” and sewage particulate without significant mobilization of any kind for most metals. Consistent with this interpretation is an estimate that on the order of 1% of the total sewage particulate—and 1% of the total sewage metals—is deposited. Myers has estimated that 0.5% of the sewage organics could be accounted for in these sediments. Differences in the fate of various metals can, in some cases, be explained on the basis of different chemical behavior—e.g., the more soluble characteristics of cobalt, nickel, and manganese—while in other cases, differences in physical (sedimentation, flocculation) or biological (microorganism uptake) behavior have to be postulated to explain the data as is the case for the relative enrichment of lead and cadmium in the reduced sediments.

This study points out important research needs in the area of analytical chemistry of wastewaters as well as in the area of physical transportation processes in coastal waters. Specifically a new direct or indirect method of evaluating the oxidation-reduction level of reduced solutions should be developed, and much theoretical and experimental research on the interactions of suspended particulate matter is necessary to upgrade our understanding of the fate of metal pollutants in waste water.

It should be emphasized that the very reduced and metal-rich nature of the JWPCP sewage is not typical of all

sewage discharged from marine outfalls. For example, Chen and Rohatgi (14) have found the metals in the Los Angeles City sewage to be rather easily solubilized in contrast to the situation in the Los Angeles County sewage—reflecting assuredly the differences in treatment processes. Extension of the methodologies used in this study to other particular situations is certainly warranted; extension of the results is not.

Acknowledgment

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New Orleans Drinking Water Sources Tested by Gas Chromatography–Mass Spectrometry

Occurrence and Origin of Aromatics and Halogenated Aliphatic Hydrocarbons

Betty J. Dowty, Douglas R. Carlisle, and John L. Laseter*

Department of Biological Sciences, University of New Orleans, Lakefront, New Orleans, La. 70122

■ Low-molecular-weight volatile organics were thermally extracted from water samples before, during, and after processing by a New Orleans area municipal water treatment facility. The volatile components were trapped on a solid polyphenyl ether adsorbent and resolved by high resolution gas chromatographic procedures. A gas chromatography–mass spectrometer–computer combination was used to identify major aromatic and halogenated aliphatic components. Approximately 60–70 organics were commonly present in finished water. They varied considerably from day to day in their relative concentrations. A commercial source of artesian water, as well as deionized charcoal-filtered finished water, was also analyzed. These latter water sources contained a wide variety of organics of which many are common to finished water.

There are several techniques, such as liquid–liquid solvent extraction techniques (1), recovery on ion-exchange resins such as Amberlite (1), carbon adsorption (2), and head space sampling techniques (3, 4) to extract organics from water for analysis. A novel technique described herein has been successfully applied to the qualitative analysis of trace volatile organics in water following their thermal extraction. Previous reports by this laboratory have employed this new technique to monitor low-molecular-weight organics present in blood plasma of New Orleans residents and their drinking water (5), and body tissues (6). These studies revealed many halogenated hydrocarbons in New Orleans drinking water, several of which had not previously been identified. Another study conducted to locate the origin of these halogenated hydrocarbons (7) revealed that some of the compounds appear to be introduced in the water treatment process itself, at the chlorination step of the procedure.

This is not the first time that the chlorination process has been suspect. Independent studies by another laboratory also indicate that it is likely that chlorination introduces new compounds into the water (8), although identification of these compounds was incomplete. Because little is known of the origin of these compounds, this study was undertaken to identify by mass spectrometry the low-molecular-weight organics isolated at various stages of the water treatment process. Finished water used in this investigation was derived from the lower Mississippi River. Two alternate sources—i.e., deionized charcoal-filtered water, and bottled artesian water were also studied. Major emphasis was placed on the identification of halogenated aliphatic and aromatic constituents of water, as these are the compounds of interest from a health standpoint. Little is known of the toxic and health aspects of these compounds when ingested by man over long periods of time. Even less is known about antagonistic or synergistic effects elicited by these compounds acting in the presence of one another.

Experimental

Sample Collection and Source Description. Water samples were collected and stored in 1-liter acid-washed glass bottles with screw caps until analyses were performed. One-liter water samples were collected for chromatographic analyses, whereas approximately 3-liter samples were collected for mass spectrometric analyses. Samples representative of various steps in the water treatment process were collected from the local treatment plant that receives its water supply from the lower Mississippi River. Water treatment procedures at this plant were those common to solid contact, up-flow type units. The water is initially treated with several chemicals to control alkalinity, soften the water, and oxidize organics present. Next, the water sample is treated to remove colloidal and larger size particles at the clarifier stage of the water treatment process. En route from the clarifier to the sand and gravel filter beds, chlorine and ammonia are added to the water. In this latter process mono- and dichloramines are formed. Water samples were analyzed by gas chromatography–mass spectrometric methods from the treatment plant entrance, the clarifier effluent (which is after sedimentation and some chemical treatment, but before chlorination), and the finished water (tap water). Bottled artesian water from a local supplier was also analyzed, as well as water from a commercial laboratory charcoal filtering–deionizing unit. The commercial filtering unit (Continental Deionized Water Service, New Orleans, La.) is comprised of 0.0070 meter³ of 18–40 mesh, grade 718 charcoal contained in a glass fiber tank, as well as Amberlite IR 120 cation-exchange and Amberlite IRA 410 anion-exchange resins in a 2–3 ratio.

Sample analyses were performed according to the technique described earlier (5, 7). Volatile organics were eluted from the water sample by heating to 95°C under a stream of ultrapure helium. Totally stainless steel valves and regulators (Matheson, LaPorte, Tex.) ultrasonically cleaned, were incorporated into the helium flow system. Additionally, one molecular sieve 5A (Linde, Applied Science, State College, Pa.) and two activated charcoal (Adsorbit, Curtin, New Orleans, La.) filters were employed. The helium stream was passed over the water sample contained in a 1-liter round bottom flask and exited through a series of glass condensers to eliminate the bulk of water vapor. Volatile organics were trapped for 1 hr on poly *p*-2,6-diphenyl phenylene oxide adsorbent having 35–60 mesh size (Applied Science, Laboratories, Inc., State College, Pa.) attached to the end of a condenser train. After the polymer was trapped, it was transferred to a glass injection port liner.

The injection port of a Hewlett-Packard 7620-A gas chromatograph has been modified to accommodate the larger diameter liners. The liners containing the trapped organics were placed into the injection port maintained at 200°C. A helium stream of approximately 16 ml/min was used to transfer the volatile components onto a 1.5 m ×

Table I. Organic Constituents Identified by Gas Chromatography–Mass Spectrometry in Mississippi River Clarifier Effluent and Finished Water

Chromatographic peak no.	Compounds identified	Relative concentrations ^a		
		Finished	Clarifier effluent	Mississippi River
1	Acetaldehyde	1.28	1.38	2.10
5	Acetone	7.29	0.96	5.60
6	Diethylether	0.77	0.34	2.20
9	<i>tert</i> -Butylalcohol	4.18	3.11	11.13
14	Dichloromethane	0.33	0.25	0.77
21	Dichloroethylene + tetrahydrofuran	0.64	1.27	0.93
22	Chloroform	8.73	1.87	1.17
26	Benzene, carbon tetrachloride, dichloroethane	36.61	3.26	12.27
28	3-Methylbutan-1-al	1.11	0.20	—
31	Trichloroethylene + dichloropropane	8.28	11.48	20.87
32	Dichloropropene	0.29	0.34	1.00
34	Bromodichloromethane	12.31	38.46	2.00
37	Toluene	1.51	0.57	0.67
39	C ₈ H ₁₈	0.51	0.20	—
43	Trichloroethane	1.02	2.03	5.67
44	Tetrachloroethylene	0.31	0.64	1.87
49	Dibromochloromethane	2.48	18.16	2.17
58	(2- or 1-Naphthyl)dichloromethane	0.98	0.90	0.80
65	Xylene	0.29	0.47	0.60

^aAs computed from gas chromatographic data.

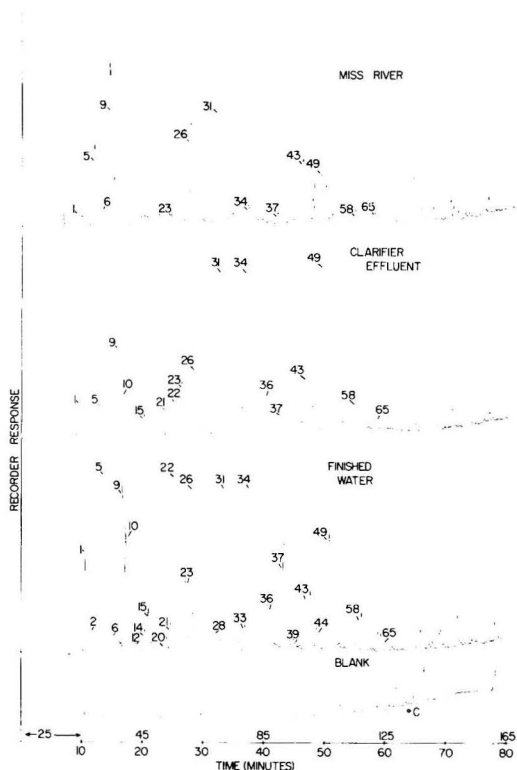


Figure 1. Gas chromatographic separations of volatile organics collected from one-liter samples of Mississippi River water at the purification plant entrance (upper trace), the clarifier effluent stage (second trace), and the finished water (third trace). A glassware and gas chromatographic system blank is also shown (lower trace). Chromatographic conditions are described in the text. Identification of numbered peaks is given in Table I

0.05 cm precolumn coated with either Emulphor ON-870 or GE SF-96 and Igepal CO 880 (Applied Science Laboratories, Inc.) held in a Dry Ice–methanol bath. After a 7-min trapping period, the cold bath was removed and the collected organics were swept onto a capillary chromatographic column (9). All glassware was cleaned with chromic acid solution and purged with an ultrapure gas stream for 1 hr while being held at a temperature of 165°C. This operation will tend to remove residual traces of organics from previous analyses and thereby reduce background. Blanks were run immediately before a given analysis to ensure that the helium carrier gas, glassware, and chromatographic system were free of any interfering organic volatiles.

Mass spectrometric analyses were performed on 3-liter water samples by venting the gas chromatographic effluent from the end of the column through a heated (200°C) stainless steel transfer line into the ion source of a Du Pont 21-491 double-focusing mass spectrometer. The source was maintained at 210°C and an ionizing voltage of 70 eV was used. The signal from the electron multiplier amplifier was processed by a PDP-12 LDP (Digital Equipment Corp., Maynard, Mass.) computer for analysis and data reduction.

Results and Discussion

Figure 1 illustrates the typical gas chromatographic separation of organic constituents present in the Mississippi River water at the plant entrance (upper trace), the clarifier effluent stage of the water treatment process (second trace), the finished water (third trace), and a glassware and chromatographic system blank (lower trace). Mass spectrometric identification of these compounds and their relative percent abundances in the chromatograms are presented in Table I. Of the approximately 70 organic constituents present in finished water that can be detected in any single analysis of liter size, the preponderance of organics present is either aromatic or halogenated aliphatic and aromatic. As can be seen, the major constituents of finished water are benzene, carbon tetrachloride, and dichloroethane (which remained unresolved in peak 26), bromodichloromethane

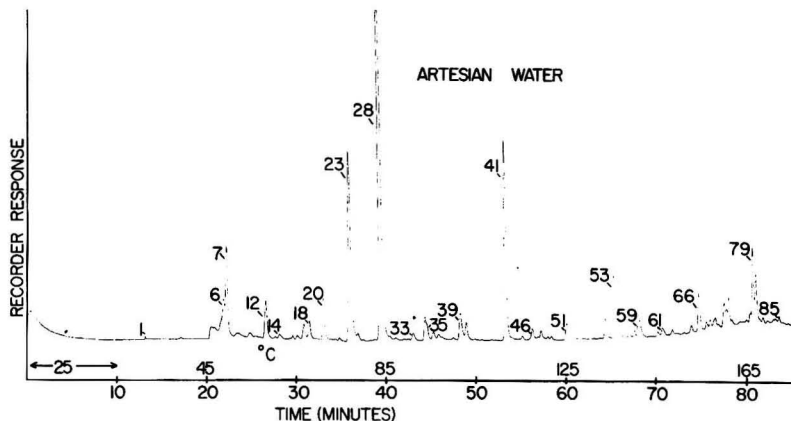


Figure 2. Gas chromatographic separation of volatile organics collected from a commercial source of bottled artesian water. Chromatographic conditions are described in the text. Identification of numbered peaks is given in Table II

(peak 34), and chloroform (peak 22). Many halogenated and aromatic organics such as trichloroethylene (peak 44), (2- or 1-naphthyl)-dichloromethane (peak 58), and xylene (peak 65) pass through the treatment plant unaltered in concentration. By contrast, however, dichloroethylene (peak 21), chloroform (peak 22), benzene, carbon tetrachloride and dichloroethane (peak 26), bromodichloromethane (peak 34), toluene (peak 37), and dibromochloromethane (peak 49) are enhanced greatly in the water treatment process. Rise in concentrations of these compounds after chlorination strongly suggests they are formed by chlorination of precursor organic molecules. Many aromatic compounds, as well as bromine-containing compounds, also appear elevated after the chlorination procedure. This strongly implies that any accidental or industrial pollution does have a direct bearing on the quality of the finished water. It should be noted that essentially every compound observed in finished water was present, usually in a much lower quantity, in the precursor river water. Previous work (7) indicates that many compounds generated in the purification process are discharged into the river. One may assume that the presence of trace quantities of such compounds may have originated from water treatment plant discards occurring upstream. Many of the halogenated and aromatic

compounds present in the river water are still present in the finished water (Table I). This suggests that they pass through the treatment plant without removal.

A commercial source of bottled artesian water was also examined, as it serves as an alternative to drinking finished

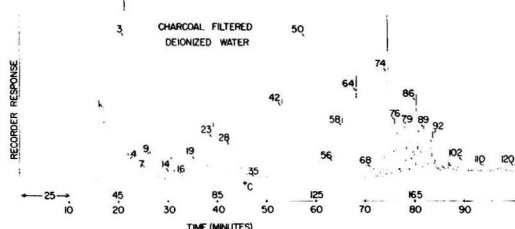


Figure 3. Gas chromatographic separation of volatile organics collected from finished water following treatment by a commercial deionizing-charcoal filtering unit. Chromatographic conditions are described in the text. Identification of numbered peaks is given in Table III

Table II. Organic Constituents Identified in Commercially Bottled Artesian Water

Chromatographic peak no.	Comps identified	Relative ^a concns
6	Acetone	1.22
7	Diethylether	2.79
12	Dichloromethane	0.96
20	Ethylacetate	1.31
23	Chloroform	5.72
28	Benzene	16.16
33	Dichloropropane	0.26
39	Bromodichloromethane	0.87
41	Toluene	6.11
51	Dibromochloromethane	0.48
53	Xylene	1.97
59	C ₉ H ₂₀	0.66
61	C ₁₀ H ₂₂	0.13
66	C ₁₁ H ₂₄	1.22
79	Dichlorobenzene	2.40

^a As computed from gas chromatographic data.

Table III. Organic Constituents Identified in Commercial Deionized Charcoal-Filtered Water

Chromatographic peak no.	Comps identified	Relative ^a concns
1	Acetaldehyde	2.71
3	Acetone	7.43
4	Diethylether	0.91
9	<i>tert</i> -Butylalcohol	1.09
19	Chloroform	1.00
23	Benzene	2.17
28	Trichloroethylene	1.74
30	C ₇ H ₁₄	1.00
32	Methylmethacrylate	0.46
42	Toluene	3.00
50	Tetrachloroethylene	13.77
56	Monochlorobenzene	0.89
57	Ethylbenzene	1.94
58	Xylene	2.31
63	Xylene	0.71
64	Styrene	3.86
74	Methylethylbenzene	6.00
89	Dichlorobenzene	1.94

^a As computed from gas chromatographic data.

water in the local area. The chromatographic results are shown in Figure 2. Compound identification and the relative percent abundance are shown in Table II. By examining Figure 2, it is evident that there are much lower concentrations of organics in the artesian water. However, it can be seen that many of the organics are the same as those in the finished water. In this particular sample, chloroform, benzene, and toluene are the major constituents. Toluene concentrations appear to be enhanced over the concentration in finished water. Variations in organics present and their relative concentration varied from container to container of artesian water from the same commercial supplier.

Because charcoal filtering is currently being suggested as a means to eliminate the problem of organics in water, a study was undertaken to evaluate the efficiency in removal of organics in this process. Water from a commercial deionizing-charcoal filtering unit was analyzed, and its chromatogram is depicted in Figure 3. Table III identifies the compounds, their gas chromatographic peak number, and their relative percent abundance. Chloroform, benzene, and toluene are still present in the water. Chloroform and benzene show reduction in concentration over those amounts present in finished water; toluene, on the other hand, appears to have increased somewhat. Tetrachloroethylene shows a marked increase over the amount found in finished water or commercial sources of bottled water. Of interest is the appearance for the first time of compounds such as methylmethacrylate and styrene. These

compounds could have originated from the plastics used somewhere in the preparation or storage of the ion-exchange resins or charcoal. Our preliminary data seem to indicate that further studies are needed to determine the value of charcoal filtering before its incorporation on a large scale into water treatment plants.

Acknowledgments

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NOTES

Trace Elements in Corn Grown on Long-Term Sludge Disposal Site

M. B. Kirkham¹

Plant Physiologist, Advanced Waste Treatment Research Laboratory, Environmental Protection Agency, Cincinnati, Ohio 45268

■ Corn plants (*Zea mays* L.) grown on soil treated with municipal sludge (28 metric tons/ha/yr) for 35 years were analyzed for Al, Cd, Cu, Fe, Mn, Ni, Pb, and Zn. Soil was analyzed to the 91-cm (36-in.) depth for total and dilute acid extractable concentrations of the trace elements. Total concentrations of the trace elements in the 0- to 30-cm (0- to 12-in.) depth of soil were increased by sludge additions by the following factors: Al, 1.1; Cd, 35; Cu, 16.5; Fe 1.1; Mn,

1.2; Ni, 2; Pb, 16.5; Zn, 13. The results indicated that, even though large amounts of trace elements accumulated in the soil, these elements did not accumulate appreciably in the grain of the corn plants when compared with the accumulation in the control crop and normal levels reported in the literature. The roots, however, contained large amounts of the elements. Concentrations of Cd and Cu in the leaves were higher than normal concentration ranges.

Sludge has been applied to land for decades in the USA for disposal purposes and to use it as a soil conditioner and fertilizer (1). Long-time spreading of sludge on land, however, can result in high concentrations of trace elements in soils because many metals present in sewage are removed by sewage treatment and are concentrated in the sludge (2). There is concern that plants grown on these soils may accumulate trace elements in amounts toxic to man and animals eating the crop. Almost no information has been published on the concentration in soils of available trace elements from sludge being applied to land over many years. Most studies on metal concentrations in sludge-treated

soils have been started within the last five years (3, 4). This paper reports the concentrations of trace elements in corn plants and soil treated with sludge for 35 years.

Materials and Methods

Corn plants (*Zea mays* L.) were sampled on October 19, 1973, at the Dayton, Ohio, Sewage Treatment Plant. The soil type at the plant is Warsaw silt loam (5). The amount of erosion is slight (slope of land, 0-2%). The well-drained soil with moderate permeability is over limestone bedrock and has formed in alluvium of calcareous glacial till. Two plant samples were obtained from each of three different locations: a control plot (1.2 ha) that had never received sludge; a plot (0.2 ha) that had been saturated with supernatant from sludge-holding lagoons between 1968 and

¹ Present address, Department of Plant and Soil Sciences, University of Massachusetts, Amherst, Mass. 01002.

Table I. Characteristics of Sludge from Dayton, Ohio, Sewage Treatment Plant

Measured parameter or element	1931 ^a	1971 ^b	1973 ^b
Wet solids produced, kg	2,286,900	8,798,900 ^c	...
pH	6.7
Total solids, %	4.8	6.2	5.4
Volatile solids, %	58	...	50
	Mg/kg		
N	34,000	23,400	...
P	...	24,000	17,800
K	...	2,000	...
Ca	...	26,000	...
Mg	...	4,100	...
Ag	...	360	...
Al	...	12,550	...
As	...	1,800	...
Ba	...	3,020	...
Cd	...	830	800
Cr	...	5,900	...
Co	...	ND ^d	...
Cu	...	6,020	4,100
Fe	...	20,370	...
Hg	...	11.5	15.0
Mn	...	1,140	1,200
Na	...	1,800	...
Ni	...	ND	400
Pb	...	6,940	4,000
V	...	ND	...
Zn	...	8,390	10,500
PCB (polychlorinated biphenyls)	...	105	12.0

^a From Tatlock (18). ^b From B. V. Salotto, National Environmental Research Center, Environmental Protection Agency, Cincinnati, Ohio; personal communication. ^c From the records of the Dayton, Ohio, Sewage Treatment Plant, 1970 data. ^d Not detected.

1971; and a plot (0.8 ha) that had received surface applications of dried sludge every year between 1930 and 1965.

The corn plants were separated into roots, stems, leaves, husks, and grain, dried at 80°C, and ground in a Wiley mill. Elemental composition of the plants was determined (6) using a Perkin-Elmer 303 Atomic Absorption Spectrophotometer with a graphite furnace attachment.

Soil was sampled using a soil auger (2-cm diam) at one location in each of the fields. Samples were taken every 30 cm (12 in.) to a depth of 91 cm (36 in.). Extractable cations were analyzed on the atomic absorption spectrophotometer following the procedure described by Issac and Kerber (6). Total concentrations of the elements in the soil were determined using the procedure of Gish and Christensen (7). Phosphorus in the soil was analyzed following the procedure described by Kirkham and Dotson (8)

Results and Discussion

The amount and characteristics of the sludge treated by the Dayton Sewage Treatment Plant in 1931, 1971, and 1973 are given in Table I. No metal analyses of the sludge are available before 1971.

The extractable and total concentrations of Al, Cd, Cu, Fe, Mn, Ni, Pb, and Zn in the control, supernatant-treated, and sludge-treated soils at the 0- to 30-cm, 30- to 61-cm, and 61- to 91-cm (0- to 12-in., 12- to 24-in., and 24- to 36-in.) depths are shown in Table II. Each value represents the analysis of one sample. At the 61- to 91-cm depth, the sludge-treated soil was too gravelly to sample. The concentrations of elements in the control soil are within the range observed in soils (9, 10). The total cadmium concentration was high (2.0 ppm), but it was not greater than the 0.01-7 ppm range present in soils, according to Allaway (9). In general, extractable and total concentrations in supernatant- and sludge-treated soils were much greater than those in the control soil.

The 0- to 30-cm depth of sludge-treated soil had the highest concentration of total elements, except for Al, Fe,

Table II. Extractable and Total Concentrations of Trace Elements at Different Depths in Soil

Characteristic or element	Control, cm			Supernatant-treated, ^a cm			Sludge-treated, ^b cm	
	0-30	30-61	61-91	0-30	30-61	61-91	0-30	30-61
Cation exchange capacity, meq/100 g ^c	21.1	20.4	22.1
Organic matter, % ^c	3.9	1.5	1.2
pH ^c	6.2	5.0	5.0
P, %	0.07	0.03	0.01	0.59	0.03	0.01	0.57	0.08
	Extractable Concentration, Ppm							
Al	2.8	3.0	0.2	<0.2	<0.2	<0.2	0.2	0.4
Cd	0.4	0.2	<0.2	1.6	0.2	<0.2	2.0	0.6
Cu	0.4	<0.4	<0.4	0.6	<0.4	<0.4	2.0	0.4
Fe	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Mn	13.9	12.1	0.4	10.0	8.1	28.2	4.1	6.1
Ni	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Pb	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Zn	17.9	4.0	<1.0	46.0	<1.0	<1.0	73.0	12.1
	Total Concentration, Ppm							
Al	14,850	19,008	34,200	17,850	12,850	12,850	16,850	16,980
Cd	2.0	0.5	2.0	54.6	4.4	2.0	70.5	23.2
Cu	51.0	30.8	40.8	330	73.3	20.3	843	341
Fe	15,700	15,700	25,500	18,400	18,400	17,900	17,700	18,950
Mn	580	780	980	580	780	680	680	680
Ni	71.5	14.9	30.0	195	92.9	71.0	147	138
Pb	61.3	25.6	61.1	526	58.6	25.4	1,015	380
Zn	158	108	117	988	214	91	2,065	863

^a Treated for three years with supernatant liquid from sludge-holding lagoons. ^b Treated for 35 years with dried sludge. ^c From Montgomery County, Ohio, Soil Inventory, 1970.

Table III. Trace Element Concentrations in Corn Plants,^a Ppm

Element	Roots			Stems			Leaves		
	Control	Supernatant ^b	Sludge ^c	Control	Super-natant	Sludge	Control	Supernatant	Sludge
Al	15,500	12,900	8,750	104	<100	<100	648	760	646
Cd	9.0	21.5	48.7	2.1	9.0	5.0	2.1	24.0	13.9
Cu	85	214	617	26	17	10	10	63	40
Fe	18,900	13,000	11,400	146	146	169	549	700	696
Mn	796	469	467	19	115	25	72	225	99
Ni	27.8	26.3	46.7	2.1	1.0	1.0	2.0	4.1	2.0
Pb	114	245	542	<5	<5	<5	<5	<5	11
Zn	236	421	1,349	165	221	320	67	202	196

Element	Husks			Grain			Literature ref ^d		
	Control	Supernatant	Sludge	Control	Super-natant	Sludge	Leaves	Grain	Toxic
Al	200	102	200	100	<100	<100	50-200	20-100	...
Cd	4.0	5.1	5.0	0.8	1.0	0.9	0.1-5	0.1-1	...
Cu	17	41	22	8	11	12	2-30	4-17	>20
Fe	220	296	359	160	101	122	20-250	50-200	...
Mn	18	117	28	5	10	5	20-150	1-10	...
Ni	1.0	2.5	2.0	1.0	1.0	1.0	0.1-5	0.1-5	>50
Pb	<5	<5	<5	<5	<5	<5	0.1-12.4	0.03-5	...
Zn	72	105	202	12	56	79	5-400	20-100	>400

^a The average coefficients of variation for the different plant parts were as follows: roots, 38%; stems, 16%; leaves, 27%; husks, 28%; grain, 11%. ^b See Table II. ^c See Table II. ^d Range found in Alloway (9), Beeson (11), Chapman (12), Hinesly et al. (13), Jones (14), and in a personal communication from W. J. Bauer, Bauer Engineers, Chicago, Ill. 1973.

and Ni, which were highest in the supernatant-treated soil. Total concentrations of the elements in the soil from the supernatant-treated field showed that large amounts of the elements built up during the three-year period that the soil was saturated with supernatant from sludge-holding lagoons. The buildup of certain elements (total concentrations) in sludge-treated soil over a 35-year period was greater than that in the supernatant-treated soil, except for Al, Fe, and Ni in the surface layer. Total concentrations in the 0- to 30-cm layer of the sludge-treated soil were increased over those in the control soil by the following factors: Al, 1.1; Cd, 35; Cu, 16.5; Fe, 1.1; Mn, 1.2; Ni, 2; Pb, 16.5; and Zn, 13.

Table III shows the average concentrations of Al, Cd, Cu, Fe, Mn, Ni, Pb, and Zn in the two plant samples obtained from the control, supernatant-treated, and sludge-treated soils. Except for Al and Fe in the leaves, concentrations of elements in the stems, leaves, husks, and grain of the control plants were within ranges observed in these plant parts (11-14). Ranges normally observed in roots are not given by these authors. The data from the present experiment showed that the concentrations of the elements in the roots were higher than those in any other plant part. Some soil contamination might have occurred because the roots were not washed. However, the air-dried roots were wiped clean of soil before they were oven dried.

In general, the roots, stems, leaves, and husks from plants treated with the supernatant and the sludge had much higher concentrations of the elements than those from the control plants. The concentrations of Al, Fe, Mn, Ni, and Pb in the grain from sludge-treated plants were not greater than those in the grain from control plants. Concentrations of Cd, Cu, and Zn in grain of the sludge-treated plants were only slightly greater than those in grain from control plants. Concentrations of the elements in the grain from the supernatant- and sludge-treated plants were within the range normally observed in corn grain and corn meal (11, 12, 15).

Table IV. Total Amount of Sludge and Trace Elements Added to Soil by Sludge Spread for 35 Years

Element	Metric tons/ha	
	Estimated amount of sludge applied to soil over 35 yr	Amount of elements found in soil, 1973
Al	637	8.0
Cd	456	0.36
Cu	1075	4.41
Fe	1030	21.0
Mn	333	0.40
Ni	1990	0.79
Pb	1310	5.23
Zn	1010	10.65

Phosphorus was not analyzed in the plant tissue. However, the high Al and Fe content of the leaves from the control plants suggests that the plants may have been P deficient. Phosphorus deficiency is often a prominent symptom of Al toxicity (16). Also, the amount of Fe that a plant takes up is dependent on the P concentration in the soil. Phosphorus competes with Fe in the uptake process (16). Cadmium content in the leaves and grain of the control plants was high, even though it was within the range of values given in the literature (see Table III). The high Cd content in the control plants also suggests that the plants may have been P deficient. However, the supernatant- and sludge-treated plants probably were not P deficient. Phosphorus content in the soil from the supernatant- and sludge-treated soils was higher than that in the control soil (Table II). A high P content in the supernatant- and sludge-treated plants could explain the minimal transport of the elements to the grain.

The measured concentrations of elements in the sludge-treated soil and the control soil can be used to determine

the total element loadings deposited on the land. The bulk densities of the control soil and supernatant- and sludge-treated soils are unknown. Therefore, a bulk density of 1.33 metric tons/m³ was chosen, which is an average value for many textural classes of soils (4). If we accept this density, the total amount of each element contained in the soil to a depth of 61 cm has been calculated (Table IV). Subtracting the control field figures from those for the sludge field gives the total element loading from the sludge. The loadings are biased to the low side because losses from leaching below depths greater than 61 cm, crop uptake, and erosion have not been considered. Loadings of Cu, Ni, Pb, and Zn are approximately 40–50 times higher, and loadings of Cd about 100 times higher, than those recommended by Chaney (17). Yet the previously discussed uptake into the corn grain is small. However, organic matter content, cation exchange capacity, and pH of the supernatant- and sludge-treated soils are unknown. These analyses are needed to fully evaluate the mobility of trace elements in soil used as a sludge disposal site (4, 17).

From the amount of elements found in the soil as the result of the 1973 analysis of the Dayton sludge (1971 analysis used for Al and Fe), the total sludge loading has been estimated (Table IV). The average loading is 980 metric tons/ha (431 short tons/A). The annual loading rate over the 35-year period is 28 metric tons/ha/yr (12 short tons/A/yr).

Acknowledgment

I thank Mr. DeFro Tossey, Superintendent of the Dayton Sewage Treatment Plant, for his help in obtaining the corn and soil samples and in providing information about the sewage treatment plant.

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Chromium and Lead in Colored Printing Inks Used for Children's Magazines

Diana F. Eaton, Gerald W. A. Fowles,* Michael W. Thomas, and G. Brian Turnbull

Department of Chemistry, The University, Whiteknights, Reading, UK

■ Lead chromate-based inks are used for printing the colored pages of some children's magazines (comics) and tests have shown that high levels of lead and chromium can be extracted by dilute (0.1M) hydrochloric acid at body temperature. This paper reports investigations of 48 United Kingdom, 9 Spanish, and 5 Austrian comics.

It is well-known that heavy metals, such as cadmium, lead, and mercury, constitute a serious health hazard even in quite small amounts, and there has been considerable public anxiety and debate about these dangers. Much of the discussion (1–4) has been concerned with contamination of food and water supplies, or of the atmosphere. Increasing attention has been given recently (5) to the problem of young children who face a greater risk in view of the

susceptibility of the immature central nervous system, particularly to lead poisoning. For this reason it is essential that children should not be exposed unnecessarily to materials containing significant amounts of such heavy metals, and it would be prudent to exclude them as far as possible from children's toys and printed papers (comics), since many children are inclined to chew and sometimes swallow such materials.

Of course it may be argued that these heavy metal compounds, normally used as pigments, are not necessarily dangerous, because the pigment particles may be insoluble or well protected by suitable coatings—as for instance in many plastic toys that use cadmium-based or lead-based pigments. Hence there is need for an extraction test simulating the conditions of the human stomach rather than an analysis for the total lead.

We have accordingly devised simple test procedures that roughly correspond to the conditions under which the ma-

Table I. Lead and Chromium Content of Colored Pages of United Kingdom Children's Magazines^a

Magazine	Lead, ppm	Chromium, ppm	Magazine	Lead, ppm	Chromium, ppm
1-27	<50	<20	38 (3)	4815	570
28 (3)	480	110	39 (3)	2480	430
29 (6)	745	120	40 (2)	2720	290
30 (2)	430	80	41 (6)	4000	420
31 (4)	80	15	42 (5)	3230	410
32 (3)	525	90	43 (3)	1070	160
33 (5)	820	140	44 (6)	2560	460
34 (3)	2880	315	45 (3)	3010	340
35 (1)	2540	290	46 (3)	3230	380
36 (4)	3590	560	47 (2)	1610	340
37 (2)	1540	200	48 (1)	3200	400

^aThe magazines were published between March 1973 and September 1974. Each magazine is given a code number and the number of issues analyzed of each is given in parentheses. The lead and chromium levels quoted are the average found for all the issues. For magazines 28-48, the colored printing inks were changed to lead-free inks in May-June 1974; analysis of subsequent issues showed lead and chromium levels to be below 50 and 20 ppm, respectively.

terials might be chewed and swallowed, and applied them to comics and other printed papers, various paints, glazes and enameling powders, and a wide range of plastic toys, commonly available to children in European shops and schools. In this paper we report the results of our survey into magazines (comics).

Hankin and co-workers (6) investigated the total lead content of colored pages of several American magazines and the possible relationship with high blood-lead levels of children known to chew paper. We show the problem to be one found in more than one country. Our work is extensive, covering 48 UK and 14 European comics, and we have shown both lead and chromium to be extracted. Both elements are hazardous. Also, we have been concerned with the amounts that can be extracted rather than the total present. This happens to be almost the same with our printed papers, but it would not be true with materials such as plastics and pottery materials.

Experimental

Test Procedure. The colored page (normally the cover) of each magazine was shredded in a paper shredder and then pulverized in a coffee mill. Four grams of this pulverized paper were placed in a 250-ml stoppered conical Pyrex flask together with 125 ml of 0.1M hydrochloric acid. These conditions would seem to be a fair reflection of retention time (3-4 hr for meat) and acid levels (0.05-0.1M HCl) commonly found in the stomach (7), but to simplify subsequent analysis, pepsin was omitted from the synthetic gastric juice. The flask and contents were placed in a thermostat bath at 37.5°C and shaken gently at 30-min intervals over a total period of 4 hr. The contents of the flask were filtered with suction through Whatman No. 1 papers, and the filtrate was examined for its chromium and lead content by the standard atomic absorption procedure; a Perkin-Elmer 2908 instrument was used, the samples being diluted as necessary. The results (Tables I and II) are expressed as parts per million ($\mu\text{g/g}$) of dried paper. A sample of each pulverized comic was dried to constant weight at 110°C and allowance made for the moisture content (~7%) in calculating the levels of chromium and lead.

Since it is possible that some of the chromium or lead might come from other sources than the pigment of the printing ink (e.g., impurities in the paper, drying additive in the oil, introduced by the type face or by the sampling

procedure), blanks were carried out on black and white pages when these were present in the comic. In every case these blanks gave near zero extract levels (<10 ppm) for both metals. It was further shown that our procedure extracted virtually all the heavy metals present in the paper.

Normally only one sample of each issue of a given comic was examined, but since the ink density on the printed page may vary appreciably over a long printing run, tests were made on six copies of comic number 36 (Table I) issue October 6, 1973, samples being purchased from widely separated retail outlets. Lead values were 5140, 4690, 4920, 4570, 4730, and 4870 ppm, with a mean of 4820 ppm and a mean deviation of 3.2%.

A number of the comics were examined for extractable cadmium, but in no case did this level exceed 50 ppm.

Results and Discussion

Tables I and II summarize, respectively, results obtained in a one-and-a-half year survey of comics available in the United Kingdom and other European countries. The results show that up to March 1974, 15 of the 48 United Kingdom comics had extractable lead levels in the 1500-6000-ppm range, with a further five comics with lead levels between 500 and 1500 ppm. Hankin and co-workers (6) in their brief study of six American magazines found total lead levels of between 1140 and 3170 ppm in the colored pages but very low levels with black and white pages. Our studies further showed that substantial amounts of chromium (160-570 ppm) could also be extracted from the colored pages, and the source is clearly the lead chromate type of pigment used in the ink. These inks are commonly used in printing by the rotary letterpress method, but comics printed by the offset process contained low lead levels.

It is clear that such high-lead and chromium levels constitute a real risk to children, especially "pica" children, who might chew and swallow paper, and Hankin et al. (6) refer to three known cases. The problem may be put in perspective by reference to the FAO/WHO Expert Committee on Food Additives (8), which considers the "tolerable" weekly intake of lead from both food and water to be 3000 μg for adults. For reasons of body weight alone, this figure must be reduced two or three times for children, and in addition it must be recognized that a child's central nervous system is more sensitive to lead poisoning; recent experiments have shown that an average of 53% of ingested lead was absorbed by the gut of young children, which is roughly five times that found in adults (9). On these grounds a

Table II. Lead and Chromium Content of Colored Pages of Austrian and Spanish Children's Magazines

Country	Magazine	Lead, ppm	Chromium, ppm	Comments
Spain	1 ^a	4280	420	Inside page
	2 ^a	2450	270	Inside page
	3	910	115	Inside page
	4	780	140	Cover
	5	490	55	Cover
	6	295	35	Cover
	7	150	15	Cover
	8	20	0	Cover
	9	0	0	Inside page
Austria	1	141	27	Inside page
	2-5	0	0	Inside page and cover

^aBeing printed with lead-free inks since November 1974.

level of about 100 μg per day would appear to be a sensible maximum, although King (10) quotes 300 μg per day as being potentially hazardous to children.

A comic containing about 5000 ppm of lead has an average level of about 30 $\mu\text{g}/\text{cm}^2$, so that ingestion of as little as 10 cm^2 would provide King's quoted maximum, and this would be in addition to lead from all other sources!

Our limited European survey showed that comics on sale in Austria contained very little lead, but that several Spanish comics had high levels. Since our results were made available to United Kingdom and Spanish publishers in 1974, their printing inks have been changed to "lead-free" inks, which in the case of the United Kingdom are of the quality approved for food wrappings.

However the use of lead chromate-based inks for printing children's papers and books is unlikely to be confined to Spain, United Kingdom, and the USA, so more extensive surveys are called for.

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INDUSTRY TRENDS

General Motors will conduct an extensive research experiment to obtain data on actual atmospheric effects of exhaust from a large fleet of automobiles with catalytic converters.

Romicon, Inc. has introduced a 4-gpm portable pilot system to evaluate hollow fiber ultrafiltration that removes virtually all suspended solids, bacteria, and viruses from pre- and post-deionized water.

The Electric Power Research Institute (Palo Alto, Calif.) gave Gibbs & Hill, Inc. (New York, N.Y.) a \$200,000, one-year contract to prepare a comprehensive assessment of coal preparation for combustion and conversion.

Dames & Moore (Los Angeles, Calif.) has organized a new professional service group to consolidate its expanding facilities in computer mapping and automated data management.

The Permutit Co. has received a \$6 million contract from General Electric Co.'s San Jose, Calif., office of nuclear reactor feedwater flow meters.

RP Industries, Inc. (Hudson, Mass.) and **Accelerators, Inc.** (Austin, Tex.) have agreed to form a jointly held company, Environmental Ion Industries, Inc. (EIII). EIII will work in air and water pollution control, and water purification with ozone.

Union Camp Corp. (Wayne, N.J.) has donated 49,097 acres of its landholdings in the Great Dismal Swamp (Va.) to the U.S. Department of the Interior's National Wildlife Refuge System.

WAPORA, Inc. has established two new branch offices. One is in Cincinnati, Ohio, and the other is at Marquette, Mich.

The Jeffrey Manufacturing Division of Dresser Industries, Inc. (Columbus, Ohio) has completed the first of three new solid waste processing plants for the City of Columbus.

Roe Associates (Hempstead, N.Y.) has prepared a conceptual study of a research laboratory heated and cooled by solar wall panels for the U.S. EPA.

Charles River Associates (Cambridge, Mass.), an economic research firm, predicts that iron and steel scrap shipments would decline by almost 13% in 1975, but will rise in 1976 and 1977.

Camp Dresser & McKee designed the new \$5.3 million, 60-mgd rapid sand fil-

tration water plant that has just gone into operation for the City of Springfield, Mass.

Andco Torrax Ltd. has been organized at Toronto, Canada, to market the Andco-Torrax solid waste conversion system, based on high-temperature slagging pyrolysis, in Canada.

Energy Information Service, Inc. (New York, N.Y.) has formed a "Speakers' Bureau" to obtain qualified people to speak on all aspects of energy and energy-related issues.

Universal Oil Products Co. (UOP) has merged its Fluid Sciences and ROGA Divisions, both of San Diego, Calif., into one single unit, the Fluid Systems Division.

Roy F. Weston, Inc.'s principal officers and **Philip S. Steel and Associates** have formed The Steel-Weston Partnership at West Chester, Pa., to offer architectural services.

Nitrogen Service Co., a subsidiary of **Union Carbide**, handled delivery and pumping of nitrogen gas to help startup of a synthetic natural gas (SNG) plant (125 million ft³/day) of Public Service Electric and Gas Co. in New Jersey.

C-E Power Systems (Windsor, Conn.) will supply two multi-fueled boilers, valued at over \$8 million, to the Kerr-McGee Chemical Corp., at Trona, Calif.

Exxon Research and Engineering Co. (Linden, N.J.) has announced a new method of removing lead contamination from gasoline. The suspect gasoline is passed through a fixed bed of carbon or silica gel impregnated with cupric chloride.

Dow Chemical U.S.A. plans two new plants to make alkanolamines and glycol ethers. Alkanolamines remove acidic contaminants from gas and oil, and glycol ethers combat air pollution problems in mass production of painted products.

Foote Mineral Co. (Exton, Pa.) has completed financing of air pollution control equipment at its Graham, W. Va., ferroalloys plant with tax-exempt Mason County, W. Va., revenue bonds totalling over \$6.4 million.

The Electric Power Research Institute (EPRI, Palo Alto, Calif.) has awarded a \$250,000 contract to Environmental Research and Technology, Inc. (Concord, Mass.) to investigate coal-fired power plant emissions on a regional basis.

Pearl Brewing Co. (San Antonio, Tex.) won the 24 Carat Golden Circle Award from Affiliated Advertising Agencies International for Pearl's aluminum can recycling program called "Pearl Can Pickin' Time."

Proler International Corp. (Houston, Tex.) announced net income of over \$4.2 million for the three months ended April 30, 1975, the second most profitable first quarter in company history. Proler is a leading firm in processing metals for recycling.

Lonza Inc. (Fair Lawn, N.J.) has received registration approval from EPA for a disinfectant-sanitizer-fungicide-deodorizer based on the company's Bardac-22 (didecyl dimethyl ammonium chloride).

Davy Powergas (Lakeland, Fla.) is performing engineering and procurement services for a \$40 million pollution abatement system on a coal-fired power plant jointly owned by Public Service Co. of New Mexico and Tucson Gas and Electric Co.

Research-Cottrell has received \$14 million worth of orders for four electrostatic precipitators. Two, for \$10 million, will go to American Electric Power System, and two "hot" ones to Alabama Electric Cooperative.

Catalytic, Inc. has been granted an exclusive right by Westvaco Corp. for international marketing of the Westvaco flue gas desulfurization process. The process makes elemental sulfur.

Xonics, Inc. has contracts worth over \$5 million to manufacture and install air and water pollution monitoring systems. Two contracts are with the U.S. Army Corps of Engineers, and a third is for 13 air monitoring stations in the Middle East.

Environmental Data Corp. has recently opened an area service office in Farmington, N.M., in order to provide full maintenance for stack monitors in various southwestern states.

Combustion Equipment Associates, Inc. (CEA) reported operating income of over \$9.4 million for the year ended March 31, 1975. Per-share earnings were \$1.59 as compared to \$1.35 for the previous year.

The Manufacturing Chemists Association (Washington, D.C.) honored Canadian Industries Ltd. (Montreal) and Ventron Corp. (Beverly, Mass.) with the Lamot du Pont Safety Award bronze plaques for outstanding safety records.

Dames & Moore (Los Angeles, Calif.) has been retained by the EPA to prepare an environmental impact statement on sewage sludge dumping at new sites in the New York Bight.

NEW PRODUCTS

Conductivity instrument

Measures conductivities from below 1 and up to 10,000 micro-ohm/cm. Applications include boiler waters, cooling waters, waste streams and incoming raw water. Nalco Chemical Co. **101**

KF reference material

Potassium fluoride reference material (SRM 2203) for the standardization of fluoride ion-selective electrodes. National Bureau of Standards **102**

Filter photometer

Features a 4-in. meter with sensitivity and zero adjustments; readout is linear with concentration. It can be used as a colorimeter, fluorometer and nephelometer; applications include the use in pollution monitoring and liquid chromatography. TCS, Instrument Division **103**

CO₂, O₂ analyzer

For routine use in laboratory testing including environmental chambers. The rapid, accurate testing takes less than a minute to complete. Bacharach Instrument Co. **104**



Liquid/solids separator

Compact square design allows for higher capacity in the minimum space. Applications include wastewater cleanup, solids recovery, dewatering, wet sizing or any other removal of free moisture down to 37 μ . Rotex Inc. **105**

Low flush toilets

Uses only two quarts of water for each flush cycle, and operates on 50-70 psi compressed air. Unit can be used with any type of sewage treatment system. Microphor **106**

Vibration monitor

Single channel unit provides a real-time check on machine performance to prevent the machine from reaching harmful vibration levels. Monitors vibration levels on motors, pumps, compressors, generators and turbines. Endevco Machinery Health Monitoring **107**

Wastewater sampler

Self-contained unit has an automatic valve that can accurately measure specific sample sizes. Sample volume and sampling intervals are adjustable. It is available in refrigerated and non-refrigerated models. Can-Tex Industries **108**

Integrator, pyranometer sensor

Weatherproof combination permits untended long- or short-term totaling of global radiation; applications include solar energy research and utilization and environmental quality studies. The unit is resistant to harsh environmental conditions. Lambda Instruments Corp. **109**



Water quality checker

Operator can select the parameter to be measured; parameters include pH, dissolved oxygen, conductivity, temperature or turbidity. This hand-held, battery-operated instrument weighs less than 3 lb. Horiba Instruments Inc. **110**

Wet electrostatic precipitator

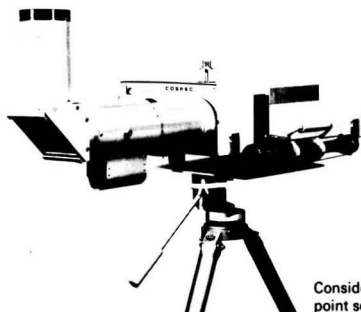
Designed to solve emission control problems in small-volume gas streams of between 1,000-2,000 ft³/min. These mini-units are particularly applicable for use in emission control of gas streams from glass container coating and meat-smoking processes. Fluid-Ionic Systems **111**

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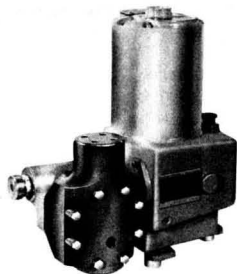


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Gas chromatograph

Portable flame ionization GC has been modified to accept new detector and valve options. With these options, SF₆ tracer studies, freon and low-level chlorine analysis, and analyzation of sub ppm levels of CO, methane and total hydrocarbon are possible. Analytical Instrument Development, Inc. **115**

Moisture analyzer

Measures water content with an accuracy of $\pm 2\%$ in thermoplastic and thermosetting resins, dry chemicals, pharmaceuticals and foodstuffs. Moisture levels from 0.1–999.9 μg may be measured in sample sizes up to 3.5 cc in volume, weighing from 0.1 mg to 2 g. Du Pont Co. **116**

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Tip loading system

Disposable micropipette tips (0.005–0.2 ml volumes) are designed for use with hand-operated pipetting systems. Tip-loading system permits more rapid and safer pipetting of corrosive materials, wastewater and other liquids in pollution control laboratory testing. Oxford Laboratories, Inc. **119**

Air pollution balance

Extra wide weighing chamber is equipped with a special supporting rack (for weighing filter sheets) that is interchangeable with a conventional weighing pan. Load capacity is up to 200 g, with read-out to 0.1 mg. Brinkmann Instruments Inc. **120**



Solar collector

Tubular collector incorporates a coated flat absorber plate housed within an evacuated glass tube. Collector tubes are mounted in modules of from six to ten tubes. The units are presently being manufactured in limited quantities for experimental and demonstration purposes. Corning Glass Works **121**

Boomerang camera

Camera can be used to take photographs at specific sites in the deep sea or in shallow water. It free falls to the ocean floor, takes pictures and then resurfaces. Applications include survey studies for manganese nodule deposits, and biological, ecological and geological surveys. Benthos, Inc. **122**

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Designed for use in industrial and commercial recirculating cooling water systems, the oxidizing microbicide exhibits broad spectrum activity against bacteria and algae with no residual toxicity effect. Dearborn Chemical (U.S.) **123**

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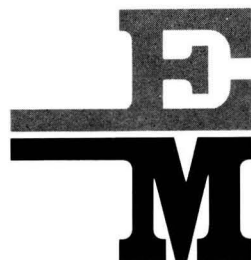
Meteorological system

Measures and records wind speed and direction in compliance with state agencies and the EPA for direct and indirect source monitoring. It is available in rack and field configurations. TechEcology, Inc. **125**

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NEW LITERATURE

Lime slaker. Brochure describes and lists specifications for a continuous slurry-type lime slaker used for municipal and industrial water treatment, and producing a 20–30% slurry. PORTEC Inc., Butler Division **151**

Spectrophotometry. Bibliography of 50 articles relating to various applications of fluorescence spectrophotometry, including environmental analysis, is now available. Perkin-Elmer **152**

Chlorinator. Bulletin 1001 illustrates complete line of ADVANCE chlorinators, gives a glossary of terms, and provides a list of dosage rates in ppm or mg/liter. Capital Controls Co. **153**

Process equipment. Bulletin PE-1A covers a complete line of equipment for chemical process industries, including material preparation and feeding, and dry, semidry, and paste material mixing. Beardsley & Piper **154**

Industrial water pollution control. Brochure describes a compact packaged horizontal tube-type concentrator especially suitable for high BOD/COD waste streams containing hard-to-handle dissolved solids. aqua-chem, Inc. **155**

Flow measuring. Product guide lists a complete line of flow measuring instrumentation according to type, application, flow range, temperature, and pressure rating. Brooks Instrument Div., Emerson Electric Co. **156**

"Hay Fever Holiday". Brochure with map describes the allergy, its form of treatment, and good and bad spots for hay fever sufferers. Abbott Laboratories **157**

Vinyl chloride detection. Application note ANG 1-75 describes how a gas chromatography system can be configured for vinyl chloride to help manufacturers stay within safe limits. Hewlett-Packard **158**

Gas desulfurization. Bulletin PES-10 describes a range of gas desulfurization processes for industry and electric utilities. Peabody Engineered Systems **159**

Crusher/mutilator. Catalog sheet describes the model T270 "Tubar" crusher/mutilator that reduces glass, metal, and brittle plastic bulk by 80%. Uhrden, Inc. **160**

Self-cleaning pH/redox probes. Brochure describes the new Polymetron line of heavy-duty industrial self-cleaning pH/redox probes and accompanying pH/redox meter. Polymetron **161**

Transfer pumps. Bulletin 3A.5 describes vertical industrial turbine, canned type pumps for secondary recovery, chemical, cryogenic, and other applications. Goulds Pumps, Inc. **162**

Wastewater samplers. Brochure describes sequential and composite samplers, as well as new refrigerated samplers and explosion-proof samplers. ISCO **163**

Line strainers. Bulletin 735 describes Sani-Filtration line strainers, including conical line strainers, trap strainers, and flat plate strainers. Newark Wire Cloth Co. **164**

Programmed fermentation. New booklet, "Computer Analysis and Control of Biochemical Processes," is aimed at optimizing product yield. New Brunswick Scientific Co., Inc. **160**

Pinch valves. Technical packet describes uses of pinch valves in piping systems, with special data concerning transporting abrasive slurries. Red Valve Co., Inc. **161**

Calibration instruments. New general catalog for precision calibration instruments for metrology and oceanography is now available. Applications and technical diagrams are included. Guildline Instruments, Inc. **162**

Fluorocarbons and ozone. "Management Bulletin" Vol. 4/No. 1, February 1975 discusses in depth the question of whether fluorocarbons are damaging the atmospheric ozone layer. Du Pont **163**

Industrial fans. Bulletin 164 lists over 250 models of heavy-duty industrial fans. Many meet OSHA quiet-operation requirements. Aerovent Inc. **164**

Ferric chloride. Bulletin S-202B tells about expanding markets for ferric chloride for sludge conditioning, phosphorus removal, and industrial waste and water treatment. Pennwalt Corp. **165**

Air flow monitoring. Form 4071 describes new air flow indicator for monitoring air flow through filter elements in a spray paint booth. Has OSHA applications. Conco, Inc. **166**

Environmental design. Booklet describes company's design capabilities in air, water, and noise pollution, and solid wastes. The Anaconda Co., Brass Division **167**

Chemical tanks. Data sheet No. 68 describes reinforced tanks for storage and

shipment of chemicals. Baltek Corp. **168**

Material handling. New product catalog covers material handling and storage in all industries, warehouses, and the like. Jarke Corp. **169**

Dust collection. Ten-page brochure details company's HyPulse dust collection system designed to capture particulate matter with better than 99% efficiency. Carborundum Environmental Systems, Inc. **190**

Water testing. Product Bulletin 323, revised, covers biological water testing and suspended solids testing, and includes membrane filtration procedure. Gelman Instrument Co. **191**

Epoxy embedding media. Data sheet EEK-1150 describes epoxy embedding media for electron microscopy applications. R. P. Cargille Laboratories, Inc. **192**

Pilot plant services. Brochure describes new chemical pilot plant service offered by the company. Applied Science Laboratories, Inc. **193**

Strip-chart recorders. Catalog 4024 lists entire line of Rustrak miniature strip-chart recorders. Applications are in pollution monitoring, oceanography, and other fields. Gulton Industries, Inc. **194**

Stack monitoring. Six-page brochure describes the state-of-the-art in stack gas analysis for sulfur compounds. Tracor Instruments **195**

Lab integrator. Brochure describes Model CSI-38 Mini Lab Integrator for use with gas and liquid chromatographs. Least expensive on the market, according to the company. Columbia Scientific Industries **196**

Fluorescence spectra. Flyer sheet describes two new volumes of fluorescence spectra for identifying unknown compounds. Sadtler Research Laboratories, Inc. **197**

Humidity monitoring. Catalog covers complete line of instrumentation for monitoring humidity and moisture, and includes environmental applications. General Eastern Corp. **198**

Corrosion control. Bulletin 5-24 describes Flakeline 300, an inert flake-reinforced polyester coating for steel and concrete surfaces. The Ceilcote Co. **199**

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.

BOOKS

Cooling Tower Environment—1974.

Steven R. Hanna and Jerry Pell, coordinators. x + 648 pages. National Technical Information Service, U.S. Department of Commerce, Springfield, Va. 22161. 1975. \$13.60 (\$16.10, foreign), paper.

Portraying the state-of-the-art of many aspects of the cooling tower environment, this book comprises the proceedings of a symposium sponsored by the U.S. Atomic Energy Commission (now ERDA), and the State of Maryland. Advanced concepts in cooling tower research and environmental assessment are presented. Ask for CONF-740302.

Environmental Sources and Emissions Handbook.

Marshall Sittig. xii + 523 pages. Noyes Data Corp., Publicity Dept., Mill Road at Grand Ave., Park Ridge, N.J. 07656. 1975. \$36, hard cover.

In this book, origins of both air and water pollution are considered comprehensively, as are the types of pollutants encountered. Moreover, intermedia pollution is covered. Composition and quantities of raw waste effluents (to air and water) are discussed, and perhaps the only data on effluents following in-plant control, in certain instances, are available.

Primary Productivity of the Biosphere.

H. Lieth and R. H. Whittaker, Eds. 325 pages. Springer-Verlag New York Inc., 175 Fifth Ave., New York, N.Y. 10010. 1975. \$29.80, hard cover.

This book aims at bringing together and summarizing current understanding of the primary productivity of the world as it is realized in different kinds of communities. Aquatic and terrestrial communities are considered, as are more specialized problems, such as regional problems, production analysis, calorific values, modeling, and use of crop data.

Fluid Mechanics and Thermodynamics of Our Environment.

S. Eskinazi. 436 pages. Academic Press, Inc., 111 Fifth Ave., New York, N.Y. 10003. 1975. \$26.

This book unifies oceanography and meteorology into a single environmental science that deals with the atmosphere and oceans as a geofluid. It provides a generalized treatment of basic principles of motion and energy transfer in the atmosphere and oceans, and applies these principles in many ways of interest to engineers, meteorologists, oceanographers, and environmental scientists.

A Feasibility Study of Lawn Sod Production and/or Related Activities on Dredged Material Disposal Sites.

National Technical Information Service, Springfield, Va. 22151. 1975. \$3 (\$0.95, microfiche).
Work is in progress to develop improved disposal facility operation and management procedures, as well as techniques to reclaim potentially valuable materials. These efforts can increase disposal area life expectancy and improve aesthetic and environmental characteristics. Contract Report D-75-1 reports on this work by the U.S. Army Engineer Waterways Experiment Station (Vicksburg, Miss.).

Regional Environmental Management.

L. Edwin Coate and Patricia A. Bonner, Eds. xi + 348 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1975. \$19.95, hard cover.

This book contains the papers presented at a conference held at San Diego, Calif., in February 1973. It was aimed at determining the validity of the regional (both physical and political) concept of environmental management, identifying the most productive approach, and ascertaining the best means of solving problems.

Energy, Environment, and Building.

Philip Steadman. ix + 287 pages. Cambridge University Press, 32 E. 57th St., New York, N.Y. 10022. 1975. \$14.95, cloth; \$5.95, paper.

Here is a comprehensive approach to energy conservation, "clean" energy sources, and composting, as well as other pertinent environmental considerations with respect to building. Complete technical data and cost figures are given. The book was written as a report to the Academy of Natural Sciences of Philadelphia (Pa.).

Control of Environmental Impacts from Advanced Energy Sources.

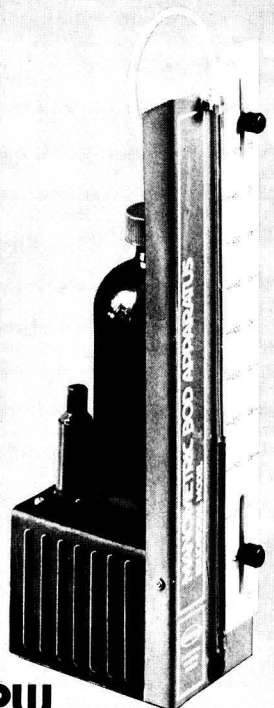
326 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1974. \$4.

New and advanced sources of energy will have considerable technological and environmental effects. The EPA points out major problems associated with geothermal energy, oil shale, underground coal gasification, process water, exotic pollutants, and land. The study was done by Stanford Research Institute (Menlo Park, Calif.). Ask for EPA-600/2-74-002.

Face-to-Face With Environmental Problems.

117 pages. AATCC, P.O. Box 12215, Research Triangle Park, N.C. 27709. 1975. \$15, paper.

This volume encompasses the proceedings of the Textile Technology/Ecology Interface Symposium held at Charlotte, N.C., in May, and sponsored



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by the American Association of Textile Chemists and Colorists. It describes pollution control work being done by the textile and dye industries, as well as EPA and OSHA regulation problems that the textile industry faces.

Pollution Control in the Plastics and Rubber Industry. Marshall Sittig. ix + 306 pages. Noyes Data Corp., Mill Road at Grand Ave., Park Ridge, N.J. 07656. 1975. \$36, hard cover.

No. 18 in the Pollution Technology Review Series, this book fully covers plastics and rubber manufacturing processes, as well as pollution control in these industries. New, timely reviews of industrial practice are integrated with considerations of air and pollution, and solid waste. Many tables, flow diagrams, and schematics are presented.

A Homesite Power Unit: Methane Generator. Les Auerbach. 50 pages. Edmund Scientific Co., 555 Edscorp Bldg., Barrington, N.J. 08007. 1975. \$5.

Produce your own gas (biogas) and valuable fertilizer at home. Full instructions are given for designing and building a methane generator for home, farm, cottage, or business. The gas can provide heat for cooking or hot water, or power internal combustion engines; compost is a by-product. Odor, pest, and health problems associated with

improperly managed wastes are eliminated by a gas-tight system. Ask for book No. 9485.

Hydrogen Energy, Part A and B. T. Nejat Veziroglu, Ed. xxvi + 1369 pages. Plenum Publishing Corp., 227 West 17th St., New York, N.Y. 10011. 1975. \$95 per set, hard cover.

Where will abundant, clean energy come from? Is hydrogen the most viable answer to this question? This two-volume publication discusses the approaches to answering these questions. Part A covers primary energy sources, hydrogen production by nuclear, solar, and other means, and its storage and transmission. Part B discusses use of hydrogen industrially, commercially, and residentially; environmental considerations, and alternative systems.

A Solid Waste Technology Assessment Study. 350 pages. Frost & Sullivan, Inc., 106 Fulton Street, New York, N.Y. 10038. 1975. \$450.

Compiled by General Electric solid waste experts, this volume makes available process facility and resource recovery strategy information previously classified as "company confidential." It deals with resource and fuel recovery processes, composting processes, landfills, baling, and front-end systems in exhaustive detail. The book contains

93 illustrations and 80 tables. Ask for Report GE101.

Transition. Joel Schatz. Research Coordinator, Office of Energy Research and Planning, Office of the Governor, Salem, Ore. 97310. 1975. \$5.

Surprisingly, solar energy is applicable to Oregon, according to the report that explains how a "solar farm", on a square of land 12 mi on a side, can supply the state's electrical needs. The report also describes the use of pumped storage for nights and overcast days. Examining Oregon's clean energy resources, the report emphasizes the desirability of solar energy and expresses strong reservations concerning nuclear-fission energy.

Survival 2001: Scenario from the Future. Henry E. Voegeli and John J. Tarrant. Van Nostrand Reinhold, 450 West 33rd St., New York, N.Y. 10001. 1975. \$5.95.

During the fifth decade of the 21st Century, people looked back to 1975 when it was thought that the earth was dying, choking on its own affluence and effluents. The authors present over 100 ideas on how known technology (1975) can be used to obviate all these horrors and vastly improve the quality of life. Heat pumps, ocean energy, use of reclaimed waste, alternatives to fossil fuels, and similar ideas are proposed.

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MEETING GUIDE

August 24-30 Boston/Cambridge, Mass. **6th Triennial World Congress of the International Federation of Automatic Control.** American Automatic Control Council and others

Theme is "Control Technology in the Service of Man." Environmental topics will be discussed. *Write:* IFAC/75 Secretariat, 400 Stanwix St., Pittsburgh, Pa. 15222

September 8-10 Newton, Mass. **Symposium on Enzymatic Conversion of Cellulosic Materials.** U.S. Army Natick Development Center and the Advisory Board on Military Personnel Supplies of the National Research Council

Write: Frank R. Fisher, executive director, Advisory Board on Military Personnel Supplies, National Research Council, 2101 Constitution Ave., N.W., Washington, D.C. 20418

September 8-12 Berkeley, Calif. **Nuclear Power and Environmental Assessment.** Continuing Education in Engineering University of California—Extension

Write: Continuing Education in Engineering, University of California—Extension, 2223 Fulton St., Berkeley, Calif. 94720

September 11-12 Chicago, Ill. **Third Annual Illinois Energy Conference on Nuclear Power in Illinois.** The Energy Resources Center, University of Illinois at Chicago Circle and the Office of Intergovernmental Science and Research Utilization, National Science Foundation

Write: Dr. James P. Hartnett, Director, Energy Resources Center, University of Illinois at Chicago Circle, Box 4348, Chicago, Ill. 60680

September 14-19 Las Vegas, Nev. **International Conference on Environmental Sensing and Assessment (ICESA).** American Chemical Society, U.S. EPA, World Health Organization and others

Write: EPA/NERC-LV, P.O. Box 15027, Las Vegas, Nev. 89114 or IEEE-TAB, 345 E. 47th St., New York, N.Y. 10017

September 15-17 Gaithersburg, Md. **1975 National Conference on Noise Control Engineering.** Institute of Noise Control Engineering and the National Bureau of Standards

Write: Institute of Noise Control Engineering, P.O. Box 3206, Arlington Branch, Poughkeepsie, N.Y. 12603

September 16-18 Madison, Wis. **Secondary Fibers/Testing Conference.** Technical Association of the Pulp and Paper Industry (TAPPI)

Environmental topics are included. *Write:* W. H. Gross, TAPPI, One Dunwoody Park, Atlanta, Ga. 30341

September 16-19 Denver, Colo. **Third University of Minnesota International Conference on Personal Rapid Transit.** University of Minnesota

Write: Gordon J. Amundson, 207 Nolte Center for Continuing Education, University of Minnesota, Minneapolis, Minn. 55455

September 17-19 Dayton, Ohio **32nd Annual Meeting.** East Central Section of the Air Pollution Control Association

Write: Regional Air Pollution Control Agency, Attention: Mr. William T. Burkhardt, 451 W. Third St., Dayton, Ohio 45402

September 17-19 Washington, D.C. **Nuclear Legislation Update.** American Nuclear Society

Write: James T. Ramey, Stone & Webster, 7315 Wisconsin Ave., N.W., Washington, D.C. 20014

September 18-19 Nashville, Tenn. **Sixth Annual Meeting.** Southern Section of the Air Pollution Control Association

Write: Mr. Gordon Nix, Optimal Systems, Inc., P.O. Box 1182, Atlanta, Ga.

September 21-26 Pacific Grove, Calif. **Risk-Benefit Methodology and Application.** Engineering Foundation

Attendance limited to 100. *Write:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

Courses

August 18-22 Ann Arbor, Mich. **Industrial and Municipal Water Pollution Control: Physicochemical Processes.** University of Michigan, College of Engineering

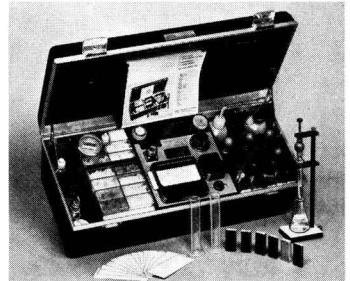
Fee: \$300. *Write:* Engineering Summer Conferences, 400 Chrysler Center, North Campus, The University of Mich., Ann Arbor, Mich. 48105

August 18-22 Seattle, Wash. **Fundamentals of Interpreting the Mass Spectra of Organic Molecules.** Finnigan Corp.

Topics will include a discussion of "Computerized GC/MS" and "Demonstration of International Mass Spectral Search System (MSSS)." Fee: \$275. *Write:* Finnigan Corp., Attn. Ms. Karen Hansen, 845 W. Maude Ave., Sunnyvale, Calif. 94086

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August 27-29 Los Angeles, Calif.
Resource Recovery from Municipal Solid Waste. University of California at Los Angeles Extension, Dept. of Engineering

Write: Dept. of Engineering, UCLA Extension, P.O. Box 24902, Los Angeles, Calif. 90024

September 4-5 Pittsburgh, Pa.
Occupational Health Approach to Cardiovascular Diseases—Evaluation, Assessment, Rehabilitation. Industrial Health Foundation

Designed for the occupational health nurse. Fee: Not established yet. *Write:* George Reilly, Director of Safety and Training, Industrial Health Foundation, 5231 Centre Ave., Pittsburgh, Pa. 15232

September 4-5 Madison, Wis.
Pulp and Paper Mill Sludge Management. University of Wisconsin—Extension

Fee: \$110. *Write:* Robert C. Lutton, P.E., Dept. of Engineering, University of Wisconsin—Extension, 432 N. Lake St., Madison, Wis. 53706

September 8-10 Washington, D.C.
Energy Conservation, Opportunities and Guidelines for Existing Buildings. Short Course No. 339.

Fee: \$345. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

September 15-19 Austin, Texas
Advanced Water Pollution Control: Biological Waste Treatment. The University of Texas at Austin, College of Engineering

Fee: \$300. Applications must be received by August 15. *Write:* The University of Texas at Austin, Engineering Institutes of the College of Engineering, Ernest Cockrell Hall 2.102, Austin, Tex. 78712

September 17-19 New York, N.Y.
Dynamics and Control of Air Pollution. American Chemical Society

Write: Department of Educational Activities, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036

International

August 17-21 Quebec City, Quebec
Third International Conference on the Physics and Chemistry of Asbestos Minerals. Dept. of Natural Resources of Quebec

Write: G. J. Foy, Dept. of Natural Resources of Quebec, 1180 Dufresne St., Quebec City, P.Q., Canada

August 18-20 Copenhagen, Denmark
Nitrogen as a Water Pollutant. International Association on Water Pollution Research (IAWPR), the Danish National Committee

Write: Asst. Prof. J. Lønholdt, Dept. of Sanitary Engineering, Technical University of Denmark, Building 115, DK 2800 Lyngby, Denmark

September 15-19 London, England
First European Plant Engineering and Maintenance Conference and Exhibition. Clapp & Poliak, Inc.

Topics will include pollution control, and health and safety law compliance. *Write:* Clapp & Poliak, Inc., 245 Park Ave., New York, N.Y. 10017

September 22-24 London, England
Water Conservation and Management—An International Symposium. The Cooling Water Association

Write: Secretariat, The Cooling Water Association, 74, Queensway, London, W2 3RW

September 29-October 3 Naples, Italy
4th International Symposium on Engine Testing Automation: Performance, Emission & Diagnostics. Automotive Automation Ltd.

Write: Secretariat, ISETA, 62 High St., Croydon CRO 1NA, England

October 6-7 Sudbury, Ontario
Hydrometallurgy—Selection of Equipment and Materials. Hydrometallurgy Section of CIM

Write: I. J. Itzkovitch, Ontario Research Foundation, Sheridan Park, Mississauga, Ontario, Canada, L5K 1B3

October 27-31 Toronto, Ont.
International Conference on Heavy Metals in the Environment. Institute for Environmental Studies of the University of Toronto, and the National Research Council of Canada

Write: M. K. Ward, Executive Secretary, International Conference on Heavy Metals in the Environment, c/o National Research Council of Canada, Ottawa, Canada K1A 0R6

November 3-5 Montreux, Switzerland
Conversion of Refuse to Energy: First International Conference and Technical Exhibition. World Environment & Resources Council, Institute of Electrical and Electronics Engineers, American Institute of Chemical Engineers and others

Write: Ms. E. Aubert, CRE Conference and Exhibition 1975, Secretary's Office, 42, Grand-Rue, Box 97, 1820 Montreux, Switzerland

Call for Papers

August 15 deadline
Fifth Mineral Waste Utilization Symposium. IIT Research Institute and the U.S. Bureau of Mines

Conference will be held April 13-14, 1976, in Chicago, Ill. *Write:* S.A. Bortz, IIT Research Institute, 10 W. 35th St., Chicago, Ill. 60616

September 15 deadline
8th International Conference of the International Association on Water Pollution Research (IAWPR). IAWPR

Conference will be held October 17-22, 1976, in Sydney, Australia. *Write:* Chairman of Program Committee, IAWPR, Headington Hill Hall, Oxford OX3 0BW, England

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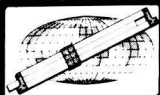
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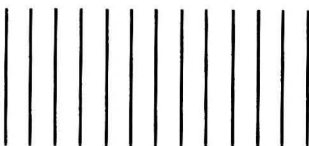
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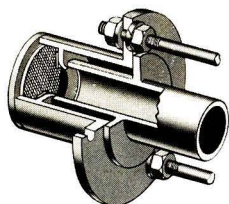
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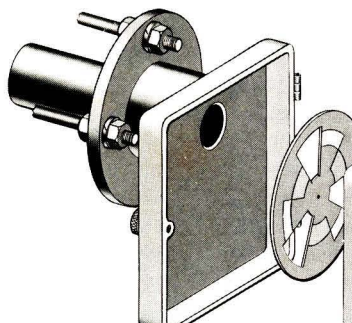
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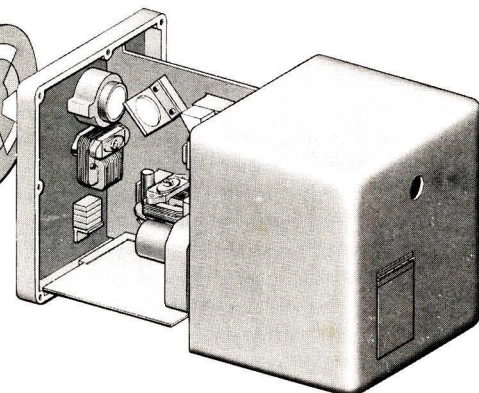
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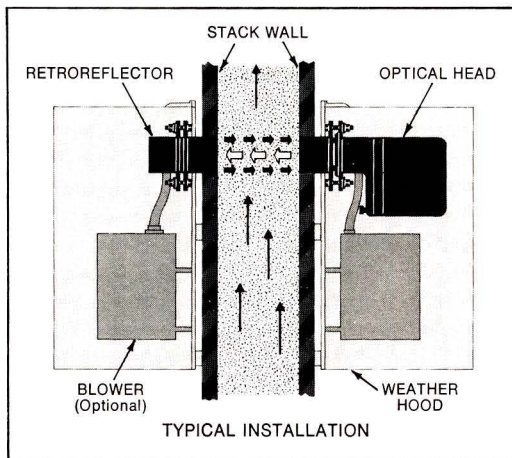
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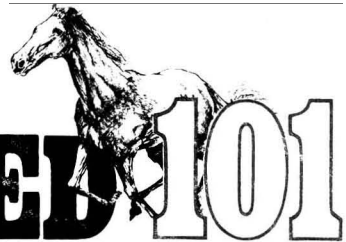
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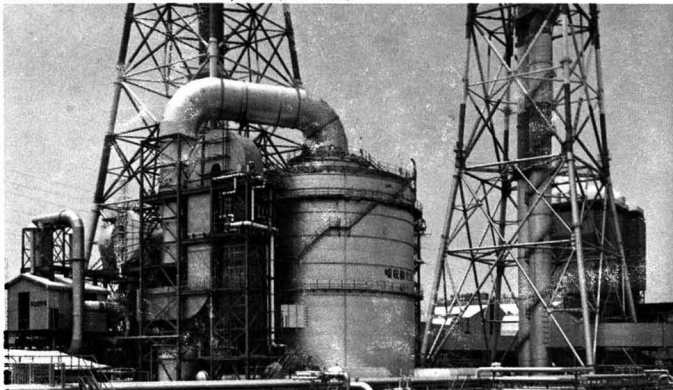
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