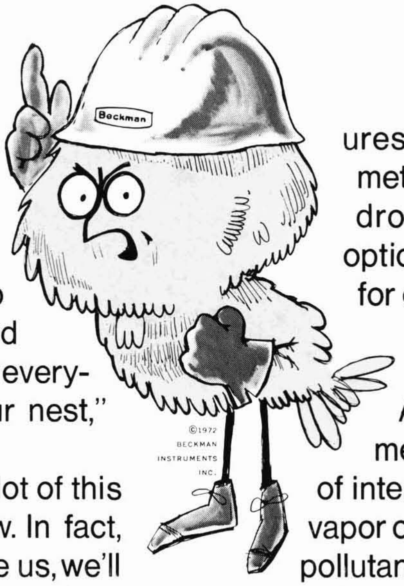
Environmental
Science & Technology

August 1972

SCRAP RECYCLING

Does anyone else remember sky blue?



Remember the miner's canary? Luckily, he no longer lays his life on the line detecting poisoned air. He's out now to keep reminding us that polluted air isn't new. And that it's everyone's job to "clean up our nest," to see the sky blue again.

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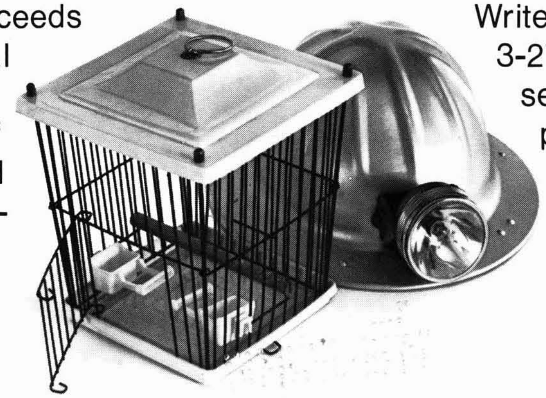

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Environmental
Science & Technology

Volume 6, Number 8
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contents

AMERICAN CHEMICAL SOCIETY
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Washington, D.C. 20036

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For author's guide and editorial policy, see June 1972 issue, page 523 or write Norma Yess, Manuscript Reviewing Office.

In each paper with more than one author, the name of the author to whom inquiries should be addressed carries a numbered footnote reference.

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Special Report

Feature

Outlook

Departments

Current research

Identifying sources of lead contamination by stable isotope techniques 705

M. B. Rabinowitz and G. W. Wetherill

It is now possible to distinguish among sources of lead contamination on the basis of stable isotopic measurements. For example, the lead sources—lead in gasolines, soils near freeways, and air in urban traffic—show one set of values whereas other lead sources—lead in lead ores, refined metal, topsoils and dusts near smelters—show another set of values. The technique has been applied to lead poisoning of horses near Benicia, Calif.

Continuous analysis of reactive organics by selective combustion 710

W. B. Innes

Reactive organic hydrocarbons (photochemical smog-forming materials) in automotive exhaust gases or condensates can now be analyzed by a selective and continuous combustion method. A knowledge of these materials is essential for effective evaluation of exhaust control devices for automobiles. The instrument described has a fast response time, high sensitivity, and negligible inlet system losses.

Production of fungal protein from cellulose and waste cellulosics 715

C. J. Rogers, E. Coleman, D. F. Spino, T. C. Purcell, and P. V. Scarpino

Fungi can be used to produce high-quality protein from cellulose waste such as kraft paper, agricultural waste, and urban refuse, but the cellulosic fiber must first be separated from the noncellulosic material by a process such as hydropulping. For the recycling of cellulose to be economically feasible, an effective pretreatment process is necessary. Several processes were investigated but only a photochemical one proved significant; its use reduced the cellulose fermentation time by one fourth to one half the time required for untreated cellulose.

Relationships between lake trophic state and nitrogen and phosphorus loading rates 719

E. E. Shannon, and P. L. Brezonik

So-called partial budget calculations for nitrogen and phosphorus nutrients estimate gross supply and loading in lakes. Data are presented for 55 lakes in north-central Florida. The problems of relating trophic state and nitrogen and phosphorus supply are discussed.

Concentration of mercury in the manufacture of fish protein concentrate by isopropyl alcohol extraction of sheepshead and carp 726

T. A. Gasiewicz and F. J. Dinan

In the production of fish protein concentrate using this extraction technique, it has been noted that the alcohol does not remove mercury from the starting material. It has also been observed that an enrichment factor of 5 is operative so that only fish of low initial mercury concentration may be used as starting material if the resulting fish protein concentrate is not to exceed the maximum allowable mercury concentration (0.5 $\mu g/g$).

Critical evaluation of rate-controlling processes in manual determination of nitrogen oxides in flue gases 727

G. Margolis and J. N. Driscoll

The wet chemical analysis of NO in the presence of SO_2 can now be expedited. At 10 atm the absorption of NO is complete in about 10 min whereas under atmospheric conditions the absorption takes 5 hr. The complete analysis is performed within a few hours instead of the 30 hr required earlier.

Effect of chemical structure on microbial degradation of methyl-substituted aliphatic acids 732

M. W. Hammond and M. Alexander

The ability of pesticides, detergents, and industrial organic wastes to persist in the environment for long periods may be traceable to the organic structures of these materials. It has been found that substituted aliphatic acids are not degraded by soil microorganisms, whereas the unsubstituted acids are.

Relationship between atmospheric carbon dioxide amount and properties of the sea 736

G. N. Plass

Carbon dioxide continually interchanges in the atmosphere and the oceans; if the amount of carbon dioxide is changed in one, it must eventually change in the other, resulting in climatic changes. The equilibrium equations for the interaction of this gas between the sea and atmosphere are discussed.

Isolation of metal-binding fractions from tobacco smoke condensate 740

V. N. Finelli, E. E. Menden, and H. G. Petering

The tobacco smoke condensate from nonfilter research cigarettes has been separated by on exchange technique into three different materials, two of which bind transition metals. This binding ability may be involved with chronic diseases, chemical carcinogenesis, and artherosclerosis. Studies on the biological and biochemical activities of these fractions are currently under way.

Notes

Chemiluminescent reactions of oxygen atoms with reactive hydrocarbons. I. 7000–9000Å 742

B. Krieger, M. Malki, and R. Kummler

This reaction offers a direct measurement potential for reactive hydrocarbons under conditions analogous to their direct role in photochemical smog formation. The method uses low-pressure, rather than a high-pressure discharge. Earlier, measurements of these hydrocarbons were obtained by subtracting a so-called methane equivalent from a total hydrocarbons value.

Mercury uptake by polyamine-carbohydrates 745

M. S. Masri and M. Friedman

Natural and synthetic polymers containing amino groups are useful for removing mercury as mercuric chloride from aqueous solutions. Specifically, polyamine derivatives of carbohydrates are useful.

Credits: 677, ES&T's Marty Malin; 681 (lower) National Steel Corp.; 683, C&EN's Dermot O'Sullivan; 693, 695, ES&T's Stan Miller; 700, NASMI
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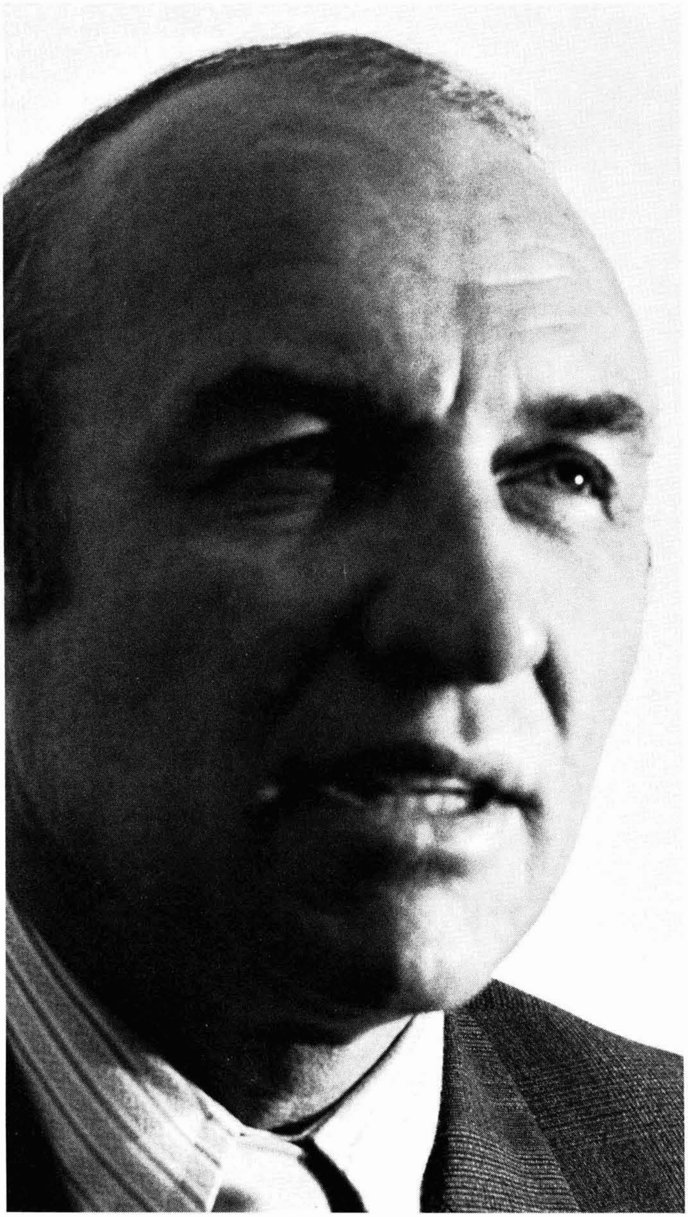
RENT J-M's JACK GARBER.



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letters

Thermal discharges

DEAR SIR:

We have read with considerable interest the article on thermal discharges by authors from Battelle Laboratory in your March 1972 issue, p 224.

Their summary of the observed effects, or rather the lack of observed effects, on the aquatic environment of thermal discharges from power plants closely parallels the results of similar work in Britain over the past two decades. Lengthy ecological surveys at a number of power station sites on rivers and estuaries in this country have consistently failed to disclose measurable effects of heated condenser discharges on local aquatic species, except within a few meters of the outfalls. One of these studies is now in its 14th year, having commenced four years before the plant concerned came into operation, and so far no indication at all has been found of long-term or sublethal effects on the wide range of species studied.

With results like these to hand, from a growing number of countries, it is perhaps permissible to doubt whether the popular image of "thermal pollution" from power plants is justified. Indeed it is doubtful whether this term has any real meaning in temperate latitudes where the seasonal and diurnal variations in natural water temperature to which local species are adapted greatly exceeds the heating effect from the power plant. No doubt instances could be found where, by bad or careless engineering design of the outfall structures, an adverse effect has been created, but at most modern plants the lack of observable effects is not even surprising.

The authors' comments and recommendations on future control practices are equally of interest, and show convergence of views in Britain and the U.S. In effect, they recommend:

- the planned multiple use of waterways, including their use for industrial cooling purposes, to the maximum advantage of the community.
- that each discharge must be considered on its own merits and in relation to the circumstances at the specific site.

These two principles have been the cornerstones of British water pollution control policy for the past 20 years or more.

Under the Rivers (Prevention of Pollution) Act of 1951, details of the flow rate, quantity, temperature, and chemical quality of a proposed effluent have to be disclosed. In return, the River Authorities, before imposing limits on any of these factors, have to justify these limits in relation to the present condition and future use of the waterway itself. Rigid, numerical standards of water quality, applied universally and indiscriminately, have no place in this system. The aim is steady and sustained improvement over the years, rather than instant Utopia, and practical results are the more readily achievable.

The River Thames in the center of London, which 15 years ago was virtually lifeless, now supports almost 50 species of fish and the reintroduction of game fish in the near future is no longer a pipe dream. At the same time, the many direct cooled power plants on this relatively short stretch of the Thames, totaling 3400-MW output capacity, continue to discharge about the same quantity of heat that they did 15 years ago, with no measurable ill effect. In contrast, the improvement in water quality has brought with it problems of corrosion and biological growth in the power plant cooling systems which did not previously exist, and only illustrates that there is no such thing as a simple environmental problem.

A. J. Clarke and F. B. Hawes
Central Electricity Generating Board
London E.C.1, England

Retraining aerospace engineers

DEAR SIR:

The aerospace industry employs engineers having a variety of engineering backgrounds, such as aeronautical, civil, mechanical, sanitary, metallurgical, industrial, chemical, and so forth. In general, these engineers are referred to as aerospace engineers simply because they are associated with the aerospace industry and not because they are degreed as aerospace engineers. As an engineer with a bachelor's and master's degree in mechanical engineering, a doctorate in sanitary engineering, and currently employed by Grumman Aerospace Corp., I am therefore an aerospace engineer.

Having been closely associated with the development of the curricula and the teaching of the retraining program in pollution control with the emphasis on water quality as a specific, critical issue in the environment (ES&T, April 1972, p 316), I must take issue with Professor Okun's letter (your June 1972 issue, p

(Continued on p 672)

478) on the retraining of aerospace engineers for water pollution control.

Prof. Okun's stigmatization that the unemployed aerospace engineer is not likely to have been among the best of those who have been employed by the industry is quite unfair and untrue. It is this type of branding that is harming the unemployed aerospace engineer by creating a severe obstacle to the employment of these highly trained, competent engineers in areas where their talents can be useful. Okun's generalization as to the lack of quality of these engineers is misleading and highly improper without having first ascertained the reasons for their unemployment.

If Prof. Okun's inference as to the unemployment of the thousands of aerospace engineers being due mainly to their lack of quality were true, then it is truly a sad reflection on the quality of our engineering education at the universities. I wonder if Prof. Okun would apply his stigmatization of lack of quality to those professors whose positions may be terminated at one of our largest eastern universities? It seems to me that the university does not operate on a "cost-plus" basis so quality must be very important. This same university is in the process of divesting itself of its school of engineering, which offers both the master's and the doctorate degree in sanitary engineering. The basis for the cutback action of the aerospace industry and the university is *not* lack of quality of personnel, but economic survival.

Prof. Okun says, "If it turns out that the Grumman graduates are not highly sought after, it is no condemnation of retraining. It may just possibly signify that retraining should be done in a university which is equipped for the purpose." I agree with him on the need for retraining; however, I disagree with his narrow-minded pedagogical viewpoint that retraining should be done within the ivory towers of academe.

In my opinion, the parochial attitude expressed by Prof. Okun and others in industry and government has unfairly stigmatized the aerospace engineer to such a degree as to inhibit his employment in any field other than aerospace. Until this attitude is changed, it may make no difference where the aerospace engineer gets his retraining—industry or university. We will be creating a new category of engineer—Retrained Unemployed Aerospace Engineer.

Lawrence Slote
Grumman Aerospace Corp.
Bethpage, N.Y. 11714

Can degraded air be clean air?

Deterioration of air quality to the levels represented by secondary standards won't be the disaster many fear

A June 2 decision by the U.S. District Court in the District of Columbia has once more brought to the fore an issue of the highest importance to all who grapple with the complexities of environmental protection: whether the government can allow a pristine resource to deteriorate in quality. Previous attempts to elucidate this point, in reference to a "nondegradation" clause in water quality standards required by former Secretary of Interior Stewart Udall, never did get resolved. The D.C. decision raises the matter again—this time in connection with air quality.

In this recent court ruling, Judge John H. Pratt imposed a preliminary injunction on the administrator of the federal EPA, requiring him to disallow portions of any state implementation plan that would allow existing air quality to deteriorate. (Implementation plans are required under provisions of the 1970 Clean Air Act; in them, states must specify what steps they will take to achieve certain air quality standards established by EPA within a given time.)

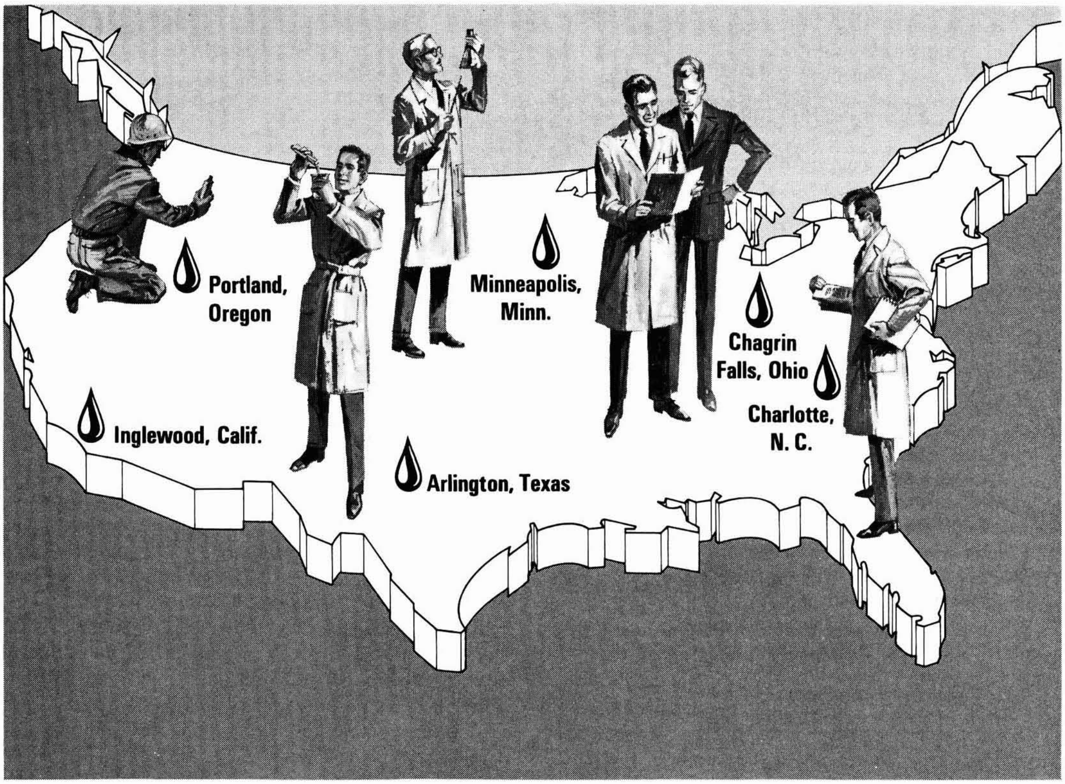
There are two types of standards—a primary standard, at which level public health is deemed to be adequately protected, and a more stringent secondary standard that will prevent damage to plant and animal life. At the time these standards were promulgated, they were widely regarded as being tough, even by EPA, and so close to "background" are the secondary levels that many doubted they could be achieved. It may come as a surprise, therefore, to discover from EPA's own data that quite a few places in the U.S. actually have air that is of better quality than that called for in secondary air quality standards. The pure regions include much of the nonurban west and sizeable chunks in the rural portions of many eastern states.

The court's decision prohibited EPA from approving implementation plans that do not specifically spell out how a state intends to keep air in the pure regions pure in perpetuity. EPA's position, rejected by the court, was that it has no statutory authority to do anything but require states to achieve air quality standards in those regions where the air is now of a quality worse than in the standards. The arguments presented in court, however, make clear that the intent of Congress in passing the Clean Air Act—to "protect and enhance" air quality in the U.S.—is of paramount importance. The contention, upheld by the court, of the plaintiffs in the suit (spearheaded by the Sierra Club), was in essence that protection and enhancement of air quality cannot possibly be consistent with deterioration of air quality.

Notwithstanding a certain logic in the court's decision, something troubles us about it. It would appear to lock up large areas of the country against any sort of development, since it is difficult to see how any human activity could in practice fail to degrade pristine air quality at least a tiny bit. All development would have to be conducted in those parts of the country where existing air quality is worse than the standards—in other words, in areas where the air is already dirty and where states are now trying manfully to clean up. EPA has already appealed the District Court verdict and, in view of all the contradictions and problems, it seems certain that the Supreme Court will eventually be asked to rule on the matter.

The sensible middle ground on the nondegradation issue, it seems to us, is to allow degradation of air quality to secondary standard levels. Air as clean as secondary standards is something that New Yorkers would dearly like to have. Of course, for Miles City, Mont., air that clean would indeed represent deterioration, but without the option to let its air quality deteriorate a small amount, it is difficult to see how Miles City could do anything but stagnate. The plain fact is that air "degraded" to the secondary standard level is *clean* air. To call it dirty air, even in good faith, is to obstruct the effort to attain a rational balance between environmental health and economic development.

D. H. Michael Bowen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environmental currents

WASHINGTON

CEQ's Train sums up U.S. position at Stockholm

Council on Environmental Quality chairman Russell Train, who led the U.S. delegation to the U.N. Conference on the Human Environment (this issue, p 682) called for action on 12 proposals. Train said, "We need not act in hysteria, nor credit every prophecy of ecological doom—but act we must." The 12 items for which he urged support were:
• establishment of a 27-nation commission of the Economic and Social Council, • creation of a $100 million U.N. environmental fund, • regional action for management of environmental resources, • global monitoring and assessment, and • international agreement on control of dumping waste into the ocean.

EPA bans most DDT uses, readies lead action...

• Effective the last day of this year is the Environmental Protection Agency ban on almost all uses of DDT. Three crops—cotton, soybeans, and peanuts—account for the domestic agricultural use of the material. New crop growers will begin to use a substitute material, methyl parathion. DDT use will still be permitted to protect public health in emergencies—for example, in an outbreak of disease following a flood.

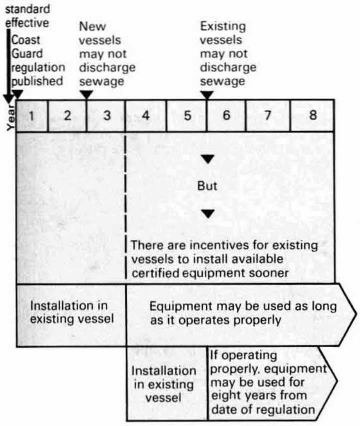
• On July 14, the period for public comments on the lead in gasoline issue ended, and EPA regulation is due imminently. The regulation proposed by EPA called for a two-third reduction in the lead content of leaded gasoline by 1977, but congressional and public pressures are demanding the removal of all lead from gasoline by 1977.

...issues boat standard, and charges for training

• On June 23, EPA issued its final regulation on waste discharge from vessels. Essentially, it's a no-discharge standard. Holding devices are specified and require on-shore pump-out facilities. Although the standard is effective now, it will not be implemented or enforced until the Coast Guard publishes its related regulation, expected toward the end of this year.

• Last month, EPA started charging for its training courses. Some 334 different courses are offered in air, water quality, water hygiene, solid wastes, radiation, and pesticides. In fiscal year 1973, it is estimated that 8000 persons will be enrolled; half of the students will come from state and local agencies; the other half will come from federal agencies, industries, and universities.

Time table for vessel sanitation standards



Congress works on NEPA amendments and water bill

Although the House last year passed its bill (H.R. 56) for a national environmental data system (one amendment) and despite the fact that the Senate passed its version on June 29 this year, the proposal has hit a congressional jurisdictional snag. Basically, the proposal authorizes an office within CEQ for the collection and evaluation of environmental data; this information would then be made available not only to federal agencies but to the public. Meanwhile, House-Senate conferees still labor over this year's Clear Water Amendments.

Commerce extends worldwide monitoring activities

Department of Commerce scientists plan to measure atmospheric carbon dioxide, fine particles, trace materials, and solar radiation attenuation. Dubbed Geophysical Monitoring for Climatic Change, the new program is headed by Donald Pack, director of the National Oceanic and Atmospheric Administration's Air Resources Laboratory (Silver Spring, Md.).

INDUSTRIAL ENVIRONMENTAL HEALTH—The Worker and the Community

editor: LESTER V. CRALLEY, Environmental Health Services, Aluminum Co. of America, Pittsburgh, Pa.

associate editors: LEWIS J. CRALLEY, U.S. Dept. of Health, Education and Welfare, Public Health Service, Health Services and Mental Health Admin., National Inst. of Occupational Safety and Health, Cincinnati, Ohio, **GEORGE D. CLAYTON,** George D. Clayton and Assoc., Southfield Mich., **and JOHN A. JURGIEL,** Industrial Health Foundation, Inc., Pittsburgh, Pa.

Increasing public concern over environmental forces and hazards has led to awareness of the need for improved working conditions in all phases of industry. This book covers both basic research and field studies dealing with all aspects of environmental health, including air and water pollution, as related to industry. It centers attention, however, on evaluating the specific health hazards covered by the Occupational Safety and Health Act of 1970.

August 1972, about 515 pp., $24.00

ENVIRONMENTAL TOXICOLOGY OF PESTICIDES

edited by FUMIO MATSUMURA and G. MALLORY BOUSH, Dept. of Entomology, Univ. of Wisc., Madison, **and TOMOMASA MISATO,** Inst. of Physical and Chemical Research, Wakoshi, Saitama, Japan

CONTENTS: Introduction: Patterns of Pesticide Usage and Occurrence of Residues. Mercury Transformation in the Environment. Chlorinated Hydrocarbon Insecticides in the Environment. Fungicides, Herbicides, Organophosphates, and Carbamates. Photodecomposition of Pesticides. Toxic Effect of Pesticide Residues on Wildlife. Design of New Pesticides.

1972, 662 pp., $17.50

MULTIPLE FACTORS IN THE CAUSATION OF ENVIRONMENTALLY INDUCED DISEASES

edited by DOUGLAS H. K. LEE and PAUL KOTIN, Temple University, Philadelphia, Pa.

This book discusses the effects produced by common combinations of environmental agents and considers measures for optimum control of these complex situations. It contains a wealth of information on such topics as: diseases caused by environmental agents (e.g., cancer, liver cirrhosis, arteriosclerosis, chronic obstructive lung disease, and nephritis); the interaction of environmental agents with each other and with constitutional factors in the pathological process; and instances in which two or more environmental agents are known to interact in the production of effects on tissue function.

4Q1972 in preparation

MUTAGENIC EFFECTS OF ENVIRONMENTAL CONTAMINANTS

edited by H. ELDON SUTTON, Dept. of Zoology, Univ. of Texas at Austin **and MAUREEN HARRIS,** The John E. Fogarty International Center, National Inst. of Health, Bethesda, Md.

New products are being introduced into our society faster than their safety can be ascertained, and both governmental agencies and public groups have expressed concern about the possible mutagenic effects of some of these products. This book provides a comprehensive treatment of this problem, for both the nonspecialist and the many scientists interested in: the current burden of mutation as human genetic disease, the molecular biology of mutation, practical and feasible tests (using a variety of organisms) for screening potentially mutagenic agents, and methods of determining the human mutation rate and the consequences of an increase in the rate.

1972, 214 pp., $7.50

SYSTEMS ANALYSIS AND SIMULATION IN ECOLOGY, Volume 2

edited by BERNARD C. PATTEN, Department of Zoology, Univ. of Georgia, Athens

TENTATIVE CONTENTS: ECOSYSTEMS: DYNAMIC ANALYSIS. ECOLOGY SYSTEM GROUP: A Dynamic Analysis of Grassland. M. BRYLINSKY: Sensitivity Analysis of Energy Flow in a Marine Ecosystem. G. I. CHILD and H. H. SHUGART: Frequency Response Analysis of Magnesium Cycling in a Tropical Moist Forest. THEORY: H. T. ODUM: An Energy Circuit Language for Ecological and Social Systems: Its Physical Basis. R. B. WILLIAMS: Steady State Equilibriums in Simple Nonlinear Food Webs. G. C. GALLOPIN: Structural Properties of Food Webs. B. C. PATTEN: Some Odd (and Even) Relationships in Food Webs and the Inverse Modeling Problem. APPLICATIONS AND PROSPECTS: S. B. SAILA: Systems Analysis Applied to Some Fisheries Problems, G. J. PAULIK: Digital Simulation Modeling in Resource Management and the Training of Applied Ecologists. O. L. LOUCKS: Systems Methods in Environmental Court Actions. T. C. FOIN, Jr.: Systems Simulation and the Future of Human Society. A. BEN CLYMER: Next Generation Models in Ecology.

1972, about 635 pp., in preparation

Advance Announcement...

FUNDAMENTALS OF AIR POLLUTION

by ARTHUR C. STERN, Dept. of Environmental Sciences and Engineering, School of Public Health, Univ. of N. C., Chapel Hill, **HENRY WOHLERS,** Depts. of Environmental Science and Engineering, Drexel Univ., Philadelphia, Pa., **RICHARD W. BOUBEL,** Dept. of Mechanical Science and Engineering, Oregon State Univ., Corvallis, **and WILLIAM P. LOWRY,** Dept. of Atmospheric Sciences, Oregon State Univ., Corvallis

FUNDAMENTALS OF AIR POLLUTION is divided into four parts. Part 1 examines the scale of the air pollution problem from local to global levels, encompassing ecology, pollution, air quality and air chemistry. Part 2 covers air sampling and analysis, discusses the effects of pollution on inert materials, vegetation, animals, and man, and relates these effects to air quality criteria and standards. Part 3 deals with the meteorology of air pollution, including the bases of climate, climatology, atmospheric radiation thermodynamics, precipitation, and atmospheric motion. Part 4 outlines the sources of air pollution and discusses source sampling, engineering and regulatory control, and means of organization for air pollution control.

1973, about 500 pp., in preparation

METALLIC CONTAMINANTS AND HUMAN HEALTH

edited by DOUGLAS H. K. LEE, National Inst. of Environmental Health Services, Research Triangle Park, N.C.

Here is an authoritative review of current knowledge of the principal metallic contaminants in the environment and their effects upon human health. The book concentrates on discussions of mercury, lead, and cadmium, but it also includes indepth discussions of chromium, manganese, nickel, vanadium, and arsenic. In addition, the book discusses the fluorides because of public interest in possible effects from industrial use and fluoridated water.

1972, 260 pp., $7.00

ENVIRONMENTAL FACTORS IN RESPIRATORY DISEASE

edited by DOUGLAS H. K. LEE

This book is divided into three major sections. Following an introductory chapter, the first section discusses the physiology of the lung, tracheobronchial responses to insult, alveolar response to insult, and the effects of chronic respiratory disease on the function of the lungs and heart. The second section deals with lung responses to environmental factors, environmental factors in chronic lung disease, pulmonary responses to the environment, and the interaction of infectious disease and air pollutants. The final section discusses such special problems as the relation of smoking and air pollution to lung cancer, occupational lung diseases, epidemic asthma, and environmental factors in bronchial asthma.

1972, in preparation

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STATES

Pa., Okla. regulate solid wastes; N.Y. utilizes glass

- After solid waste management plans mandated by Pennsylvania's Solid Waste Management Act are approved, five counties (Bucks, Chester, Delaware, Montgomery, and Philadelphia) have from six months to a year to phase out the illegal dumping of solid wastes into unpermitted landfills and to make other arrangements for disposal of these wastes.
- The Oklahoma Department of Health has set a July 1974 deadline for every Oklahoma community to have a sanitary landfill or other acceptable solid waste disposal operation. State permits will be issued.
- Glasphalt pavement, utilizing more than 90,000 waste bottles and jars, has been installed on a heavily traveled roadway (3000 vehicles/day) at John F. Kennedy International Airport by the Port of New York Authority.

Shoreline zoning studied for Maine law requirements


Zoning the Maine shoreline

The University of Maine has received a $100,000 Ford Foundation grant to support planning and research on zoning and subdivision control in Maine shoreline areas. The University hopes to assist local, regional, and state agencies in responding positively to a Maine law requiring the zoning of all lands within 250 ft of water bodies by June 30, 1973.

New environmental agencies in Idaho, Colo.

- Idaho's Department of Environmental Protection and Health officially came into being last month. The new department includes the former department of health and combines the forces of environmental concern from other agencies into one organization.
- Colorado is turning toward the public utility concept with solid waste services. At present, private collectors are licensed by the Public Utilities Commission; with the new system, to be operating within two to three years, the state will regulate rates as it does with common carriers.

Ocean dumping prohibited, recycling studied in Calif.

- California has banned ocean dumping of sludge from sewage treatment plants, "high level" industrial wastes, and chemical, biological, or radiological "warfare agents." Under these controls, municipal and industrial wastes must (by 1977) receive secondary treatment before disposal.
- Under contract to the San Francisco District, the U.S. Army Corps of Engineers, and the engineering, architectural, and planning organization of Parsons, Brinckerhoff, Quade & Douglas, Inc. (New York, N.Y.) are investigating alternative means of recycling effluent from secondary sewage treatment plants in the San Francisco Bay–Delta area.

Colo. sets up toxic spill warning, tests enforcement

- Colorado's Department of Health has developed a procedure for quick evacuation of an area in the event of an accidental spill of toxic materials into the air. By knowing the type and quantity of material emitted and the wind speed and direction in the spill area, meteorologists will plot the direction and range the toxic material will travel. Affected areas can be determined in minutes and evacuation started.
- Fry Roofing Co. is appealing a decision of the State Air Pollution Variance Board that the firm violated Colorado's air pollution control law. As the first such case to go to the state Supreme Court, the decision will have a far-reaching impact on air pollution control in Colorado.

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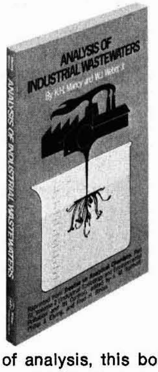

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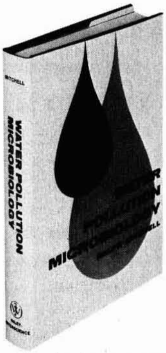

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environmental currents

TECHNOLOGY

Hydrolysis holds promise for cyanide destruction

It may be better to detoxify metallic cyanide compounds by hydrolysis rather than by chemical addition, according to a German scientist, who has applied for a patent on his process. By hydrolysis, cyanides can be converted to ammonia and salts of formic acid, according to a reaction first observed 140 years ago. At room temperature hydrolysis doesn't work well, but at temperatures above 150°C the reaction proceeds fast enough to allow continuous detoxification of most simple metallic cyanides. Transition metal–based cyanide complexes require a somewhat longer detention time or elevated temperature. The higher temperatures and pressures necessitate high-alloy steel reactors, according to the process inventor U. Schindewolf.

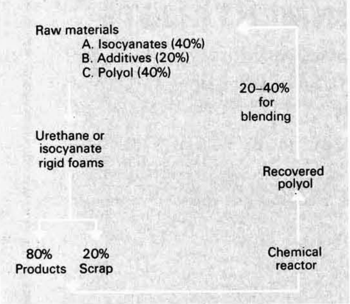
R_x for mine water: keep it out of mines

In some cases the best way to clean up acid mine drainage might be to intercept groundwater before it seeps into a mine, according to Richard Parizek, a hydrogeologist at the Pennsylvania State University. Using aerial photography, he pinpoints underground collection points for groundwater above mines and then sinks wells into them. Where the geography is favorable, water from the collection reservoirs could be drained out by gravity. Even if it were necessary to pump water from the well, the hydrogeologist estimates that the total annual cost per installation would be only about $^{1}/_{20}$ as much as treatment.

Closing the loop on plastic solid wastes

The Upjohn Co.'s Chemical Division has pilot-tested a process for recycling rigid urethane foam and says the process should be ready for scaleup to a commercial-size plant next year. Details of the process have not been fully revealed, but the process is known to convert scrap rigid urethane or other polymeric isocyanate–based foams into a polyol. The recovered polyol costs about two thirds as much as the virgin material to produce, and can be blended in amounts of 20–40% with virgin polyols to make foam. About 20% of the rigid foam produced each year in the U.S. ends up as scrap which must be landfilled, according to Upjohn.

Upjohn's recycle scheme

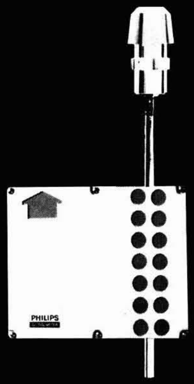


Nature makes 10 times more CO than man

Mother nature puts 10 times more carbon monoxide into the atmosphere than all industrial and automotive sources combined, according to a study by scientists at Argonne National Laboratory (Argonne, Ill.). Natural processes—oxidation of methane and the decay and growth of chlorophyll—release about 3.5 billion tons of CO annually to the atmosphere, according to the Argonne data. All man-made sources contribute about 270 million tons per year. The findings do not "exonerate man or minimize the need for reducing emissions," according to Alan Zengel, project manager for the Coordinating Research Council (New York City) which sponsored the Argonne study, but they demonstrate that the balance of CO in nature is "much more complicated than originally supposed."

Converting tannery effluents to proteins

Lime–sulfide solutions used in tanneries to unhair hides have high COD but with proper treatment can yield potentially valuable protein, according to Steven Feairheller of the U.S. Department of Agriculture. The solutions are clarified by filtration or centrifugation; dissolved solids are removed by dialysis and dried. The solid product shows promise as an animal foodstuff and for uses in adhesives and cosmetics.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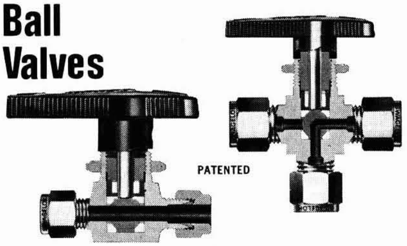
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environmental currents

INDUSTRY

Business International's President Freeman

U.S. exporters should adopt EEC standards

U.S. exporters must be prepared to meet the stringent environmental protection standards likely to be adopted by the European Economic Community (EEC) or face the prospect of being shut out of the market, according to Orville Freeman, president of Business International Corp. (New York City). The implementation of such regulations is still several years in the future, says Freeman, a former Secretary of Agriculture, but he warns that American firms should "ready themselves now for what's ahead." The proposed regulations were submitted to members and pending members of the EEC this spring. The standards would become applicable in the next few years. Once accepted by the EEC, the standards would in effect become applicable to the entire industrialized world.

Alaskan firm plans to use north slope oil

Should the long-delayed Alaskan oil pipeline eventually be built, at least one company is hoping to tap into the line before the oil reaches the ice-free port of Valdez. Energy Co. of Alaska (a subsidiary of Earth Resources Co., Dallas, Tex.) plans to erect a $45 million industrial complex 12 miles from Fairbanks. The complex would include a 15,000 bbl/day refinery and a 30-MW-plus power plant fired by desulfurized fuel oil from the refinery. The complex could provide roughly 85% of the electric power and all the petroleum products for the Alaska interior at a substantially lower cost than is now being paid. More than $5 million will be spent for environmental controls.

Steel cans to be recycled

Steel recycles its cans; tax relief in the wind

- The steel industry now "guarantees" that all steel cans produced in the United States contain at least 25% recycled material. The American Iron and Steel Institute says that about 2¹/₄ billion steel cans will be reclaimed in 1972 by the 22 municipalities now using magnetic separation in refuse disposal plants, and predicts that more than 3 billion cans may be salvaged in 1973.
- A tax incentive bill, introduced in the House of Representatives by Congresswoman Martha Griffiths (D.-Mich.), would provide deductions for companies using recycled materials for manufacture in useful raw materials of salable products, and would allow amortization of solid waste material facilities on a five-year basis to those firms recovering, processing, converting, and manufacturing solid wastes into raw materials and products.

Detergent maker will list all ingredients

Procter & Gamble (Cincinnati, Ohio) will begin listing ingredients on all packages of its household laundry, dishwashing, and cleaning products in a move to assure consumers of P&G's "continued commitment" to provide them with information about its products. All major ingredients will be identified by chemical name, while those ingredients used in small amounts will be identified by function. The listing on P&G's Tide, for example, would read: "Ingredients: Tide contains ingredients to lift dirt from clothes (anionic and nonionic surfactants), soften water (complex sodium phosphates) and protect washer parts (sodium silicate). There are also processing aids (sodium sulfate) and small quantities of soil-suspending agents, fabric whiteners, and perfume." The new labeled packages will begin to appear in the next few months.

U.N Conference: idealism has its day

The question now is whether national truculence will swamp good intentions

"Things will never be the same again," an observer was moved to remark as he gazed out over one of Stockholm's crowded assembly halls where delegates were hunched in concentration over the documents before them. In front of each group was a card plainly marking the country it was representing. One read Afghanistan, another, Algeria, a third, Argentina, and so on down the list of the alphabet of nations; 113 in all, each playing its role in the two-week deliberations of the U.N. Conference on the Human Environment. In addition to national delegates, there were representatives from 37 intergovernmental organizations as well as observers from special interest groups.

The comment reflected the consensus of opinion at Stockholm, that matters of the environment had indeed been lifted out of the narrow context of national policy to become a subject of international discussion. Reinforcing this idea is the decision reached at Stockholm to set aside June 5 each year as World Environment Day. Said Maurice Strong, secretary general of the Conference, "We have taken the first steps on a new journey of hope for the future of mankind."

The Conference was more than three years in the making; the U.N. General Assembly endorsed the idea back in December 1968. Even so, there were some who held that the agenda was too ambitious to be adequately covered in the 12 days between June 5 and 16. And there were plenty of moments when it seemed they were justified in their opinion, as discussions got bogged down over seemingly nit-picking arguments revolving around definitions of terms and the recasting of phrases.

Symbol. *Conference logo represents underlying theme, "only one earth"*

Nevertheless, by the time Conference president, Ingemund Bengtsson, Sweden's minister of agriculture, formally declared the meeting closed, the more than 1400 participants had put their approval to a Declaration on the Human Environment, and had endorsed the more than 100 proposals that make up an Environmental Action Plan. "The success of the Conference offers great hope both for further joint international action in this immensely important area and for the strengthening of the United Nations as a whole," said Dr. Bengtsson. The documents now go before the U.N. General Assembly in the fall for acknowledgment and, the organizers hope, acceptance.

Cliff-hanger Declaration

The Declaration centers around "the need for a common outlook and for common principles to inspire and guide the peoples of the world in the preservation and enhancement of the human environment." Although an extensive amount of pre-conference work on the Declaration had seemed to ensure it plain sailing at Stockholm, it was in fact the subject of considerable debate, initiated by the Chinese delegation. The Chinese argued that since the Peoples Republic of China was not a U.N. member when the document was drawn up, it should be allowed an opportunity to have a say in its content. A hastily assembled ad hoc working committee sequestered itself in a hideaway outside Stockholm and in true cliff-hanger fashion finally emerged with a revised Declaration draft that was generally acceptable to all at 5 A.M. on the closing day of the Conference.

In its seven-point Proclamation, which opens with the statement "man is both creature and moulder of his environment," the Declaration spells out the reasoning underlying the need for a greater sense of international environmental awareness. Then follow 26 Principles that span every aspect of the influence of environmental conditions on mankind, from "racial segregation and discrimination" to "the effects of nuclear weapons and all other means of mass destruction."

The 60-man U.S. team that went to Stockholm, led by Russell Train, chairman of the U.S. Council on Environmental Quality, was among those who harbored strong doubts about the advisability of opening up the original draft of the Declaration to debate. But in a statement issued at the close of the Conference, Train's group noted that "although the resulting text is uneven in quality, it contains important principles which may serve as a foundation for future international law; and its Preamble contains concepts which may serve a wide educational value."

While each of the 26 Principles of the Declaration (they exceed by three the number in the original draft) embodies a profound concept, the U.S. delegates cite several that they consider particularly significant. For instance, Principle 2 calls for safeguarding the earth's living and nonliving resources for future generations, Principle 6 demands a halt to the discharge of toxic substances and of the release of heat beyond the capacity of the environment to render them harmless, and Principle 16 deals with population density.

Also highlighted were Principle 21, urging nations to be aware of their responsibility "to ensure that activities within their jurisdiction and control do not cause damage to the environment of other States or to areas beyond the limits of their national jurisdiction," and Principle 25, which declares that "States shall ensure that international organizations play a cooperative, efficient and dynamic role for the protection and improvement of the environment."

Framework for action

During their deliberations on the Action Plan, drawing up of which was a major conference goal, the Stockholm

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This story was written especially for ES&T by Dermot A. O'Sullivan, London Bureau Head for our sister publication, Chemical & Engineering News, who attended the U.N. Conference in June.

Optimist. *Chairman Strong sees conference as beginning "a journey of hope"*

conferees were grouped into three committees. Each met concurrently to debate the issues of two subject areas. One discussed approaches to planning and management of human settlements for environmental quality, as well as the educational, informational, social, and cultural aspects of environmental issues. The second reviewed environmental aspects of natural resources management and the very broad subject of development and the environment. The third considered identification and control of pollutants of broad international significance, and the international organizational implications of action proposals. The aim of the Action Plan is to provide a framework "to establish the basis for a concerted international attack on major specific environmental concerns and long-term objectives."

Many far-reaching recommendations were adopted at these sessions. One urges a global convention to restrict ocean dumping; the convention is to be completed by the end of this year. Another recommendation spells out steps that should be taken to minimize the release into the environment of heavy metals and organochlorine compounds.

There was agreement on the need for an Earthwatch program, in which satellites could play a key role, to monitor and assess environmental trends in the atmosphere, oceans, and land masses. An international program was called for to collect and safeguard plant and animal resources on which stability of ecosystems and future breeding stocks depend. Keyed to this would be a referral service to facilitate exchange of data and technical developments in environmental matters. Other proposals range from the need to expand education and training programs to steps that should be adopted to prevent national environmental actions from creating trade barriers against the exports of developing nations.

Perhaps most important from the standpoint of keeping alive the "spirit of Stockholm" were proposals to establish the organizational and management machinery to ensure that the recommendations of the Action Plan are carried out. One of these is the setting up of a voluntary Environmental Fund. The delegates adopted President Nixon's earlier proposal to raise $100 million for this fund, toward which the U.S. has pledged $40 million, to help meet the costs of the various programs during the coming five years. Although the amount falls short of the $164 million that Maurice Strong estimates would be nearer the figure needed, it is, as he puts it, "a good beginning."

To manage the Fund, and to help coordinate the environmental programs already under way or planned by various U.N. organizations, would be a U.N. Environment Secretariat headed by an executive director elected by the General Assembly. The secretariat itself would be funded out of the regular U.N. budget, but details as to its size and location are yet to be worked out.

The delegates also recommended establishing a Governing Council for Environmental Programs. This body, comprised of 54 members chosen by the U.N. General Assembly, would "provide general policy guidance for the direction and coordination of environmental programs within the U.N. system." Its members, appointed for three-year terms, would be chosen "on the basis of equitable geographical distribution."

Paper tiger

The less optimistic at the Stockholm meeting cite several issues that raise a question mark over the degree of its ultimate success. They noted, for instance, the boycotting of the Conference by the Soviet Union and most of the Communist bloc countries over the failure of East Germany (which isn't a U.N. member) to gain an active role in the proceedings. There were several instances, too, when discussions on particular environmental issues couldn't be pursued without touching on a country's political or national aims. Typical was Brazil's quashing of attempts to open up for deliberation the environmental consequences that many fear will result from the extensive development programs under way in the Amazon Basin.

Even two firm recommendations handed down by the delegates failed when put to the test soon after the Conference. The International Whaling Commission, meeting in London two weeks later, voted against adopting a 10-year moratorium on whaling agreed to at Stockholm. And France turned a deaf ear to urgings to halt atomic bomb tests in the Pacific.

Dr. Barbara Ward of Columbia University and coauthor with Rene Dubos of "Only One Earth," sounded a note of caution when she admonished the participants against falling into the trap of thinking they had gone a long way toward solving environmental problems, simply on the basis of having spent many hours discussing them. The best laid plans are of little consequence if the will and determination to see them come to fruition are lacking, she observed. Moreover, she pointed out that while it's possible to justify to ourselves our particular stand on moral issues, "you can't fool DNA, and you can't fool the genetic code."

In-plant control of workaday hazards

The Occupational Safety and Health Act affects you and your boss more than you know

With a congressional mandate of assuring, so far as possible, safe and healthful working conditions for every working man and woman in the U.S. and preserving our human resources, the Occupational Safety and Health Act became law more than one and one-half years ago. The law covers 60 million workers in 5 million workplaces. It essentially covers all business establishments engaged in interstate commerce with the exceptions of coal mining and atomic energy, for each of which other federal occupational safety and health laws are applicable.

Everyone hears that the new act is causing a quiet revolution in the job health area. Certainly, it is safe to say that the law has at least initiated a new beginning in the job health area.

One consequence of the new law was the creation of two new federal agencies—the Occupational Safety and Health Administration (OSHA) in the Department of Labor, and the National Institute of Occupational Safety and Health (NIOSH) in the Department of Health, Education and Welfare. Administration and enforcement of health standards are vested in OSHA which is headed by Assistant Secretary of Labor George Guenther, whereas research and related health standards functions are dealt with in NIOSH, headed by Assistant Surgeon General Marcus Key.

Today, approximately 1000 personnel are on board in OSHA, and although the federal manpower ceiling for NIOSH was 702 in fiscal year 1972, only 600 persons are employed at present. Nevertheless, with a manpower ceiling for fiscal year 1973 of 720, NIOSH expects to fill all these positions by July 1, 1973.

The OSHA program is truly decentralized. Of its 1000 personnel, 317 are located at the national office in Washington, D.C.; the other two thirds are in the field—in the 10 regional and 51 district and area offices of OSHA. On the other hand, of the 600 NIOSH personnel, about 100 are at national headquarters in suburban Washington, D.C. (Rockville, Md.), another 100 at the black lung research center at Morgantown, W.Va., 40 at the western area research lab at Salt Lake City, Utah, and the remainder in field offices.

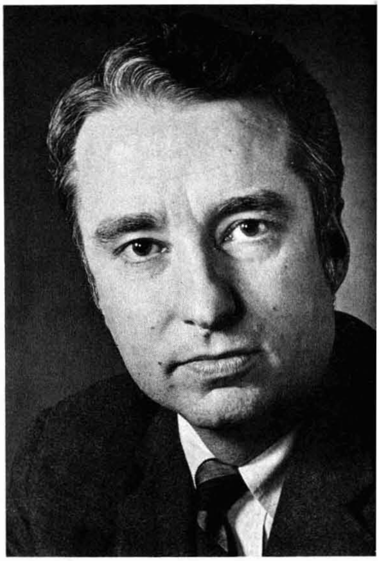
As for funding, OSHA received $36.5 million in fiscal year 1972, and NIOSH received $26.5 million, of which 67% went for research on new standards, and the remainder was earmarked for manpower training. However, the budget request for both agencies is greatly increased for fiscal 1973—$67.5 million for OSHA and $29.5 million for NIOSH. On June 16, the House passed an appropriation of $29.5 million for NIOSH, the amount requested. But on June 27, the Senate appropriated $64.5 million for NIOSH. The $35 million difference between the House and Senate versions (to be settled in conference) include two additional big items of $20 million for black lung research and $11 million for research on occupational standards outside of coal mining. The big increase in the OSHA budget request is a $21 million item for state planning.

What has been achieved?

The Occupational Safety and Health Act has set the ball rolling in several areas. OSHA authorized development and enforcement of standards to assure safe and healthful working conditions for employees in the private sector. What's more, Executive Order 11612, signed by President Nixon on July 26, 1971, established an occupational safety and health program in federal departments and agencies, requiring an equivalent safe and healthful workplace for federal workers.

OSHA announced two programs—a target industries program and a target health hazards program (see box). Inspection and compliance are in full swing in each program as well as in all industrial workplaces under the auspices of the act.

Today OSHA has approximately 400 compliance officers and inspectors in the field and will, more than likely, have 600 in the field by next June 30. Candidates coming to OSHA for compliance work receive four weeks of intensified training at the OSHA training institute near O'Hare field in Chicago, Ill. All compliance officers are in the safety engineering field, and virtually all are college graduates.



OSHA's Guenther
promulgating standards, inspecting and enforcing them

In addition to compliance officers necessary for enforcing standards, industrial hygienists play an important role. Approximately 50 industrial hygienists (one in each district and area office) conduct inspections in the workplaces for the five in-plant pollutants specified in the target health hazards program.

The target industries program pinpointed those industries which were more accident-and-injury prone than others. Each of the five cited industries (box, p 686) had an injury rate more than double the national average figure of 14.9 injuries per million employee hours worked. The goal of OSHA compliance inspectors was to visit all establishments in each of the five target industries program by June 30, 1972. One of the main priorities of this program is to reduce the number of injuries per million employee hours worked at least to the earlier national average of 14.9.

What really has been accomplished was summed up at a press conference on the first anniversary of the new law. In the first nine months of fiscal year 1972, 400 OSHA compliance officers and industrial hygienists conducted a

NIOSH's Key

ascertaining if indeed there is a health hazard

total of 26,868 inspections in 20,688 establishments employing 4,064,205 workers. Although only 23% of the establishments were found to be in compliance with safety and health standards, Assistant Secretary Guenther seemed pleased. Realizing that these inspections were conducted in the target areas, he indicated that "this percentage (23%) is a respectable indication that employers and employees are addressing themselves to the improvement of job safety and health conditions."

On the other hand, NIOSH provides the scientific base for establishing occupational health standards. This federal agency provides so-called criteria documents to the Labor Department with recommended threshold limit values (TLV). However, the Department of Labor does not have to accept the values that NIOSH recommends.

By the end of calendar year 1971, NIOSH had identified some 15,000 harmful materials to which workers should not be exposed, but industrial hygiene standards existed only for approximately 500 of these materials. Mainly, these industrial hygiene standards are the TLV's developed by the American Conference of Governmental Industrial Hygienists. Basically, the TLV is the safe level at which workers can be exposed to a certain material for an 8-hour day, 40 hours a week.

Before the target health hazards program was announced, NIOSH submitted a list of 10 materials to the Department of Labor based on the prime considerations—toxicity of the material and the number of workers exposed. With these two considerations in mind, OSHA then narrowed the list to the five announced health hazards based on additional considerations of reliability and currentness of the standard and capability for compliance and inspection.

NIOSH top priorities are the development of criteria documents on occupational hazards. Their first document on asbestos was finalized this February. A second one for beryllium and a third one for carbon monoxide were under way at press time, with projected completion by June 30, 1972. Then, early in the 1973 fiscal year budget cycle, NIOSH expects to issue additional criteria documents on other occupational hazards (see box).

Compliance and inspection

In the target health hazards program, each of the materials must be capable of inspection and compliance. In this program, OSHA industrial hygienists, who generally have received college training in the industrial hygiene field earlier, receive additional training before embarking on inspection and compliance tours in the workplaces. For example, they learn:

- how to sample
- how to classify violations
- where to sample
- methods of analysis.

In this target program, 25 Standard Industrial Classification (SIC) industrial categories are the prime targets, but the program, of course, is not limited to industries within these 25 codes.

Compliance inspectors concentrate on the five toxic materials—lead, carbon monoxide, silica, cotton dust, and asbestos. They use a carbon monoxide detector—a Hopkalite meter which reads ppm CO directly. Each inspector also has a battery-operated personal sampling pump with a variety of filter papers for the different materials to be sampled. Three of the toxic materials listed are major dust hazards—asbestos, cotton dust, and silica. For inspecting each of these dusts, a sample is collected using the hand pump with a certain airflow rate setting. The filter paper sample is then submitted for analysis to the Salt Lake City office. For example, fiber counts are performed on the asbestos samples using a phase-contrast illuminating microscope—fiber particles larger than 5 μ in length are counted. On the other hand, cotton dust samples are weighed on an analytical balance in the area offices.

Several different types of meters are used for noise inspections. Regular sound level meters can be used to measure noise levels in certain industrial operations, for example, in textile mill operations. Manufacturers of regular sound level meters include

- B&K (Bruel and Kaeger) meters (Cleveland, Ohio)
- General Radio (Boston, Mass.)
- Columbia Research Labs, Inc. (Woodlyn, Pa.).

In general, these meters have a slow response time and cannot be used to measure noise at high speeds such as jet aircraft noises. Impact meters, such as one manufactured by General Radio, are needed for this purpose.

Remaining chores

Obviously, many problems remain to be achieved under the new act: getting the word out about the more than one-year-old act, state involvement with inspections and compliance, and record-keeping requirements that industries must maintain.

Spreading the word about the act is still under way. OSHA conducts one-day seminars for both employers and employees in each of the 51 district and area offices. About 100 are held every month. What's more, OSHA expects to schedule about 1200 seminars during fiscal 1973. OSHA also put out a compliance manual; however, the 25,000 copies were depleted within six weeks.

The states have a major role yet to play under the new act. Before the end of this calendar year, states must come forth with their plans for compliance and inspections within their jurisdictions. All told, plans for 56 jurisdictions—50 states plus 6 territories—are expected by OSHA. At press time, 15 states had finalized contract agreements with OSHA to conduct inspections in the target health hazards industry program. South Carolina was the first state to comply.

At the press conference on the first anniversary of the new act, Guenther said, "During the coming year OSHA will be involved in the critical transition from state planning to state operations—achieving the intent of Congress to have the states assume full responsibility for development and enforcement of occupational safety and health standards."

Fiscal year 1973 is the last year that states can receive 90% federal grants to plan their programs as authorized by Occupational Safety and Health Act (P.L. 91-596). The assistant secretary expects 20–25 state plans to be in operation by the end of next June—boosted perhaps by the $31 million increase in the 1973 budget request for OSHA, $21 million of which goes for state programs.

Record-keeping is another needlesome aspect. Under the act, all employers are obligated to maintain records of the cause and prevention of occupational accidents and illnesses. Although only those employers who are contacted by the Bureau of Labor Statistics have to submit their records to OSHA, records must be kept for a period of five years.

The nationwide record-keeping and reporting system will provide data on occupational injuries and illnesses and was in fact developed in cooperation with the Bureau of Labor Statistics. Some 35–40 states are expected to participate in a statistical survey this calendar year.

OSHA says that the record keeping has been simplified. Forms have been standardized and definitions clarified. Now, employers must not only report injuries and illnesses, meaning any situation which resulted in lost work days, but, more importantly, must also include any situation which resulted in medical treatment, loss of work or motion, loss of consciousness, or transfer to another job, even if no work day was lost. The latter requirement gets away from "the safety job" where workers were put on light duty because they could not perform their own jobs.

What use OSHA will make of the records that employers keep it is too early to say. But with such records in certain critical industry areas, the federal regulatory agency could, for example, perform in-depth studies of injury producing patterns within industry. After finding out where injuries are occurring, then OSHA could determine why.

The law also created an Occupational Safety and Health Review Commission. Employers dissatisfied with alleged violations can appeal such violations to the panel. Of the cases appealed, penalties were reduced in 43% of the cases, but stiffened in 15%. In the establishments that did not comply, (in the first nine months of fiscal year 1972), some 63,573 violations resulted in 16,370 citations to employers amounting to proposed penalties totaling $1.4 million.

It is noteworthy that the new law provides that citations and penalties can be imposed only against the employer, despite the fact that the employee's action may result in the actual violation. Nevertheless, compliance inspections will increase in fiscal 1973. Is your establishment ready? SSM

Timetable, targets and provisions of the new law

The Williams-Steiger Occupational Safety and Health Act
P. L. 91-596, signed on Dec. 29, 1970

April 28, 1971

Law became effective (OSHA established)

May 26, 1971

NIOSH established

June 30, 1971

Target industry program announced for five top injury-prone industries:

- longshoring
- roofing and sheet metal
- meat and meat products
- lumber and wood products
- miscellaneous transportation equipment (manufacturers of cargo trailers, mobile homes, and snowmobiles)

Jan. 4, 1972

Target health hazards program announced: (including standards for five materials)

- lead
- carbon monoxide
- silica
- asbestos
- cotton dust

Apr. 28, 1972

First anniversary of new law (see text)

OSHA priorities

- reduction in workplace deaths and catastrophes
- response to complaints initiated by the work force
- special programs—the target industries and target health hazards programs
- inspection and compliance for a random cross section of industries

NIOSH priorities

- research and development of criteria for standards in the area of occupational health

NIOSH activities and plans

- produced asbestos criteria document and transferred it to Department of Labor in Feb. 1972
- was completing a second document on beryllium and a third on carbon monoxide which were to be submitted before the end of fiscal year 1972
- expects documents on heat stress and noise by early fall
- expects documents on cotton dust and uv radiation somewhat later

Typical violations in the health hazards area:

- asbestos (if the workplace concentration level exceeds 5 fibers/ml greater than 5 μ in length)
- cotton dust (if the workplace concentration exceeds 1 mg/m^3 of air)
- silica (if the workplace concentration exceeds 10 mg/m^3 of air divided by the percentage of SiO_2 plus two)
- lead (if the workplace concentration exceeds 0.2 mg/m^3 of air, (8-hr time-weighted average)

Violations

- civil penalties up to $1000 . . . are provided for each violation; each day constitutes a new violation
- willful or repeated violations, the penalty increases to $10,000
- criminal penalties are set for willful violations resulting in death

Information tips

- any employee who believes that a violation of job safety or health standard exists which threatens physical harm, or that an imminent danger exists, may request an inspection by sending a signed written notice to the Department of Labor

Adsorption process eases acid recovery

New continuous technique has been used with success on spent aluminum cleaning solutions

Pennsylvanians seem to be famous for encouraging frugality. "Waste not, want not," and "A penny saved is a penny earned," Benjamin Franklin said.

Another Pennsylvanian agrees. Dr. Leslie E. Lancy, founder and president of Lancy Laboratories, Zelienople, Pa., says, "To protect the environment, waste nothing. Discharge only that which absolutely cannot be reused." That philosophy, coupled with his belief that cleanup should begin near the beginning of a process and not at the end, is reflected in Lancy's new phosphoric acid recovery unit. The unit was recently unwrapped—but only partially unwrapped—for newsmen on the occasion of the dedication of the company's newly expanded research and development facilities near Pittsburgh.

Lancy Laboratories, a part of the chemical group of Dart Industries, specializes in waste treatment design and engineering for metal-finishing systems. Lancy's phosphoric acid unit is designed to clean up acid-bearing wastes from aluminum brightening and finishing operations.

In the past, acid drag-over from brightening baths contaminated with aluminum phosphate and diluted by rinse waters had to be chemically neutralized before discharge. Recovery processes have been uneconomical to date, despite the fact that commercial-grade phosphoric acid costs about $140/ton.

Lancy's technology recovers better than 75% of the acid used. The recovered dilute acid (25–30%) needs only to be concentrated for reuse. The aluminum content of the concentrated acid is negligible (about 1–2 g/l.) Lancy says, so the recovered phosphoric can be returned directly to the manufacturing process. Proper neutralization of the acidic aluminum phosphate fraction which cannot be returned to the process stream yields a sludge that is suitable for fertilizer. Alternatively, aluminum phosphate could be recovered for sale to the pigment industry, Lancy believes.

Sorption process

The proprietary package plant developed by the Lancy group is based on sorption. The heart of the unit is a U-shaped 23-ft-tall column packed with ion exchange resin. Although the packing is an ion exchange medium, the separation process is strictly adsorption and desorption. No ion exchange takes place, Lancy says, and the resin serves only as a contacting medium. Lancy is currently using Rohm and Haas's 410 resin, but he says that other anionic resins can be used as well.

The continuous loop process functions like this: A pulse of spent acid enters the loop at a given point on one of the legs of the U-shaped tubes at preset intervals. Phosphoric acid separates out in one direction and phosphate separates out in the other. When separation is complete, the products are eluted from the resin and the procedure is repeated. With the elution, the resin bed is moved countercurrently to the liquid flow direction. The 2-in. diameter columns used in the pilot operation permit a flow rate of about 70 gpd at 30–50 psi and ambient temperatures. The largest plant contemplated, Lancy says, would be on the order of 200 gpd.

Pilot. *Small unit features 2-in. diameter columns, 70-gpd throughput*

Lancy is chary with details of the process because of possible loss of international patent rights due to premature disclosure, but a key advantage of the technology would seem to be that recovery is not complicated by introducing chemicals into the column to desorb the acid. Once the capacity of the resin to adsorb phosphoric acid is reached, according to Lancy, the resin is simply backflushed with water to elute the acid fraction and the aluminum phosphate fraction.

Costs of the Lancy process are largely for capital expenditure. It would cost $70–100,000 to build a full-scale phosphoric acid recovery unit, Lancy says, although the firm has not yet decided whether it will build the plants and sell them outright or merely lease them. Operating costs are confined to water and electricity, and resin is replaced a bit at a time as the backflushing wears it down. Turnover time for the resin would be about five years. "An operator would be nice," Lancy says, but no special training or qualification would be necessary to run the unit properly.

Although he declined to put a price tag on savings effected by recycling the acid, Lancy anticipates that they will be "considerable." He sees applications for the phosphoric acid process in the automotive and appliance and construction fields, and expects to extend the basic technology to other acid-bearing wastes as well. Next in line is a nitric-hydrofluoric acid recovery system for cleaning up stainless steel pickling wastes although, he admits, there are still some problems to be solved.

Fundamental to all Lancy's systems is his belief that "good waste treatment can't be done at the end of the line." It's easier to clean up concentrated wastes of a special type than it is to create large quantities of heterogeneous sludges that often present disposal problems of their own. And, as he adds, it's more profitable. HMM

SO_2 removal technology enters growth phase

Tighter emission standards spur commercialization

To the medieval man, the pungent odor of sulfur dioxide (SO_2) in the air was proof positive that the Devil was lurking within spitting distance. Today's power plant operators are still bedeviled by SO_2 and pollution control engineers are trying everything short of exorcism to get rid of it.

How important a problem is SO_2 from stationary sources? By virtually any criterion—very important. EPA figures show that more than two thirds of the 33 million tons of sulfur oxides emitted into the atmosphere in 1969 came from stationary sources. Some 17.7 million tons—more than half the total amount—came from steam-electric power plants. Since power-generating capacity has been doubling about once every decade—most of that from conventional coal- or oil-fired steam generating plants—SO_2 has been increasing almost exponentially as well. In 1970, the National Air Pollution Control Association (NAPCA) estimated that if SO_2 emissions remained unchecked, by 1980 emissions from stationary sources would total more than 60 million tons.

Of course, EPA has no intention of letting SO_2 emissions go unchecked. The various state implementation plans recently approved in part by EPA should go a long way toward cleaning up SO_2 emissions from existing power plants, once technology has advanced a bit more and some of the snags are out of the more promising processes. In the meantime, short-term relief will be afforded by using lower sulfur fuels.

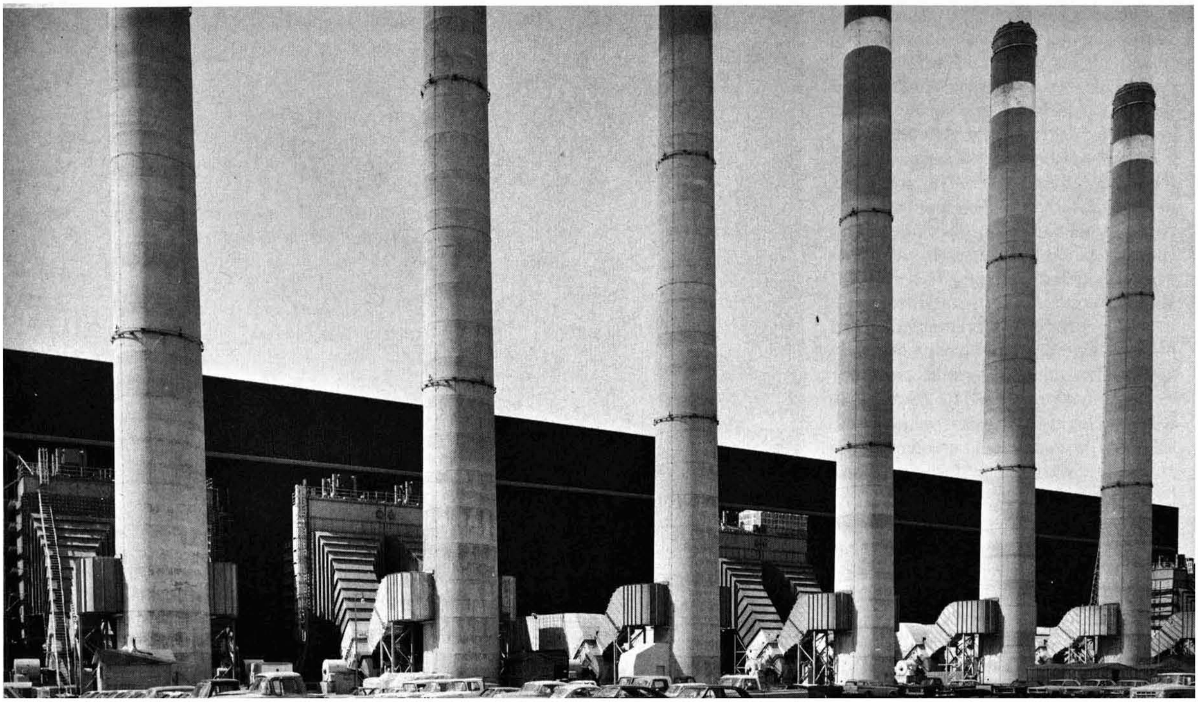
In December 1971, EPA published in the Federal Register performance standards for new stationary sources which applied to fossil fuel–fired steam generators. For large new power plants using liquid fossil fuels, standards for SO_2 are 0.80 lb SO_2 emitted for each million Btu of heat output. For plants using solid fossil fuel, the standard is 1.2 lb SO_2/million Btu. Depending upon the size, fuel type, ash content, and several other operating parameters, the standard could be achieved by burning 3% sulfur fuel with 75% of the sulfur removed—either from the fuel or from the combustion gases.

Excessive SO_2 is definitely hazardous to human health as well as plant life. A four-volume study by NAPCA, in response to a provision in the Air Quality Act of 1967 requiring the Secretary of the Department of Health, Education and Welfare to determine air quality criteria, discusses the effects of SO_2 levels on health. Adverse health effects were noticed when average SO_2 concentrations exceeded 300 $\mu g/m^3$ (0.11 ppm) for three or four days, or when the annual mean level of SO_2 exceeded 115 $\mu g/m^3$ (0.04 ppm). Adverse effects on "materials" were demonstrated with annual mean SO_2 concentrations of 345 $\mu g/m^3$ (0.12 ppm) and annual mean levels of 85 $\mu g/m^3$ (0.03 ppm) were deleterious to vegetation.

Attempts to control sulfur oxides from stationary sources are not new. The first wet scrubbing process was demonstrated in England in the 1930's. The process used aqueous lime and limestone slurries to achieve a high degree of SO_2 removal. The coming of World War II forced the plant to shut down, since stack plumes made it an easy mark for enemy air attack.

No serious attempts to remove SO_2 from flue gases were made in the United States until 1966, when small-scale

Pioneer. *TVA's Shawnee power plant in western Kentucky was first to test dry injection SO_x removal technology*



programs, funded by the U.S. government in cooperation with industry groups, were initiated. Today, the picture is vastly different. Federal expenditures to control SO_2 total in excess of $60 million—an amount which is probably more than matched by private industrial money. The EPA, Tennessee Valley Authority, and Bureau of Mines—all of which have interests in funding R&D efforts in SO_2 control—spent about $18 million in fiscal 1971.

Sources of SO_x

Stationary sources of sulfur oxides (SO_x) emissions include power plants, sulfuric acid plants, smelters, sour gas cleanup operations, refineries, and a number of less important industries. But power plants put more SO_2 into the atmosphere than all the rest combined.

SO_2 from power plants comes from three different sources in fossil fuels—organic sulfur (sulfides, mercaptans, thiols), pyritic sulfur (iron sulfides), and, to a much smaller extent, inorganic sulfates. Sulfur oxides—SO_2 and sulfur trioxide (SO_3)—are formed during combustion of fuels according to the general equations:

$$2\,FeS_2 + 5^1/_2\,O_2 \rightarrow Fe_2O_3 + 4\,SO_2$$

$$RS + O_2 \rightarrow SO_2$$

$$SO_2 + {}^1/_2\,O_2 \rightarrow SO_3$$

To control sulfur oxides, one must either burn low-sulfur fuel in the first place, clean up (desulfurize) high-sulfur fuels, or clean up combustion products. In practice, all three methods will be important. Using low-sulfur fuel promises to cut emissions for the short term. Similarly, use of desulfurization techniques may prove feasible for the long term.

Some 50 different flue gas SO_x removal processes have been evaluated and tested—at least in the laboratory—and there are now about 10 scrubbing processes plus a handful of variants which EPA thinks can be scaled up for commercial purposes. Those processes (table, p 689) are now being offered for sale by 14 engineering companies in the U.S. Of those processes, industry has already committed itself to installing four different types at 21 plant sites (table, p 690).

Process types

SO_2 removal processes are usually classified either as throwaway processes or regenerative processes. There are wet and dry throwaways and regeneratives. Furthermore, process chemistry is described as absorption, adsorption, or catalysis. Active agents may be introduced by injection into the boiler or in the scrubbing stage.

For ease of description, processes are often grouped by general categories, including dry injection, dry absorption, wet absorption, adsorption, and catalytic oxidation.

The most basic of these, dry injection, is simplest but is not generally acknowledged to be the best. Injection of pulverized limestone or dolomite directly into the firebox removes anywhere from 25–50% of the sulfur oxides during combustion. At the same time, however, there is an increased dust loading that may necessitate better particulate removal. Some work has been done with nahcolite injection (Precipitair) with results of up to 70% removal. The cost of nahcolite—a naturally occurring form of sodium bicarbonate—and the difficulty of dealing with highly soluble salts which could cause water pollution would seem to be major hurdles for the process.

Recently, another dry injection process—the Trimex process—has sparked considerable interest. Trimex—a mixture of naturally occurring calcium montmorillonite clay, phosphate, and borate salts—is fed directly into the boiler of oil-fired generators where it reacts with sulfur oxides to give a mixture of sulfates. The sulfates go up the stack to be recovered with fly ash in existing dry collectors. In tests at Savannah Electric's Port Wentworth, Ga., generating station, SO_2-removal efficiencies from 60–99% were reported. The process has yet to be tried with coal, but Trimex engineers foresee no difficulty in adapting the process for the heavier sulfur loads encountered with coals.

So-called dry absorbent processes take sulfur out of stack gases after combustion. Perhaps the most basic method—the alkalized alumina method developed by the U.S. Bureau of Mines—is archtypical. In the alkalized alumina process, hot gases pass through a filter or dust collector for particulate removal and then into a reaction chamber where the precleaned, sulfur-laden gas is contacted with the sorbent. Alkalized alumina, derived from dawsonite [$NaAlCO_3(OH)_2$] by heating it to 1200°F reacts with SO_x at about 600°F. The cleaned gases pass through a polishing precipitator to remove the remaining particulates before gas is discharged up the stack. The spent absorbent is regenerated by a reducing gas at 100°F and regenerated absorbent is recirculated to the contactor. The desorbed sulfur product—in this case H_2S—is further converted to elemental sulfur by the Claus method.

The advantage of the alkalized alumina process is that the system can produce elemental sulfur—usually prefer-

Sulfur oxide processes under active development in U.S.

Process	Company
Boiler injected lime, dry sorption	Foster-Wheeler
Boiler injected limestone, aqueous scrubbing	Combustion Engineering
Boiler injected limestone, dry sorption	(EPA—TVA)
Char sorption, thermal regeneration	Commonwealth Associates Foster-Wheeler
Char sorption, water regeneration	Foster-Wheeler
Direct catalysis to sulfuric acid	Monsanto
Lime and/or limestone slurry scrubbing, nonregenerable	Babcock & Wilcox Chemico Combustion Engineering Peabody Engineering Procon/UOP Research-Cottrell Zurn Industries
Magnesium oxide slurry scrubbing, therma regeneration	Chemico Babcock & Wilcox
Molten carbonate scrubbing, carbon reduction regeneration	Atomics International
Sodium solution scrubbing, nonregenerable	Combustion Equipment Assoc. (Arthur D. Little)
Sodium solution scrubbing, lime regeneration	Combustion Equipment Assoc. (Arthur D. Little)
Sodium hydroxide scrubbing, electrolytic regeneration	Stone & Webster/Ionics
Sodium sulfite scrubbing, thermal regeneration	Wellman-Lord
Solid sorption, reducing gas regeneration	Esso Babcock & Wilcox

Sulfur dioxide removal systems at steam–electric plants in U.S.

Utility company/plant	Unit size, MW	Scheduled start-up	Fuel	New or retro
Limestone scrubbing				
Union Electric Co. (St. Louis)/Meramec No. 2	140	September 1968	3.0% S coal	R
Union Electric Co. (St. Louis)/Meramec No. 1	125	Spring 1973	3.0% S coal	R
Kansas Power & Light/Lawrence Station No. 4	125	December 1968	3.5% S coal	R
Kansas Power & Light/Lawrence Station No. 5	430	November 1971	3.5% S coal	N
Kansas City Power & Light/Hawthorne Station No. 3	130	Mid 1972	3.5% S coal	R
Kansas City Power & Light/Hawthorne Station No. 4	140	Mid 1972	3.5% S coal	R
Kansas City Power & Light/La Cygne Station	820	Late 1972	5.2% S coal	N
Detroit Edison Co./St. Clair Station No. 3	180	November 1972	2.5–4.5% S coal	R
Detroit Edison Co./River Rouge Station No. 1	270	December 1972	3–4% S coal	R
Commonwealth Edison (Chicago area)/Will County Station No. 1	175	February 1972	3.5% S coal	R
Northern States Power Co. (Minnesota)/Sherburne County Stations No. 1 and 2	1360	May 1976	0.8% S coal	N
Arizona Public Service Co./Cholla Station	115	January 1973	0.4–1% S coal	R
Tennessee Valley Authority/Widow's Creek Station No. 8	550	April 1975	3.7% S coal	R
Duquesne Light Co. (Pittsburgh)/Phillips Station	100	February 1973	2.3% S coal	R
Louisville Gas & Electric Co./Paddy's Run Station No. 6	70	Mid–late 1972	3.0% S coal	R
City of Key West/Stock Island	37	June 1972	2.75% S fuel oil	N
Ohio Edison/Mansfield Station	1800	Late 1974	Coal	N
Sodium-based scrubbing				
Nevada Power Co./Reid Gardner Station	250	Mid 1973	1.0% S coal	R
Magnesium oxide scrubbing				
Boston Edison/Mystic Station No. 6	150	March 1972	2.5% S fuel oil	R
Potomac Electric & Power (Maryland)/Dickerson No. 3	195	Early 1974	3.0% S coal	R
Catalytic oxidation				
Illinois Power/Wood River	100	June 1972	3.5% S coal	R

able to producing sulfates because of marketability. The disadvantages are that the high temperatures required make it expensive to run. There is a high attrition of sorbent—about 7%—and to be economical the loss would need to be held at about 0.1%.

Another process of this type—the DAP–Mn process uses manganese dioxide (MnO_2) to react with SO_2 to produce manganese sulfate [$Mn_2(SO_4)_3$]. The sorbent regeneration system is more complex than in the alkalized alumina process, however, and the possibility that manganese compounds could present a health problem makes this process look less than highly desirable. A pilot plant of this type, developed by Japan's Mitsubishi Heavy Industries, reported removal efficiencies of about 90%, and further scale-up tests are reportedly in progress.

Another "dry" sorbent process which is being actively investigated in the U.S. is Atomics International's molten carbonate process. In this case, the sorbent is a eutectic mixture of sodium, lithium, and potassium carbonates which reacts with SO_2 to form sulfites and sulfates which dissolve in the molten carbonate mixture. Sulfates and sulfites are reduced to sulfides by carbon monoxide (CO) and hydrogen, and a Claus unit converts hydrogen sulfide (H_2S) into elemental sulfur. CO and steam regenerate the eutectic absorbent.

Atomics International is testing the technology at the Mohave Generating Station in Clark County, Nev.—part of the massive Four Corners Generating grid—and the company has just begun testing at Con Edison's Arthur Kill No. 2 generating station in New York City. The testing at Arthur Kill should be finished by the end of the year.

Wet absorption

Of all the process categories for SO_2 removal, wet absorption processes are held in highest favor today. Throwaway wet lime/limestone processes look particularly good because the absorbents are cheap and the end products—usually gypsum—can be discarded with little environmental consequence. Combustion-Engineering's scheme is fairly representative. The C-E process injects a pulverized alkaline earth additive into the furnace and uses wet scrubbing of flue gases to clean up sulfur oxides. The additive calcines and reacts with combustion gases to form calcium and manganese compounds—thereby removing 20–30% of the total SO_x, including all the SO_3. Flue gas, containing the remaining SO_2 and some of the calcined additive, passes through an air preheater and finally to the wet scrubber. In the scrubber, the additive reacts with water and SO_2 to form calcium and manganese sulfites and sulfates. The scrubbing medium drains into a tank at the bottom of the scrubber where solids settle out. Water thus clarified can be recirculated.

In light of its operating experience, C-E is modifying its process to eliminate direct injection into furnaces with tubular air heaters, because the additive fouls the economizer. C-E is still planning to use the process on a couple of units without these tubular air heaters.

Of course, wet limestone scrubbing can be carried out without furnace injection, simply by using a slurry in the scrubbing step. Besides C-E, several other companies have process know-how, including Zurn, Foster-Wheeler, Bahco/Research-Cottrell, Mitsubishi, Howden-ICI, Ontario-Hydro, and Chemico. The major differences in the process—aside from some engineering factors—is in the type of alkaline agent used in the scrubber. Chemico, for example, has built a plant which uses carbide sludge. Mitsubishi uses a lime–gypsum process which it says helps cut down on the scaling so prevalent with lime scrubbing.

A Japanese process, the Chiyoda Chemical and Engineering Thoroughbred 101 process uses a three-step wet scrubbing reaction which absorbs SO_2 with dilute sulfuric acid. An acid-soluble oxidation catalyst converts all sulfurous acid to sulfuric acid and the product stream is then split. Some of the acid returns to the scrubber while the rest goes to a crystallizer where it is reacted with any one of several calcium compounds such as limestone. The sulfur comes out as gypsum (hydrated calcium sulfate) according to these reactions:

Absorption

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

Oxidation

$$H_2SO_3 + {}^1/_2\,O_2 \xrightarrow[\text{cat.}]{} H_2SO_4$$

Crystallization

$$H_2SO_4 + CaCO_3 + H_2O \longrightarrow CaSO_4\cdot 2H_2O + CO_2$$

Several other inorganic scrubbing agents for limestone-type scrubbers are being investigated. Those of chief interest are ammonia (which would give ammonium sulfate) and caustic soda.

Monsanto Enviro-Chem has a "limestone" scrubbing process which uses an organic liquid for absorption of SO_x, followed by lime regeneration of the scrubbing medium. Called Calsox, the process yields a mixture of calcium sulfate and sulfite. Monsanto plans a prototype installation at an Indianapolis Power and Light Co. plant, with initial start-up expected by the end of this year.

Another wet absorption process—Chemico's MgO (magnesium oxide) process—contacts SO_x in the flue gas in a venturi scrubber, and regenerates the sorbent. The products, hydrated magnesium sulfate ($MgSO_4$) and magnesium sulfite ($MgSO_3$), form a sludge which is dewatered and dried in a kiln. Chemico has contracted with Essex Chemical Co. to calcine the sludge and regenerate MgO. In Chemico's process, particulates are removed from the gas stream before contacting with MgO. Scrubbed gas goes out the stack with about 90% of the SO_2 removed.

Like the Chemico Process, the AGS process of West Germany's Grillo-Werke, A.G., regenerates the sorbent. MgO and MnO_2 are used as absorbents in a process which results in Grillo's sludge having more sulfate than Chemico's.

The Wellman-Power Gas process uses aqueous sodium sulfite/bisulfite as a scrubbing medium to concentrate SO_2 according to the following reaction:

$$SO_2\ (\text{dil.}) + Na_2SO_3 + H_2O \longrightarrow 2\ NaHSO_3$$

Heat is then applied and the reaction is reversed, yielding a concentrated SO_2 stream:

$$2\ NaHSO_3 \xrightarrow[\text{heat}]{} Na_2SO_3 + H_2O + SO_2\ (\text{conc})$$

Besides regenerative absorption with inorganic compounds, there are at least two processes which use organic chemicals in the scrubbing step and regenerate them. The oldest, a continuing experimental process developed by the Bureau of Mines, uses a sodium citrate solution to trap SO_2. In the citrate process, hydrogen sulfide (H_2S) is bubbled through the loaded absorbent to precipitate sulfur and simultaneously regenerate the citrate.

Monsanto's Nosox process is the newest entry. A proprietary organic compound, developed especially for the process, absorbs SO_2 at a slightly acid pH. SO_2 is stripped off with water in a 212°F column, and the absorbent is recycled.

Carbon adsorption

Adsorbents, which do not have the large chemical capacity of absorbents, nevertheless enjoy one advantage—there is less need for complex regeneration. Two processes using carbon adsorption have attracted some attention recently.

The Lurgi process—also called the Sulfacid process—uses a fixed-bed carbon adsorber to collect sulfur oxides. Flue gas is first cleaned in a dust collector then cooled somewhat by weak sulfuric acid (H_2SO_4). The gas passes through the carbon bed which is intermittently sprayed with water to remove the dilute acid formed in the bed. The acid is recycled to cool the flue gas, and the process is repeated. The drawbacks: acid-resistant materials have to be used, and the acid must be concentrated if it is to be of further use.

The Reinluft process is a dry adsorption method which recovers concentrated H_2SO_4. Partially cleaned gas passes upward through two coke adsorbent beds. In the first bed, the coke removes some SO_2 and H_2SO_4 and cools the gas further for more SO_2 removal in the second bed.

The loaded adsorbent enters a desorbing unit where reducing gas liberates SO_2 and regenerates the coke. The coke moves countercurrently to the gas flow and is recirculated into the top of the stack. The desorbed SO_2 is fed to an H_2SO_4 plant.

Catalytic processes

Catalytic oxidation of SO_x to yield H_2SO_4 is a promising alternative to more conventional neutralization and scrubbing procedures. Foremost in the field is Monsanto Enviro-Chem with its Cat-Ox process. In Cat-Ox, flue gas at about 950°F comes from the boiler through a hybrid mechanical filter—electrostatic precipitator dust separator. The cleaned gas then goes to a reactor where SO_2 is converted to SO_3 with the help of a vanadium pentoxide catalyst. The SO_3 is cooled nearly to its dew point in an economizer-air preheater train. Cooled gas goes to a packed tower, where H_2SO_4 condenses out. A Brink mist eliminator removes entrained acid, and the cleaned gas is discharged to the stack.

To work well, the catalyst must be kept free of dust and periodically cleaned, sized, and partially replaced. But Monsanto says that 90% SO_2 removal with 80% acid concentration of H_2SO_4 is possible.

Another catalytic process, the Kiyourea process, uses a vanadium pentoxide catalyst with ammonia injection to produce ammonium sulfate instead of sulfuric acid. High-temperature gas is cleaned in an electrostatic precipitator before passing through the catalytic reactor and a boiler economizer. Before the air enters the preheater, ammonia is injected, reacting with SO_3 and water vapor to give $(NH_4)_2SO_4$. The Kiyourea process is expected to find far greater potential in Japan than in the United States because of the limited market potential for ammonium sulfate in this country.

Despite the multitude of process technologies available—at least on the drawing board—SO_x removal from stationary sources is still in the prototype stage. Only recently has there been a large-scale emphasis on removal technology. While engineering advances continue to be made, no process yet has been sufficiently tested in the field to the point where one can be said to be clearly superior to the other. Much depends upon application. The end product that will be desirable in one location will not be so desirable in another. And end products figure heavily in process economics. Without some potential for regeneration and sale of end products, most processes prove to be costly.

But costly or not, there can be no doubt that tighter air quality standards will soon force the processes on stream. The next two years should see SO_x removal technology come of age. HMM

Closing the loop on waste waters

The control of waste water effluents from fertilizer-producing plants is coming under more strict regulatory control, largely because of the release of the many pollutants into the nation's waterways. Various technologies have been looked at to control these effluents, but ion exchange is moving to the forefront as one of the technologies that is available to handle the wastes from actual producing plants.

The effluent from the Farmers Chemical Association, Inc. (FCAI) fertilizer plant in Harrison, Tenn., came under close surveillance by state regulatory officials in 1965. At that time, research had been done on the treatment of wastes having low nutrient levels (nutrient levels of nitrogen in the range of 10–50 mg/l.), but none of this was directly applicable to the fertilizer industry. The industry was confronted with the problem of reducing extremely large concentrations of nitrogen (1500 ppm) to levels that could be satisfactorily discharged to receiving waters.

FCAI was faced specifically with the problems of removing ammonium nitrate, a basic product of its fertilizer operation, from its waste waters and of finding ways to prevent it from entering streams and nearby waterways. Later, in 1968, FCAI was accused by the Tennessee Stream Pollution Control Board of releasing nitrogen materials to waterways, thereby causing excessive chlorine demands for purification of raw water used by the City Water Co. in Chattanooga, a short distance downstream on the Tennessee River.

Early start

The technical man behind the scenes who played an important role in bringing the new technology to the fertilizer field is Edward (Ed) C. Bingham, director of environmental and public affairs for FCAI.

Bingham says that FCAI worked with Peter Krenkel of Vanderbilt University and the Nashville-based consulting engineering firm, AWARE (Associated Water and Air Resources Engineers, Inc.). On April 18, 1969, FCAI received an R&D grant from the federal EPA to develop a feasible treatment technique (Project 12020 EGM). With AWARE as consultant, FCAI performed laboratory tests and evaluation studies on six different processes before ion exchange technology eventually won out; each of the other five, however, was limited by certain restraints:

- microbial nitrification—slow and inefficient
- biological denitrification—inefficient and expensive
- air stripping of ammonia—promising, but results in an air pollution tradeoff
- precipitation of ammonia as magnesium ammonium phosphate—problem of removing all the phosphate
- reverse osmosis—FCAI tried one vendor's equipment, but membranes were not available to give good nitrate ion rejections.

In about May 1970, FCAI discovered that ion exchange systems were in operation where the resins were regenerated by the use of nitric acid and ammonia, and about then, "We put all our hopes on ion exchange," Bingham says. "The system that came to our attention was that of a Canadian fertilizer operation—Simplot Chemical Co., Ltd., in Brandon, Man. That operation, a system designed by Chemical Separations Corp. (Oak Ridge, Tenn.), was using resins that could be regenerated by ammonia and nitric acid in the purification of well water for their boiler feed water.

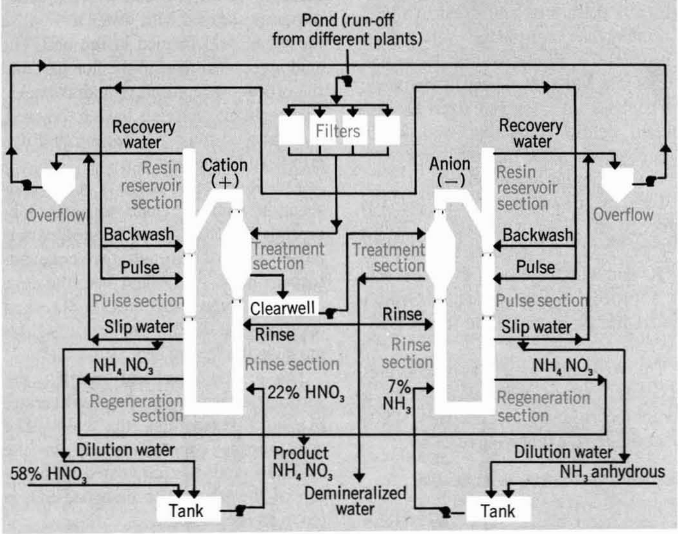
Products

FCAI produces five different fertilizer products—four at the Harrison, Tenn., plant, and an additional one at the Tunis, N.C., plant. FCAI produces ammonium nitrate (AN) for its four owner cooperatives and has a production capacity of 1000 tons a day at the Harrison plant; it will have double this capacity at its newer Tunis plant near Ahoskie, N.C., on the Chowan River. FCAI's big product item is a 30% nitrogen solution which contains AN, urea, and water. This solution is used for direct application on soils.

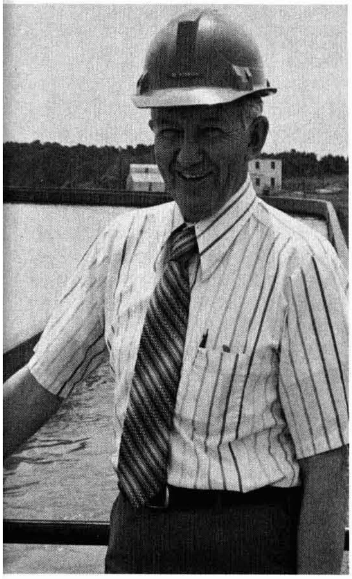
Effluent characteristics

Effluent volume from the Harrison plant is typically 0.9 million gal. of waste water each day, with a concentration of 1500 ppm AN as the essential pollutant to be removed by the ion exchange technology. Chemical Separations Corp. (Oak Ridge, Tenn.), a relatively small company, was awarded the contract to design a system for

Ammonium nitrate recovery system operates continuously



Fertilizer plants in Tennessee and North Carolina completely recycle waste waters from ammonium nitrate production



FCAI's Bingham
Bringing ion exchange to the forefront

FCAI. [Chem-Seps and the engineering construction firm of Foster Wheeler Corp. (Livingston, N.J.) have agreed in principle to a merger, subject to Securities and Exchange Commission approval.]

Bingham says that Chem-Seps actually designed a system capable of handling 1.5 million gal. throughput at a lower salt loading. In this way, rainwater could be treated along with the plant waste waters. Since the drainage system in the plant consists of open ditches, rainwater would collect in the collecting ponds. The contract with Chem-Seps was let in January 1971.

During 1971, the ion exchange recovery plant was designed and installed. It began operating in December 1971 and has operated intermittently ever since. However, the plant suffered a setback on April 16, this year, resulting in an estimated damage of $30,000. Bingham says that the problems were "mechanical in nature and have been corrected." None of the problems diminished the appeal or efficiency of ion exchange technology.

How it works

The essential steps in the ion exchange process are:

- collecting of plant waste waters, including runoff, in large settling ponds
- filtering through anthracite coal filters to remove particulate matter
- contacting waste water with strong acid cation exchange resin that removes the ammonium cation contaminant to less than 3 ppm
- contacting the "decationated" water with a weak base resin in the hydroxide form that removes the anion contaminant to 7–11 ppm nitrate
- regenerating cation resin with 22% nitric acid
- regenerating anion resin with 7% ammonium hydroxide
- combining backwash from each separate unit and neutralizing excess acid with ammonia.

The system operates by continuously cycling between the process mode and the pulse mode (see flow chart). During the process mode, the resin stays still and the ion exchanging and regenerating processes occur simultaneously in the separate ion exchange sections of the loop; the waste water and regenerants move in and out of their respective sections. During the pulse mode, the resin is moved from section to section by a pulse of water, and the waste water is used to pulse the resin.

Each loop contains about 450 ft^3 of resin; the resin life is guaranteed by Chem-Seps for five years. Dow resins are used, but resins from other manufacturers would work just as well, according to FCAI. Bingham says that there is, of course, some breakage of resin beads in movement around the loop, but all valves in the system are of the butterfly type which sweep away the resin before closing. In this way the valves do not press on the beads to break them up.

Before signing the contract with Chem-Seps, FCAI looked at other ion exchange techniques and other companies. For example, FCAI considered batch operations using both fixed and mixed resin beds, but soon became aware that in such operations there is a tremendous resin inventory problem due to loss of resin. A critical consideration in the selection of a system was a recovered waste stream of maximum concentration to preclude additional evaporation costs.

Recovery

The recovered waste stream from the Chem-Seps system turns out to be a 20% total solids solution containing at least 18% of the AN product. What happens overall is that about 6 tons of AN (100% basis) in this solution are recovered each day by the Chem-Seps system. The acid and ammonia used in regenerating the resins are combined to produce an additional 6 tons of AN in the 20% solution each day. The total amount of the AN product that is recovered, then, by the ion exchange system, is more than 12 tons each day as a 20% solution.

There is no market for the 20% solution, as such, Bingham says. But in the production of AN, nitric acid (58–60%) is combined with anhydrous ammonia in a vessel known as a neutralizer. This combination of chemicals results in the production of an 83% AN solution. This 83% solution is blended with the 20% solution from the recovery unit to make up the FCAI solution product, the 30% solution.

FCAI calculates that with the ion exchange closed loop system it would produce more than 6000 tons of AN annually and additionally. (Current price of AN is $40–45 per ton.) Of this, half is recovered from the waste stream and half is formed from the combination of the acid and base regenerants used for resin regeneration.

How applicable

Certainly, FCAI is the first in the industry to have licked a pollution problem that all AN producers share. Just how applicable the ion exchange recovery operation is to other AN producers is nevertheless subject to certain interpretations. There are 58 AN producers in the U.S., according to "Fertilizer Trends 1971," the biennial publication of the National Fertilizer Development Center (Muscle Shoals, Ala.). All companies that produce AN have this same waste problem. If the company makes a "solution" product (and it is estimated that about 31 of them do), then they might blend the recovered AN into that product. But other producers who do not make "solution" products are still faced with the problem of what to do with the 20% solution if they go the ion exchange recovery route. SSM

Jobs in the environmental field

ES&T Washington editors Stan Miller and Marty Malin find that all indicators point to more jobs, but that hard supply-and-demand numbers are not yet fully available

Environment is a field unlike most other subjects of human endeavor. The very breadth of meaning of the word "environment" is reflected in the multiplicity of disciplines and types of people who are needed to solve environmental problems. There is no one type of environmental specialist, skilled and knowledgeable in all facets of the field; instead, scientists, engineers, lawyers, technicians, aides, politicians, and hosts of other professionals are needed, in addition to park rangers, garbage collectors, and others on the environmental fringe. As the recent campaign of the Advertising Council puts it, people cause pollution, and people can clean it up.

This ES&T special report covers the supply of, the demand, and the agencies for environmental manpower. Although hard facts simply are not yet available, ES&T editors focused on a significant number of recent and new developments which point to added strength for more positions in the environmental field.

In its "Supply" section, the report details:

- the federal government's new thrust to bring all EPA's education and manpower planning efforts under a new office
- a number of surveys which attempt to get a better handle on the supply
- activities of the various associations, including the new National Association for Environmental Education.

In the "Agencies" section, the report:

- lists agencies that deal specifically with environmental manpower
- reports on the specific activities of Ability Search and a few other placement agencies.

In its "Demand" section, the report details:

- the number of people on board today in environmental jobs and the projected estimate of manpower needs in the short-term future
- a national contract to identify, for the first time, actual jobs in the area of environment
- expected salary ranges in one category of environmental protection.

SUPPLY

Indeed, there are few hard facts on the total number of environmental personnel employed today, but this is not too surprising, considering the rather sudden emergence of interest in the subject. Nor should it be alarming, because survey activities to develop such numbers are now under way, not only by the federal EPA and the Department of Labor (DOL), but also by several associations—National Association for Environmental Education (NAEE), Center for Curriculum Design, and the Education Resources Information Center (ERIC) which is on the Ohio State University campus. Although such activity is under way now, all information so far available must be regarded as embryonic, raw, and unevaluated at present; at some later time it must be further analyzed, refined, unified, and totaled.

As a general statement, it is safe to say that the majority of people in environmental positions today received their basic training either in science, engineering, or law, and then went into a job in the environmental field. Some, of course, entered the environmental marketplace after retraining. The manpower needed in the near future will most likely be supplied largely by candidates with similar training.

Obvious basic supply data that need be collected include, for example:

- the number of people in the various segments of this entity called environmental manpower
- the number of people training for later entry into the system
- the number of people coming on line for entry in the system
- the number of people being retrained for entry in the system.

After these basic facts are firmly established, the more sophisticated question becomes: What is the demand for each type of person in each of the separate categories of air pollution, water pollution, industrial hygiene, solid waste?

Until recently, each individual program office of EPA separately handled reports and statistics on its manpower needs and supply. In each case, numbers were generated but the total unified

figures have not as yet been evaluated and drawn together. EPA will shortly be attempting this synthesis of numbers, and the unified numbers may be available this time next year.

George Pratt heads the new EPA office for education and manpower planning. He reports to Thomas Carroll, EPA's assistant administrator for planning and management. Pratt is responsible not only for unifying and expanding EPA's intraagency programs in manpower development, training, and environmental education, but also for coordinating EPA's efforts in those areas with other governmental and private organizations. One of his many functions will be that of chairing a steering committee of manpower supply and demand representatives from all EPA program offices (the people who earlier pulled together the separate reports).

Although unified numbers for total environmental manpower are impossible to document at this time, a few specific numbers are available. For example, the EPA manpower ceiling for fiscal year 1972 (which ended June 30, 1972) was 8000. At the National Steel Co., the number of environmental personnel employed today is 30. The chemical industry has 6868 full-time personnel working on pollution control within the chemical industry, according to this year's survey by the Manufacturing Chemists' Association based on 130 companies. MCA found an additional 1100 people in the solid waste management area within the chemical industry.

Surveys

In 1971, the Air Programs Office of EPA performed a survey of all state and local air pollution control agencies to assess their manpower needs. It found there were 4500 persons employed in 1972 in state and local government air pollution control agencies, and that this number would increase to 8200 by 1975–76. This survey, however, was limited; it did not get into the needs for air pollution control personnel in industry, nor did it attempt to assess the needs of the federal government.

The most recent survey of manpower needs in the water category was performed, in part, by Harbridge House, Inc. (Washington, D.C.) for EPA. A report based on this survey was sent to Congress in late April. It assessed the needs not only of state and local governments, but also of industry, the federal government, and of academic positions (see box, p 698). Basically, the report substantiates earlier contentions that the need for water personnel will triple between now and 1976.

EPA's George Pratt
heads education & manpower planning

Another survey, in this case of the solid waste manpower segment, was nearing completion at press time. This survey was performed by Applied Management Sciences, Inc. (Silver Spring, Md.) under a $325,000 contract with EPA. AMSI's Robert Colonna tells ES&T that the four groups studied in the survey were:

- management people in solid waste
- employees in solid waste
- management people in scrap (SIC Code 5093)
- employees in scrap.

The criterion for classification of an individual as solid waste manpower was that he spent at least 50% or more of his time on solid waste problems.

In the AMSI survey, 5000 personal interviews were conducted. The data were broken down into five categories:

- professional, technical, and management
- clerical and secretarial
- supervisory employees and foremen (middle management)
- skilled laborers
- unskilled laborers.

For each of the five categories, the AMSI report will tell how many are hired today, how many are actively needed, and how many jobs have turned over in the past six months. Ultimately, data from this survey will be used in a report to Congress, in response to Sec. 210 of the Resource Recovery Act of 1970.

On April 13, 1972, the Manpower Administration of DOL announced that Automation Industries Inc. (The Vitro

Laboratories Division in Silver Spring, Md.) had been awarded a five-month, $97,295 contract to conduct a survey to determine the availability of job opportunities in environmental control and protection in the 1972, 1973, 1974, and 1975 calendar years.

A recent survey of consulting engineers engaged in water pollution control, based on more than 1600 responses to a national questionnaire, became available this June. It was developed by the Consulting Engineers Council, a Washington, D.C.-based organization serving U.S. engineers in private practice. A surprising result of the survey was that there will probably be a 36% increase in consultant personnel between now and 1976, even if the present level of federal assistance for waste water treatment plant construction should remain the same. The report is available from EPA.

Training

Training of various sorts is also under way today. All told, EPA currently is supporting 185 programs for training at U.S. institutions of higher learning; earlier, 103 of these federally funded programs were listed in the April 1971, ES&T feature article, "Manpower for Environmental Protection." The 185 include programs in water (94), air (45), radiation (11-12), solid waste (11-12).

In January 1967, there were only seven federal officials in the air pollution control regions of the U.S. Today there are approximately 200. To help with the supply of trained manpower in state and local air pollution control agencies, the EPA Air Programs Office established the State Air Assignee Program in June 1970. Under the program, EPA hired approximately 150 new engineers, and assigned them for a two-year period to strengthen budding state air pollution control agencies. After the two years, the state could hire them on a permanent basis. At least 47 states had at least one such assignee and it is predicted that up to 75% of these assignees will be retained when their two-year term expires. The first entries were just completing their two years this June. During fiscal year 1973 it is anticipated that 400 assignees will be detailed to help states with their air quality implementation plans.

In the water category, two federal training programs have been under way for several years, each aimed at bringing on board waste treatment operators, an earlier identified area of personnel need in the nation's water pollution control effort. In general, the supply of these operators is running at only one third the demand.

The Manpower Development and Training Administration (MDTA) program in the Department of Labor is administered in close coordination with the Department of Health, Education and Welfare (DHEW). A second DOL program is authorized by section 5G1 of the Water Quality Improvement Act and is aimed at updating operator skills to much higher levels—for example, in the area of phosphate removal.

The MDTA training consists basically of a 44-week program which includes 320 hours of classroom training coupled with on-the-job experience. Training achieved under this first program was:

Fiscal years	Operators trained	Funds expended, millions
1968/69	1000	$1.31
1970/71	1200	1.26
1972/73	870	1.00

Overall, 80% of the MDTA training went for updating the skills of existing operators; the remaining 20% went for the training of new entries to the system.

Section 5G1 training funds were expended for updating the skills of existing operators to much higher levels of performance. Training achieved under this program was:

Fiscal years	Operators trained	Funds expended
1971/72	360	$750,000 $500,000 (Training stipends)
1972/73	260	$551,000 $850,000 (Training stipends)

There are two types of training with 5G1 funds, the first is institutional training for all new entries; the other is on-the-job training. New operators receive institutional training—basically a 24-week program conducted by eight community colleges in the U.S. The training is full time, 8 hr a day, with 50% of it being in the classroom and 50% in the plant.

Yet another potential source of waste treatment plant operators is returning military servicemen. In the past two years, servicemen in the last 6 months of their military service have received waste water treatment operator training with DOL "transitional" funds. With fiscal year 1971/72 transitional funds totaling $500,000, 474 servicemen received 16 weeks of operator training; an additional 300 will receive similar training with fiscal year 1972/73 transitional funds totaling $304,000. This training is provided at centers in nine different geographic areas—Washington, California (3), Hawaii, North Carolina, Kentucky, Korea, and Okinawa; two additional training centers are planned for Germany.

To what extent these various types of training will satisfy future needs is an issue which cannot be answered with any assurance today. But with the reported decline in engineering student enrollment at universities there is the additional concern that rapidly changing technology and shifts in national priorities may adversely affect those who are either overspecialized or not well grounded in fundamentals.

Retrofit

Several retrofit programs aimed at putting top talents (mainly unemployed aerospace and defense engineers and scientists) back to work as environmental specialists have also become available over the past two years. (The Grumman Aerospace Corp. program was described in ES&T, April 1972, p 316.)

The Department of Labor also is heavily involved in retrofit studies, according to Finlay Petrie, Chief, Division of Placement at the U.S. Employment Service. Last October, the Labor department placed a request for proposals in the Federal Register to determine the availability of environmental jobs. The contract was awarded to Automation Industries. Such positions are "not readily visible," according to Petrie, since states may have legislation which authorizes environmental positions but may be short of funds to fill them. In other states, there is no legislation establishing clearly definable environmental positions.

Under its Technology Mobilization and Reemployment Program (TMRP), the Labor Department hopes to alleviate unemployment in 14 geographic areas heavily impacted with defense and aerospace personnel. The program started in April 1971 and was designed to retrain and retrofit people put out of work by the recent crunch in government space and defense spending. To be eligible for the program, the applicant must have been employed for 12 of the preceding 24 months by a company which had 40% or more of its business in aerospace or defense contracts.

Approximately 2600 applicants have

been placed under TMRP, but it's difficult to say how many of those were placed in environmental jobs, Petrie says. About 60% of those placed were engineers, 35% were technicians, and about 5% were scientists. By and large, participants were placed in positions similar in nature to their previous jobs, but at greatly reduced salaries. The average salary loss, Petrie estimates, was about $2500, from a previous job average of roughly $13,300 to a replacement job salary average in the neighborhood of $11,000.

Some fared better, however. From a cross-section survey of about 2300 engineers rehired after they lost their original jobs, 165 (about 7.2% of the sample) were rehired at salaries greater than they had before. Those hired by industry could be divided into three rough classifications: 51% in various manufacturing jobs, 24% in "service" industries, and 11% in governmental positions. As advice to prospective job hunters, Petrie suggests the best thing for an unemployed person to do is to get in touch with the state employment security agency in the state where he lives.

Project Retro is another such retraining program. It involves a consortium of three Florida institutions—Brevard Community College at Cocoa, Florida Technological University at Orlando, and Florida Institute of Technology at Melbourne—all within about 40 miles of each other. Marvin Olsen, executive director of the Retro Corp., who is on loan from TRW, Inc., and located at the Brevard Community College, tells ES&T that the training began in the fall of 1970. To date, 74 people have completed this training and 59 people are currently enrolled. At press time, 36 people were completing their training at the Master's level in environmental engineering, with degrees to be awarded this June.

All of the 74 who have completed the training were unemployed aerospace types—some with degrees in chemistry, chemical engineering, but most with degrees in electrical engineering. Of the total 74, 56 are now employed; 12 are continuing their education; the other six are still unemployed.

To place its people, the Retro Corp. office contacted state and local and county agencies as well as industries in the Southeast. This program has been successful; 90% of the people are either employed or continuing their education. About one third (24) completed a one-year technician's course (50 weeks) at the undergraduate level, a second third completed a Master's degree in environmental engineering, and the final one third completed short courses at the graduate level equivalent to six months of course work each.

AGENCIES

Ability Search is a Washington, D.C.-based management consulting firm specializing in recruiting technical personnel. Under a $30,813 contract from EPA, let in June of 1971, the firm began publishing a monthly Air Pollution Control Employment Bulletin. Ability Search publishes some 500 copies of each issue of which slightly more than half are received by state, local, or municipal air pollution control agencies.

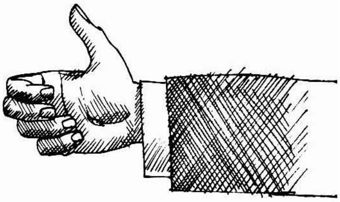
As of this spring, Ability Search had identified 432 air pollution control sector vacancies at the state, local, and municipal levels, according to Howard Payne, senior associate and director of the company's government services division. At that time, Ability Search had placed 40 people with the various agencies and another 95 were listed in the "active" category in Ability Search's files. The Ability Search Bulletin does not go to federal EPA regions or defense establishments.

Ability Search acts as a personnel broker for people looking for jobs in air pollution control. Anyone desiring to send his resume to the firm is welcome to do so. There are no restrictions on training. The jobs available in state and local agencies should appeal to applicants with a wide variety of backgrounds and interests, Payne says, and both technical and nontechnical posts are vacant.

Ability Search publishes an applicant's resume and job description in the Bulletin, and it is then the responsibility of the appropriate agency to negotiate directly with an applicant if the agency likes his credentials. Job descriptions are listed one time only.

Although most applicants are seeking jobs in air pollution control, Payne says, nearly one third of the applications received by Ability Search are from persons looking for work outside the air sector. That raises the question of whether a Bulletin such as Ability Search's might be supported by EPA on a broader basis—to include solid waste and water pollution control.

Payne says the company sent an unsolicited proposal to the EPA Office of Water Programs last September. In that proposal, Ability Search pointed out that it had identified six state and local water pollution control authorities with nearly 50 openings, of which 91% were currently unfilled yet funded positions. As of press time, the firm has not received word concerning the proposal.



Agencies to contact

Ability Search (executive search and professional recruitment)
Suite 202, Davis Building
1629 K Street, N.W.
Washington, D.C. 20006
Howard Payne (202) 296-1616

Munroe, Williams & Associates, Inc. (specializing in environmental sciences and engineering personnel)
5249 Duke Street
Alexandria, Va. 22304
Lu Griffing (703) 751-2100

National Registry for Engineers (if unemployed)
800 Capitol Mall
Sacramento, Calif. 95814
Elmer Gloer (916) 449-2160
(916) 445-4344

Associations to contact

ERIC
(Education Resources Information Center)
Ohio State University
Columbus, Ohio
Robert Howe (614) 422-4121
ERIC Center (614) 422-6717

National Association for Environmental Education
11011 S.W. 104th Street
Miami, Fla. 33156
Robert McCabe (305) 274-1212

Center for Curriculum Design
823 Foster Street
Evanston, Ill. 60204
Noel McInnis (312) 866-7830

A new twist is that firms from the private sector are now coming to Ability Search with requests for specific types and numbers of pollution control specialists. Payne says the company has requests from 20–30 firms for various trained individuals. Persons seeking employment opportunities with any of these firms should contact Ability Search (see box).

The sole business of Munroe, Williams & Associates, Inc., is in the recruiting and staffing of personnel trained

Air personnel on board today total some 15,000, should double by 1976

	Administrative	Engineers	Chemists and scientists	Technicians	Operators	Total
Private	537	1384	1142	1438	5440	9941
Federal	309	208	275	208	nil	1000
State and local	1680	804	1597	483	98	4662
Total on board	2526	2396	3014	2129	5538	15603

Source: EPA Office of Air Programs

in technical and scientific disciplines. Munroe, Williams works with all disciplines of engineering, but is a recognized leader in the growing areas of civil and environmental engineering. For the past two years, this agency has specialized in the area of the environmental sciences (air, water, waste water, solid waste, and the related engineering skills—civil, sanitary, electrical, mechanical, and chemical.

Munroe, Williams performs a recruiting service for a variety of companies on a national basis. Since its client is the company, and not the individual seeking employment, the candidate is never charged for its services. The clients pay interview and relocation expenses which may be involved. Munroe, Williams clients represent many well-known engineering companies and, through its past success, it is now able to extend its service to additional firms. Its work involves the continuous search for qualified personnel.

The National Registry for Engineers in California may prove useful to those who are unemployed. Its scope is nationwide (despite its name). The Registry was established by the Manpower Administration of DOL and serves as an exchange between job-seekers and employers. The Registry uses the services of 2000 local offices of public State Employment Services.

This National Registry is operated by the California Department of Human Resources Development in cooperation with the National Society of Professional Engineers (NSPE) and other technical and professional societies, including the American Chemical Society. Applications are made on standardized forms that are available from NRE. Engineers and scientists, as well as employers who are in search of trained manpower, may register with NRE.

Associations

Educational and technical associations also are involved with other fact-finding surveys, retraining programs, and employment clearing houses at national meetings. The National Association for Environmental Education (NAEE) held its first meeting this April in Hot Springs, Ark. The meeting was attended by about 200 educators interested in various aspects of curricula development for ongoing two-year and four-year environmental programs. At its first meeting, NAEE did not get into a fact-finding survey of how many new graduates would be entering the environmental marketplace this June. However, NAEE may be tackling this at next year's program scheduled for next spring.

Nevertheless, two fact-finding training surveys are under way today. In January 1971, the Center for Curriculum Design, a nonprofit educational foundation, mailed a survey questionnaire to just about every junior college in the U.S., in fact, to some 1200 institutions. The center received 650 returns, of which 596 were usable. Noel McInnis of the Center says that the entire study has been turned over to the ERIC clearing house and is in their hands now.

ERIC (Education Resources Information Center) is a nationwide clearing house that does work for the Office of Education–DHEW. As one of 18 information clearing houses around the U.S., it focuses on science, mathematics, and environmental education. ERIC spokesman Robert Howe says that the environmental education segment was added to the ERIC operation in September 1971. Howe says the Center regularly culls 87 journals for information of interest to users. What's more, the Center has started a survey of higher education; the results were not available at press time. ERIC mailed out survey questionnaires to more than 900 institutions of higher learning.

Specifically on environmental education, the Center is interested in:

- four-year programs at institutions of higher education
- technical two-year programs and their plans for expansion
- general environmental courses.

In June, the National Society of Professional Engineers (NSPE) announced a new nationwide program to prepare unemployed aerospace-defense engineers for careers in selected industrial and public areas. Funded by DOL, the seven-month program is referred to as the NSPE Technology Utilization Project. Twelve specialized reemployment programs have been undertaken, one of which is for environmental engineers.

Prior to the announcement of its new program, NSPE had completed a seven-month skills conversion study for unemployed aerospace/defense engineers, scientists, and technicians, again with DOL funding. In the NSPE recommendation, pollution control is the largest segment into which these people would move.

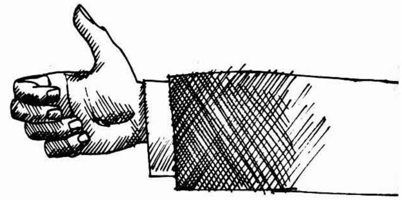
DEMAND

Nowhere is the numbers game more evident than in published projections for demand in areas of environmental employment. The second annual report of the Council on Environmental Quality (CEQ) estimates that nearly 1.2 million career opportunities in environmentally related fields will exist by 1980. While that figure is probably somewhat inflated in that it counts virtually everything which touches on the environment except construction, the percentage increase predicted may be accurate. CEQ's predictions reflect a 100% increase in environmentally related jobs in the decade 1970–80.

Writing in ES&T, Ralph Graber comes up with similar conclusions. Graber predicts that some 315,000 professional and paraprofessional environmental employees will be needed by 1975—up about 75,000 over the approximately 243,000 already on board in 1971.

Harder numbers are available in the air and water fields. The most recent study performed by the EPA Office of Air Programs defines employment needs

are expected to increase



Water personnel on board expected to grow by more than half

	Manpower on board 1971	Required by 1976	Percentage increase
Professional	25,400	42,200	66%
Operator	49,300	92,900	88%
Technician	26,900	47,300	77%
Other	47,800	71,800	50%
Total	149,400	254,200	73%

Source: EPA Office of Water Programs

Salaries in state air pollution control agencies

(in thousands of dollars)

Occupational title	Low	High
Director	$7.7	$29.9
Supervisor	7.6	27.0
Engineer	6.2	22.6
Chemist	5.0	18.1
Meteorologist	7.0	17.7
Specialist	5.6	20.4
Technician	2.9	18.5
Inspector	4.7	18.0
Aide	4.3	10.0
Administrative and others	2.9	22.6

Source: EPA

in just the air sector. It projected that about 8000 people at various state, local, and multijurisdictional agencies would be needed by 1974 to implement the provisions of the Clean Air Act of 1967. That's about double the 5111 budgeted positions available in the 264 agencies today. When that report was written, there were some 450 budgeted positions which were not yet filled either because there were no people adequately trained for the job or because salaries were too low to attract qualified applicants, or as a result of a governmental hiring or budget freeze. The Air Programs Office points out that the estimate is conservative, since it has not been updated to reflect the more stringent air quality standards brought about by the 1970 Air Act.

For water, the most recent figures from EPA's Office of Water Programs indicate that about 254,000 people will be needed to fill all the slots by 1976.

Another indication—this time from a nongovernmental source, the Manufacturing Chemists' Association—also indicates that industrial employment of environmental personnel will be up sharply in the next five years. In the water area, MCA members report that they employ 3503 full-time people—up from 2096 in 1967.

The chemical industry also employs 2255 people in air pollution control—up from 1624 in 1967. Although there are no earlier figures for industrial manpower in solid waste pollution control, MCA reports 1110 persons are so employed by the industry in 1972. In the period from 1962–72, manpower devoting full time to pollution control nearly doubled. Although MCA won't predict numbers for 1977—the next year in which a similar survey will be made—it seems reasonable to assume that numbers once again will be up substantially, particularly since industry is not yet in the enviable position of having expended enough resources to clean up completely.

How many jobs?

Perhaps the largest increase in the number of jobs available will be in the water field, particularly for in-plant operators. EPA predicts there will be an 88% increase in positions for operators by 1976, from 49,300 in 1971 to a projected 92,900 in 1976. The reason: There will be many more treatment plants built to reach water quality levels anticipated by 1976. In addition, plants will be more sophisticated and currently inadequate plants will need to be upgraded. That sophistication will have to be matched by an additional sophistication in personnel or the equipment will mean little.

There will also be a 77% jump—from 26,900 in fiscal 1971 to 47,300 projected for 1976—in technicians. There will have to be a 66% increase in professional personnel and all other personnel will need to increase by 50%.

Broken out another way, the private, nongovernmental sector will account for about 70% of the increased manpower required by 1976, EPA says. Of the 104,700 additional people that EPA predicts will be needed in the water pollution control field, 72,300 will be hired by nongovernmental employers. Local agencies will account for 23,100 positions, state agencies for 4600, federal non-EPA employers for 3300 and EPA for 1400.

What water pollution control will need most, EPA says, is more highly trained sanitary engineers. And the agency also forecasts many job openings for technicians trained specifically in one- or two-year programs.

In the air category, engineers will also be in greater demand than professionals or paraprofessionals trained in other disciplines. A breakdown of professional backgrounds of those people already working for local, state, federal and multijurisdictional agencies provides some clues. Professionals and paraprofessionals in air pollution control have widely varying backgrounds, but nearly half the people employed by the nation's clean air agencies were trained in engineering, biological or physical science, or health. Engineers make up 26% of the total, but only 17% of them work as engineers. The rest are agency directors and air pollution specialists. Most of the engineers are chemical, mechanical, and civil engineers. More than 60% of all people in the agencies have degrees beyond high school; 44% have bachelor's degrees, 10% master's, and 1% doctorates.

How much can I make?

At the top of the heap, directors make anywhere from $7700 to $34,600 in local agencies, $7700 to $29,900 in state agencies, and $8800 to $31,000 in multijurisdictional agencies. If you really want to shoot for the top, the federal EPA administrator makes $42,500 although there's no indication at this time that that post will be vacant in the near future.

Whether the supply of trained personnel will be in excess of the demand—as some readers have feared—cannot be answered now. But judging from the spate of activity in the education and manpower sectors, much more reliable numbers will appear in the next two years and perhaps as early as this time next year.

Recycling as an industry

Reclamation is a big business—$8 billion/yr—but in spite of its potential there are many real problems, such as those encountered in the recycling of paper and copper

Recycling, a word that just a few years ago was almost unknown, is now a household word. Yet, how well is it understood? What is recycling? What makes it tick? Is it something new? Is recycling just a matter of starting a "recycling center" and collecting a lot of cans, paper, and bottles? What are the economic factors that control recycling, and how can they be changed to maximize recycling?

If we are to be realistic—and if we wish to deal effectively with the solid waste problem today, considering the affluence and sophistication of our society—then the following premises should be understood. First, there always has been and always will be a solid waste problem. Even on the trips to the moon, solid waste, recycling, and disposal are critical areas. In the last few years, the magnitude of the solid waste problem has grown exponentially as a direct result of our affluent throw-away culture.

Second, recycling represents a two-pronged approach to this mountain of solid waste; it conserves natural resources, and it reduces the quantity of material to be disposed. Burning and burying should occur only after every effort has been exerted for recycling.

Finally, and probably most important, recycling will occur only when economic conditions are justified. In recycling as in any other major industry, the profit motive is a prime factor. Supply and demand must be balanced. If there is an oversupply of material, the price spirals downward, reducing the incentive on an industrywide base to supply material. Make no mistake about it; recycling is a major industry—an $8 billion industry.

The recycling industry

The recycling industry is more than 100 years old and consists of thousands of companies processing and handling a multitude of materials. These companies are usually located in the industrial centers of the country, close to their sources of supply. In fact, almost 30% of the recycling industry is located in the Middle Atlantic States (New York, New Jersey, and Pennsylvania).

To understand the recycling industry, actual flow of materials in a plant and movement of scrap from source to consumer should be analyzed. At the collection source, a vast flow of scrap materials from industry, government, farms, railroads, shipyards, etc., moves to either small scrap firms, where basic sorting and segregating is undertaken before transfer to larger scrap plants, or is shipped immediately to larger plants. The variation in the amount of recycled materials varies from 0 to almost 100% (Table 1).

At the scrap plant, material is identified, sorted into different grades, and processed (cleaned, cut, sheared, and packed by either being baled, bundled,

Howard Ness

National Association of Secondary Material Industries, Inc., New York, N.Y. 10017

or briquetted) for shipping to intermediate consumers. These intermediate consumers include secondary smelters, brass and ingot manufacturers, refiners, brass mills, foundries, etc. From this point, the secondary product made from scrap goes to fabricators, manufacturers, converters, etc., or is exported.

With some variation, this is the flow of nonferrous scrap metals as well as wastepaper or paperstock. In handling most material, there are collection, sorting, cleaning, sizing and packaging, or baling operations.

NASMI/EPA study

In response to numerous requests for information and data on the secondary materials industry, a study on the industry was authorized by the federal Environmental Protection Agency (EPA). This study, released in June, consists of nine volumes and over 1000 pages of text and charts, and was done under the direction of the National Association of Secondary Material Industries, Inc. (NASMI) by the Battelle Memorial Institute. Funded jointly by NASMI and EPA, the study covers general solid waste utilization and recycling problems and focuses on such principal recycled commodities as copper and brass, aluminum, lead, zinc, nickel alloys and stainless steel, precious metals, paper, and textiles.

Statistical tables in the study delineate the availability of various recycled materials, their flow through the industrial cycle, and the tonnages which eventually return to the economic mainstream. The report points out losses of recoverable secondary materials, analyzes the losses, and indicates moves to raise levels of recyclability. Thus, the NASMI study gives a definitive picture of recycling by the secondary materials industry, commodity by commodity, and relates these activities to the general economy and the basic industries these materials serve. A total biography and history of the recycling industry in the U.S. is developed by including such diverse factors as flow of scrap, employment factors in the industry, and geographic spread of secondary materials companies.

The NASMI study for EPA required intensive research on the part of Battelle, the Conference Board, the NASMI staff, and a 40-man industry advisory group for a year and a half. It initiated responses from hundreds of generators, processors, and consumers of all types of recycled materials as well as government agencies.

An extensive survey of the secondary industry, conducted as part of the study, discloses that the average recycling company (one engaged in the collection, processing, conversion, and sale of the selected solid waste materials) is a substantial operation. As shown in Table 2, average annual sales exceed $7.5 million, and the average company employs 71 persons. Almost 10% of the dealer/processors have more than 150 employees; almost 31% of industry have more than 50,000 ft^2 of plant under roof; and over 15% have more than $2 million invested in plant and equipment.

The huge tonnage of material currently being recycled is shown in Figure 1. Perhaps of greater importance is the tonnage still available for recycling. Only 14% of the available zinc is recycled—more than 1,000,000 tons to go to dumps. Paper (19%) and textiles (17%) show minimal recycling. The problem now is how to increase these recycling rates.

Copper

To truly understand the secondary materials industry, one must understand each component of the industry. The recycling or secondary materials industry really consists of a multitude of different industries. For example, the secondary zinc industry is very different from secondary textile industry. The federal EPA, in its publication, "Solid Waste Processing," lists some 109 items as "major waste categories." In the

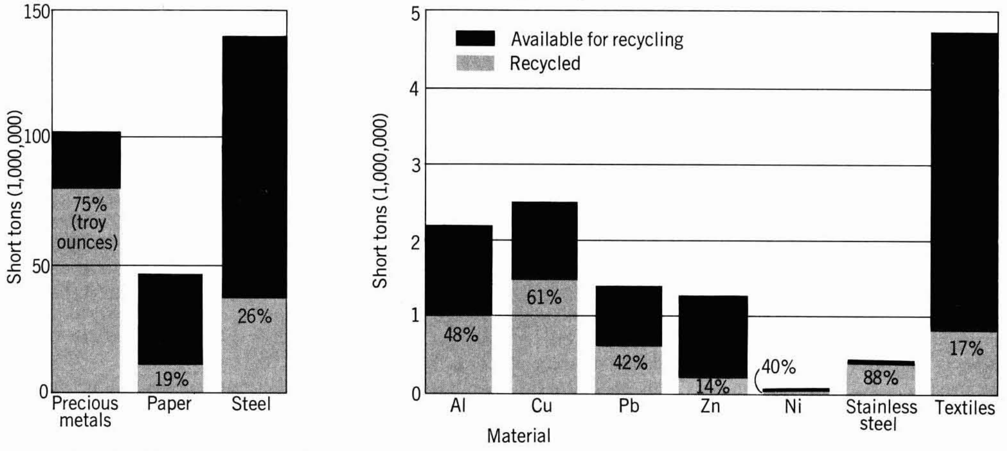
TABLE 1

Types of recyclable materials

Material type	Examples	Condition of scrap	Recycle rate, %
Manufacturing residues	Drosses, slags, skimmings	25–75% recoverable	Over 75
Manufacturing trimmings	Machining wastes, blanking and stamping trimmings, casting wastes	90% recoverable	Nearly 100
Manufacturing overruns	Obsolete new parts, extra parts	Variable compositions	Nearly 100
Manufacturing composite wastes	Galvanized trimmings, blended textile trimmings, coated paper wastes	Often not all constituents are recovered	0–100
Flue dusts	Brass mill dust, steel furnace dust	Often not economical to recover	Under 25
Chemical wastes	Spent plating solutions; processing plant sludges, residues, and sewage	Often recoverable	Under 10
Old "pure" scrap	Cotton rags, copper tubing	Over 90% recoverable material	Over 75
Old composite scrap	Irony die castings, auto radiators, paper-base laminates	Often not economical to recover valuable materials	0–100
Old mixed scrap	Auto hulks, appliances, storage batteries	Not all materials are recovered	Under 50
Solid wastes	Municipal refuse, industrial trash, demolition debris	Very low recovery rates now	Under 1

Figure 1

Recoverable material resources currently recycled



Based on Battelle Memorial Institute statistics and estimates

TABLE 2

Recycling industry companies

Average annual sales	$7,540,000
Average number of employees	71
Average value of plant and equipment	$1,480,000
Average investment per employee	20,800
Average annual sales per employee	106,000
Average investment per dollar of sales	5 cents

TABLE 3

Less than one fourth of paper consumed is recycled

(million tons) 1969

	News-papers	Container-board	Pulp substitutes and mixed papers	Permanent end use	Total U.S. consumption of paper and paperboard
Total paper consumed	9,800	15,000	22,500	10,000	58,200
Paper recycled	2,400	3,900	5,100	...	11,400
% Recycled	24	24	23	0	19
Paper not recycled	7,400	12,000	17,400	10,000	46,800
% Not recycled	76	76	77	100	81

NASMI study, 14 different materials were covered in detail. Here, two of those materials, copper and paper, are examined as examples of how the industry works, what the flow of material is, and what some of the problems are.

The importance of the U.S. copper recycling industry is reflected in the fact that almost as much copper (Figure 2), 1,375,000 short tons (2000 lb/ton), comes from recycled sources as comes from domestic ores, 1,469,000 short tons. At the present time, products made with secondary copper or primary copper are used interchangeably. Recycled copper accounts for 42% of the total copper consumed in the U.S.

Although 1,489,000 tons of copper were recycled in 1969, still some 966,400 tons were not recycled (Figure 3). Although available for recycling, 151,000 tons of copper wire, 144,500 tons of magnet wire, 76,700 tons of cartridge brass, 496,500 tons of other brass, and 153,000 tons of miscellaneous copper are not recycled.

Since copper has such a high intrinsic value, it is rather startling to learn that there is still so much copper available for recycling. Copper wire, a product highly sought by most scrap dealers, still has a way to go before it is 100% recycled. Since 18% of the available copper wire is not recycled, this appears to be one promising area where recycling can be increased.

Magnetic wire, a material used for the windings in motors and generators, is only 9% recycled. Battelle points out that it is now uneconomical to recycle all of this material since "the most common motors contain small amounts of copper individually but large amounts in aggregate." In addition, copper windings are generally surrounded by iron which makes simple recovery difficult.

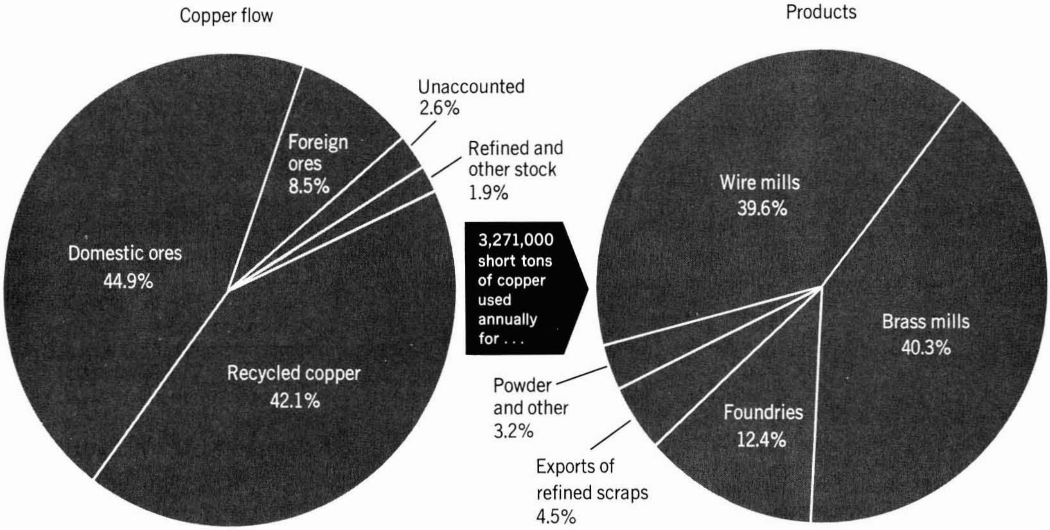
A total of 529,000 short tons of copper in brass products (40% of the available brass) is lost to use each year. Some of this is cartridge brass that is uneconomical to recycle, and the remaining includes valves, tubing, and miscellaneous brass items. Battelle suggests that many more statistics must be gathered before an accurate analysis of the problem can be made. This may be true, and more statistical data are always helpful; however, 39% of the copper that should be recycled is not and probably adds to the solid waste problem.

Paper

Recycling is both collecting and utilizing waste material. Paper recycling, more than any other material, starts with utilization. All too often col-

Figure 2

42% of copper flow recycled in 1969



lection drives for paper take place, large quantities of paper are collected, and the collected paper, with no commercial market, is dumped or incinerated.

The economics of the paper industry require that markets for paper containing recycled fibers must be available before it is collected. For most grades of paper, paper containing recycled fiber is competitive in both price and quality. Specifications for most paper being used by the U.S. government are now being changed and now require some recycled fiber content.

Of the yearly consumption of 58 million tons of paper, only 11 million tons were recycled, leaving over 47 million tons for disposal (Table 3). In its 1969 report, one of the stated goals of the Ad Hoc Committee of Solid Waste Management of the National Academy of Sciences/National Academy of Engineering is that, of the projected 50 million ton increase in paper production expected by 1985, 50% be recycled. It is further stated that "there are no major technological limitations to the reuse of newsprint and paperboard." The dollar saving on disposal costs alone of this 25 million tons of recycled paper will amount to approximately \$200 million per year. In addition, "the saving would be equivalent to 31 million cords of wood—more than two and one-half times the present total annual production of the four leading states—Georgia, Washington, Alabama, and Florida. Even by including the 25-million ton increase in recycling, the projected 1985 production will require an additional 55 million acres of forest lands. The potentials are staggering, and the national benefit to risk payoff is many thousands. This is in addition to reducing the waste load in the selected areas by perhaps as much as 25%."

The major portion of the paper stock consumed (70.5%) goes into containerboard products (Table 4). The smallest percentage goes into newsprint (3.2%); during 1969, 9,800,000 tons of paper were used to make newsprint, but of this total only 36,000 tons of it was recycled fiber.

Major problems of the paper recycling industry brought out in the Battelle study were the declining demand for products made with paperstock and the lack of tax incentives to equal those provided the virgin industries. Some solutions suggested by Battelle to combat these problems are:

- conduct technical research to improve paper, paperboard, and converted products made from paper stock
- develop strategies and educational programs to increase acceptance of, and remove stigma from, products made of paper stock
- push for nondiscriminatory purchase specifications from government agencies and others

Figure 3

61% of total available copper is recycled

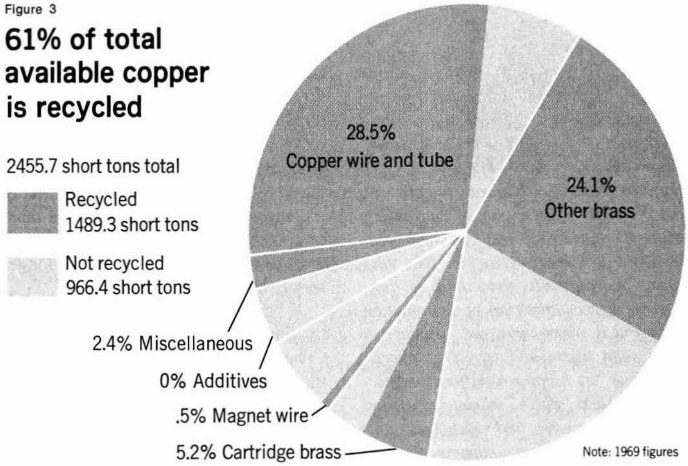


TABLE 4

Paper stock consumption in the U.S.

(thousands of short tons) 1969

	END-USE					
Category or grade	Container-board	Construction paper and board including gypsum wallboard	News-print	Fine paper	Total	% of total
Mixed paper	1,835	1,000	...	...	2,835	24.8
Old corrugated	3,468	400	...	...	3,868	33.9
News	1,455	600	360	...	2,415	21.1
High grades	1,291	...	...	1,000	2,291	20.2
Total	8,049	2,000	360	1,000	11,409	...
% of Total	70.5	17.5	3.2	8.8	...	100.0

- encourage freight rates favorable to expansion of recycled waste paper and paper stock.
- push for economic incentives to dealers or processors to increase recycling by offsetting the high costs of overseas shipments now restricting exporting.

Space limits detailed reports on the remaining commodities, but Battelle made the following suggestions to increase recycling of specific commodities:

- promote increased aluminum segregation at the source of generation, and expansion of present collection systems to broaden can and packaging scrap utilization
- initiate technical research to develop economic methods to separate zinc from die castings and from other metals
- expand research for increased use of battery lead
- for textiles, repeal Wool Labeling Act, introduce federal incentives to encourage exports, and develop new uses for synthetic blends of materials.

Howard Ness *is technical director of the National Association of Secondary Material Industries, Inc. He is a professional engineer active in the solid waste management field and is now heading a special program of coordinating government and industrial groups in their solid waste and recycling efforts. Mr. Ness has become a national authority on solid waste management and recycling, lecturing and teaching in universities throughout the country.*

Changing priorities

The National Commission on Materials Policy in its interim report of April 1972 states, "Secondary processing—i.e., recycling of materials after end-use and reclamation of waste prior to end-use—plays a major role in attaining both goals of enhancing environmental quality and conserving materials for more effective utilization of our natural resources."

Even though recycling has gone on for years, it now must be developed and increased to become a "new way of life." Maximum consideration must be directed to these questions. How can recycling be increased? How can the amount of material recycled be more meaningful in terms of total raw material supply? To do this, priorities must be reexamined; attitudes and prejudices must be changed; and man can no longer be satisfied with the status quo.

A hearing was held last November by the joint Economic Committee of Congress to discuss recycling, to identify the restraints and impediments to expanded recycling, and to project the specific legislative and regulatory policy changes that must now be projected. One of the most important obstacles to recycling, the Committee was told, is the *inequitable federal tax policies.* Present tax policies provide economic encouragement for continued and expanded use of primary or virgin products to the direct economic disadvantage of recycled material. Tax policies must be reexamined and changes made, changes that would:

- provide manufacturers a realistic incentive factor for utilizing more recycled materials through a recycling tax deduction or credit
- encourage new and expanded plant investment in recycling facilities and equipment through rapid write-off and amortization of such investments
- provide a basis for expanding research and development activities by industrial firms capable of recovering recycled materials.

Discriminatory transportation rates are a significant factor in restraining recycling. Freight rates for shipping materials to be recycled are as much as 50% higher than those rates for comparable primary or virgin materials. The complete rate structure should be reexamined with an eye toward encouraging and increasing recycling rather than the reverse.

Local, state, and national procurement policies in many cases discriminate against recycled material. Specifications that call for virgin or new materials should be changed and the specifications rewritten based on performance standards desired. Government agencies must take the lead in stimulating the demand for products made with recycled materials. Demand for these products must precede any successful and meaningful rise in the recycling rate. The individual consumer can help by requesting products made with recycled materials which creates the demand that is so vital to the recycling effort.

Many towns and cities still have antiquated licensing and zoning regulations that adversely affect recycling. While giving lip service to increasing recycling, municipalities zone and license scrap dealers and processers out of business. This *lack of leadership at the municipal and state level* inhibits recycling. As in any other major industry, *continued research and new technology* are basic growth factors and are necessary for the continued expansion of recycling efforts. These factors must change to create a climate for economic incentive for the recycling industry.

Identifying Sources of Lead Contamination by Stable Isotope Techniques

Michael B. Rabinowitz and George W. Wetherill[1]

Department of Planetary and Space Science, Institute of Geophysics and Planetary Physics,
University of California, Los Angeles, Calif. 90024

■ Investigations were undertaken to utilize naturally occurring variations in stable lead isotope abundances to determine the sources of lead in specific environments. In southeastern Missouri, measurements of lead in gasolines, topsoils near freeway, and air in urban traffic showed similar compositions; while lead ores, refined metal, and topsoils and dust near smelters displayed another distinctive set of values. The separation between these groups was about three times the variability within each group and about 12 times the experimental error. Also, near Benicia, Calif., the sources are isotopically distinguishable, as seen in roadside soil, air, and grasses on the one hand, and refined lead and grass near the smelter on the other. Smelter lead was traced to nearby pasture grass and in aerosols and dust some 20 miles downwind from the smelter. Horses which died of lead poisoning contained approximately equal parts of smelter and gasoline lead.

It has been known for several decades that the stable isotope compositions of naturally occurring lead ores are not identical; rather, there is a systematic variation reflecting the geological evolution of a specimen (Russell and Farquhar, 1960). Pb^{206}, Pb^{207}, and Pb^{208} are produced by the radioactive decay of U^{238}, U^{235}, and Th^{232} with half-lives of 4.5, 0.7, and 14 billion years, respectively. Pb^{204}, however, has no radioactive progenitor. Thus the observed isotope ratios will depend, at least in a simple case, on the U/Pb and Th/Pb ratios of the source from which the ore was derived, and the age of the ore. Although this simple model involving the buildup of lead in a closed system with time explains many situations, complicating factors such as diffusive loss of lead, multistage histories, and mixing of leads have been postulated to explain some observed isotope ratios, yielding geochronological information such as time of ore implacement, metamorphism, crystallization, and the age of the earth (Doe, 1970).

More recently, isotope ratios have been used to trace the movement of lead. Because of the small fractional mass differences of the lead isotopes, ordinary chemical reactions will not cause variations in the isotopic composition of lead. It has been demonstrated that lead in urban atmospheres (Chow, 1965), roadside vegetation (Chow et al., 1970), and roadside soils (Ault et al., 1970) is identical with gasoline-additive lead.

In this paper we report on a number of preliminary experiments designed to further explore the use of stable lead isotope measurements: to distinguish between different sources of atmospheric lead contamination, to trace the movement of lead from these sources, and to determine their relative importance in soils, air, vegetation, and animals. Two areas were examined: southeastern Missouri, an active area of lead mining and smelting crosscut by highways; and the region near Benicia, Calif., the site of a now-closed lead smelter and freeways, in which horses suffer chronic lead poisoning.

Technique

Soil samples taken from the top inch and 5-in. depth were oven-dried and screened with a 28-mesh sieve to remove large objects. Hot 6*N* HCl was then used to leach lead. This does not extract all the lead present, but only some removable portion. Six replicate analyses of each of five samples containing 90–1300 ppm lead gave repeatable data to within 10%. Grass (*Avena fatua* and *barbeta*) tops were collected, dried, and dissolved in hot concentrated HNO_3, as were animal tissues. Concentrations are reported on a dry weight basis. Aerosols were collected with Whatman No. 60 filter paper in Missouri and Millipore MF-HAWP 0.45-μ pore size in California, both filters digestible with concentrated hot nitric acid. The filter holder was shielded from large objects by an inverted plastic beaker.

Lead concentrations were measured by atomic absorption flame photometry of the acid solutions, except in air samples in which isotope dilution with a calibrated Pb^{208} solution was employed. Aliquots were extracted with dithizone to yield purified lead for mass spectrometry, run as a silicate gel on a 9 in., 60° sector, Nier-type machine equipped with electron multiplier and a Cary vibrating read electrometer with a 10^9-ohm resistor. For each reported isotope ratio, 10 sets of peaks were scanned, and an average obtained, with a standard deviation typically of 0.3%.

Several samples from the same area, prepared and measured separately, believed to represent a common pool of lead, for example, near roads in Benicia, agree among themselves to this precision. Replicate analysis of NBS equal-atom lead isotope standard gave reproducible results to at least this precision. Chemical blanks in sample preparation determined by isotope dilution were consistently less than 0.3 μg. Twenty micrograms of lead were used in the analyses.

Southeastern Missouri

An initial study was performed as a test of analytical methods and to determine if different atmospheric sources could be characterized and distinguished on the basis of isotopic measurements. Samples were collected during July 1970.

This area was chosen for investigation because it is the most active lead-producing region in the United States, with local lead ores long known to be anomalously radiogenic (Brown,

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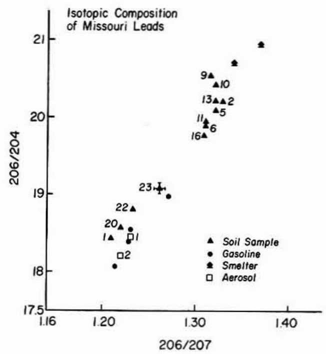
[1] To whom correspondence should be addressed.



Lower cluster of values indicate local brands of gasoline, roadside soils, and aerosols in urban traffic and a rural park. Upper cluster is samples of the local ore, soils and dust near smelters, and refined metal. Thus the two types of lead in this region may be isotopically differentiated. Error bars shown on sample 23 are typical of the analytic uncertainty

Figure 1. Isotopic composition of Missouri leads

1967) and thus likely to be distinguishable from gasoline lead which comes from a mixture of Australian, Peruvian, Mexican, and American ores as well as recycled scrap metal (Colvin, 1970) tending to average toward a fairly uniform composition.

Samples of local gasolines, purchased for mass analysis, gave a scatter of values greater than analytical uncertainties, similar to the range found among various brands by Chow et al. (1970). Samples of ore concentrate and refined metal produced from local ores are distinctly more radiogenic than this. Observed isotope ratios are displayed in Table I. The error shown for average gasoline is the standard deviation of four measurements made of four brands; for the other samples the error refers to the standard deviation of the measurement of 10 mass spectrometer isotope ratios. There is some variation of composition of lead within the extensive ore body on a kilometer and millimeter scale (Brown, 1967), but the range of values, which is comparable to that found among brands of gasoline, is about $^1/_4$ as great as the difference between gasoline and ore. The abundance of all four isotopes were measured, and it was found that samples with a high 206/204 ratio have higher 207/204, 208/204, and 206/207 ratios (see Figure 1). In reporting data the 206/207 and 206/204 ratios are graphically presented because the 206/207 ratio is most precisely measured, the accuracy of measurement of the ratio of the two nearly equal 206 and 207 peaks is the greatest. Displaying more than one of the other ratios would be redundant. The linear trend of the data as seen in Figure 1 verifies the model that the variation in composition is the result of radioactive growth and mixing of decay product leads. Any mass fractionation would produce a trend at right angles to this line, since any enrichment in 206 with respect to 204 would imply an enrichment of 207 with respect to 206.

Surface soil samples taken by a rural road (No. 1) near DeSoto removed from any known ore body gave a composition similar to gasoline and contained 135 μg/g lead while deeper soil (No. 2), which contained 32 μg/g gave a composition quite different. Thus, it appears that the surface enrichment is the result of addition of lead from above, presumably from automobile exhaust. No chemical migration within the soil could produce a surface enrichment more radiogenic. The same explanation holds for samples 22 and 23 taken from surface and deep soil near Route 66 on the outskirts of St. Louis. Here, too, the surface layer (coming from automobiles) is greatly enriched in lead distinctly different from the indigenous rock lead. An urban park in St. Louis gave soil rich in lead isotopically resembling gasoline (No. 20).

A deeper sample (No. 21), mineralogically resembling the surface, was also rich in lead (302 μg/g) indicating perhaps turnover of the soil, not unlikely in such a well-cultivated locale.

Soil samples taken from near the Indian Creek Mill at which ore is crushed and beneficiated (samples 9 and 10) showed a slight surface enrichment. On the grounds of isotopic measurements alone it would not be possible to say whether there is more than one source for the slight surface enrichment of 25 μg/g over the deeper leads. The surface and deep layers were similar in mineralogy, making doubtful the selective superficial removal of one half the soil mass which could have yielded the observed surface concentration. Deposition of fine galena dust is considered more likely but not substantiated.

In the vicinity of smelters, where the ore concentrate is roasted, reduced surface concentrations are much higher. Near the Glover smelter (samples 5 and 6) the surface was enriched by 1450 μg/g with an isotopic composition tending toward the ore locally processed and away from the deeper lead. Greater surface enrichments were found near the older smelter in Herculaneum (3600 μg/g in sample 13). This lead

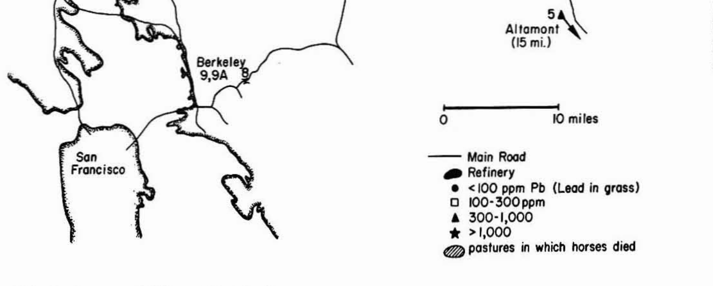


Figure 2. Map shows area with lead smelter, freeways, oil refineries, and other sources of lead where horses have died of lead poisoning; very high lead concentrations were found in grasses growing only near freeways and near the smelter

Table I. Isotopic Composition of Missouri Leads

Sample description	Lead concn, μg/g	Atomic ratios		
		206/204	208/204	206/207
Av of four gasolines	. . .	18.49 ± 0.25	36.49 ± 0.17	1.236 ± 0.018
Ore concentrate	. . .	20.98 ± 0.05	39.05 ± 0.15	1.368 ± 0.003
Refined metal	. . .	20.71	39.03	1.339
St. Louis air	18.84 μg/m^3	18.45	36.43	1.230
Rural air	0.77 μg/m^3	18.20	36.64	1.220
Av of 131 lead ore measurements (Brown, 1967)	. . .	20.81	40.08	1.303
1 Roadside topsoil along Route 67	135 ± 2%	18.43	37.22	1.209
2 5 in. beneath No. 1	32	20.20	37.89	1.328
5 Surface soil near Glover Smelter	1592	20.07	37.66	1.321
6 5 in. beneath No. 5	137	19.89	37.62	1.311
9 Surface soil near Mill	42	20.55	39.00	1.315
10 5 in. beneath No. 9	17.5	20.42	38.11	1.321
11 Fan lint at Herculaneum	71,930	19.95	38.02	1.310
13 Topsoil 900 ft from smelter	3,593	20.22	37.95	1.321
20 Topsoil Park in St. Louis	498	18.58	36.85	1.219
21 5 in. beneath No. 20	302			
22 Topsoil near Route 66	180	18.82	37.37	1.232
23 5 in. below No. 22	17	19.05	37.73	1.261

resembled lead-rich lint collected from an exhaust fan blade across the street from the smelter (sample 11) which resembled the metal produced.

In addition to the dust collection, aerosols were collected in downtown St. Louis and in a rural park 4.3 km south of Herculaneum. Both of these showed airborne lead resembling gasoline, the urban air containing more than 20 times the lead found in the rural air on those days. Neither showed any contribution from smelters.

In general, it appears that soil may have surface lead enrichments isotopically identifiable in this area of as much as several thousand μg/g within 1000 meters of a smelter, a few hundred μg/g within tens of meters of a highway, and tens of μg/g within tens of meters of a mill. These represent rapidly settling airborne particulate matter. Suspended aerosols can also be identified, and those measured in Missouri reflect automobile exhaust rather than lead-refining activity. It would be possible to seek the relative contribution of these two sources in vegetation, the human population, groundwater, etc.

Benicia, Calif.

With the experience and understanding gained from the initial study in Missouri, the area north of San Francisco was then examined. In the past two decades some 40 horses have died of respiratory complications of chronic lead poisoning in the pastures shown in Figure 2. There are a number of possible sources of this lead, including a smelter to the west, which closed at the end of 1970, and which emitted about 45 kg of lead/day (Ottoboni and Kahn, 1970). Some 15 kg of lead/day are emitted as particles by automobiles using leaded gasoline in the area. Other sources of lead include the sandblasting of lead-painted bridges across Carquinez Strait south of the pastures and ships in the bay to the east. However, these are considered of secondary importance because of generally unfavorable wind conditions for transport of dust from the bay to the pastures and because the characteristic orange paint chips found near the bridge are not seen in the pastures. Refineries in the area and industrial dumps associated with them may also emit lead as a tetraethyl (TEL) vapor and inorganic particulate matter, as could a plant manufacturing TEL 25 miles to the east. A survey of lead concentrations of grass in the area, shown in Figure 2, and displayed in Table II, including samples taken near a refinery and the TEL manufacturer, indicates concentrations as high as thousands of ppm near the smelter (No. 1) and near freeways (No. 2–5), but no extremely high concentrations were found near the refinery (No. 6) or TEL plant (No. 7). Thus the smelter and freeways were considered as the two major potential sources of airborne lead capable of contributing lead to the pastured horses; refineries and other sources of lead related to gasoline would likely be minor in comparison and would be isotopically indistinguishable from automobile exhaust.

We sought to determine the source of lead in the poisoned horses and the distance at which smelter lead is detectable and distinguishable from automotive lead of more diffuse origin. All samples were collected while the smelter was in operation, from August through November 1970.

To determine the isotopic signature of automotive lead, samples of wild grass tops (*A. barbetta*) were collected within 10 meters of freeways, far removed from other lead sources (samples 2–5). These samples with very high lead concentrations gave a cluster of isotopic values shown in Figure 3 representing the gasoline in the region averaged over all brands over the life span of grasses, many months. Dirt taken from along the inside of curbs was also analyzed (No. 8 and 9), as was aerosol (No. 9A) near a freeway in Berkeley. These samples representing a more recently averaged gasoline are in agreement with the roadside grasses. It is assumed that the high concentrations of lead in this grass represents airborne lead residing on or in the top portion of these plants (Dedolph et al., 1970).

Table II. Isotopic Compositions of Leads near Benicia, Calif.

Sample	Description	Miles from smelter	Lead concn, μg/g	Atomic ratio	
				206/204	206/207
1	Grass near smelter	0.3	9,645 ± 5%	17.33 ± 0.05	1.164 ± 0.003
2	Freeway grass	2.5	800	17.98	1.220
3	Freeway grass	8	6,141	18.09	1.204
4	Freeway grass near Lodi	54	375	17.88	1.193
5	Freeway grass near Altamont	43	707	17.97	1.215
6	Grass beyond refinery	6.6	275		
7	Grass beyond TEL plant	28	320		
8	Tunnel curbside scraping	14	5,325	18.04	1.211
9	Berkeley curbside scraping	14	...	17.88	1.201
9A	Aerosol at Berkeley	14	...	18.00	1.199
10	Ore	0	...	16.49	1.054
11	Refined metal	0	...	17.48	1.15
12	Stack emission	0	...	16.62	1.113
13	Grass at pasture	5.3	680	17.38	1.172
14	Grass at pasture	2.3	5,975	17.38	1.144
14A	Aerosol at pasture	1.8	...	17.26	1.147
15	Kidney	5.3	...	17.65	1.187
16	Kidney	5.3	9.4	17.66	1.195
17	Kidney	2.3	16	17.75	1.194
18	Liver	2.3	...	17.69	1.186
19	Bone	5.3	...	17.74	1.191
20	Grass at Brannan Island	30	268	17.78	1.192
20A	Aerosol at Brannan Island	30	...	17.54	1.157
21	Grass at Collinsville	21.5	276	17.40	1.182
22	Fallout at Grizzly Island (dust sample)	16.5	596	17.16	1.161
23	Remote grass	64	36		

Recent experiments in this laboratory involving growing oats and lettuce near a freeway in soils of unusual isotopic composition confirm that the bulk of the lead present in plant tops comes from aerosols.

Unlike the Missouri smelters, the Selby smelter does not process lead from one source, rather it processes scrap lead as well as ores from a number of California and foreign mines, hence the scatter along a line for samples of ore (No. 10), finished metal (No. 11), and stack effluent (No. 12). Thus, there are also probable temporal variations in the isotopic composition of smelter output. All samples from the smelter fall distinctly lower than the gasoline leads.

Because of this variability in the smelter lead, some means of determining an average value was required. To determine the average smelter effluent, grass was sampled 650 meters downwind from the smelter and 1400 meters upwind from the freeway, sample 1. Based on the results of other workers (Dedolph et al., 1970), we would expect only a few ppm lead in the tops of plants grown at such a distance from a road, if the road were the sole source of lead. Isotopic analysis of this extremely lead-rich sample showed it to be very similar to the refined metal produced by the smelter.

Comparing this value of smelter lead with samples 2–4, 8, and 9, all of which were collected within 10 meters of a freeway, contain lead clearly originating in automobile exhaust, and give a narrow range of isotopic values, one can see that in this instance smelter lead and gasoline lead can be isotopically distinguished.

Pasture grass measured from two sites (No. 13 and 14) gave values indistinguishable from grass grown near the smelter, as did one 12-hr air sample taken on the coast in the more western pasture (No. 14A), taken while the smelter was directly upwind.

The horses pastured there showed mild anemia, nucleated red blood cells, peripheral neuritis, and generally poor health. An autopsy revealed the sample lead content of the kidney and liver to be 9–16 μg/g fresh weight basis, by isotope dilution. These values are markedly elevated from the values of 1–5 μg/g we observe for horses which live in the Los Angeles basin and have died of intestinal rupture.

Kidney cortex and liver specimens from three horses which died of respiratory complications associated with chronic lead poisoning were isotopically analyzed (No. 15–18) in the belief that lead in these soft tissues would represent lead absorbed within a few months of death (Holtzman, 1960). A bone lead analysis was also performed (No. 19). All of these tissue samples gave a close cluster of values as seen in Figure 3, indicating a good mixing of lead within the tissue of each horse and a common exposure of these three horses. It appears from the isotopic data in Figure 3 that the lead absorbed by these horses is a mixture of approximately equal parts smelter and gasoline leads. It is noteworthy that isotopic composition of lead from the horseflesh did not coincide with their diet of pasture grass, suggesting another source of lead, perhaps respired. Grass lead is believed to originate at the smelter and be air transported, predominantly as coarse particles larger than micron size which would settle on the grass but would not be efficiently absorbed by a respiring animal. The finer particles of automobile exhaust and any TEL vapor would tend to produce more efficiently absorbed lead (Booker et al., 1969). Measurements of TEL vapor and isotopic analysis of different particle size fractions of aerosols over the pasture would test the existence and source of an easily absorbed component of airborne lead. Such measurements are in progress.

In summary, three distinct clusters of points representing different isotopic compositions are distinguishable in Figure 3. The most radiogenic cluster (samples 2–5, 8, 9, 9A) represents gasoline lead, as indicated both by their location and isotopic composition. The least radiogenic cluster (samples 1, 11, 13, 14, 14A) represent lead derived from the smelter and pasture grass on which the horses were grazing. The scatter of points within these two very distinct clusters probably reflect real differences in isotopic composition owing to temporal fluctuations in the isotopic composition of gasoline and smelter effluent. A third cluster of intermediate isotopic composition (samples 15–20) represents the lead isotopic composition of the horses which were poisoned. This clustering is statistically significant at a level of confidence greater than 99%.

The corridor for 50 miles downwind of the smelter is sparsely inhabited marshland, with some heavy industry along the south shore, as seen in Figure 2. A survey was conducted to determine the extent of smelter emission. Grass and aerosol samples were collected 30 miles downwind at the Brannan Island State Recreation Area while the wind was from the west (samples 20 and 20A). Another grass sample (No. 21) was collected 21 miles downwind at a field near Collinsville, and a fallout sample was collected at the Grizzly Island Waterfowl Management Area (No. 22), 16 miles downwind. Grass samples were also collected at 2 and 5 miles (No. 13 and 14).

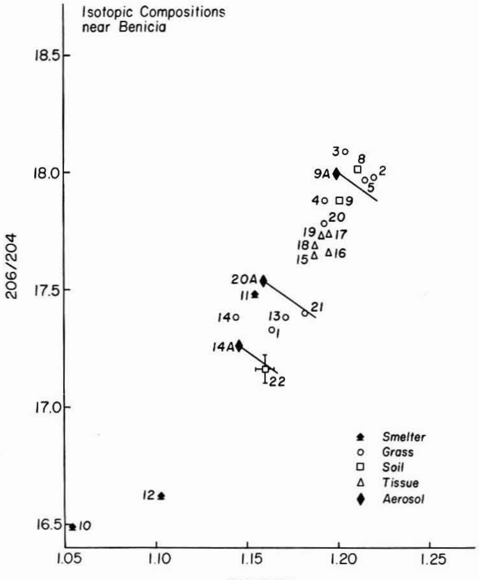


Figure 3. Isotopic composition of leads near Benicia, Calif.

Upper range of values are from roadside grass and dirt. The local smelter processes various lead ores; thus a scatter of values in the lower range. Horses which died of lead poisoning contained lead of an intermediate composition. Lines on the aerosol data points are the uncertainties generated by adding a calibrated 208 spike to the sample for concentration measurements

The lead concentration of the grass samples were all hundreds of $\mu g/g$, considerably above the background of less than 36 $\mu g/g$ observed 60 miles from the smelter on the lee side of the Diablo Range to the south (sample No. 23). This excess is thought to be deposited particulate matter, carried by the prevailing winds. It is possible that as much as about 30 ppm of the observed lead was in fact spectrophotometric interference by organic material present in the sample and introduced into the flame atomizer. If such an analytical error does exist and if it were uniform among the grass samples which all weighed about 3 grams each, then the trend seen among the samples would be unaffected, but they would all be too high. Laboratory contamination with lead is believed to be less than a microgram.

Isotopic analyses of these downwind samples displayed in Figure 3 show predominantly smelter lead in the grass out to 21 miles (No. 21), while at 30 miles the lead is tending toward gasoline (No. 20). Aerosols and fallout (samples 14A and 22) collected during periods of westerly winds showed smelter lead at 2 miles and 16 miles with lead of mixed origin at 30 miles. The area is surrounded by major interstate routes, all acting as sources of lead, observed to be isotopically uniform.

Conclusion

In the two areas examined it is possible to distinguish among sources of lead contamination on the basis of stable isotopic measurements. Identifiable lead can be traced from ore or gasoline, as an aerosol, to soils, vegetation, and animals. The horses which suffered from chronic lead poisoning near Benicia, Calif., absorbed approximately equal parts of smelter and gasoline lead.

Acknowledgment

The Ethyl Corp., St. Joe Minerals Co., and the American Smelting and Refining Co. provided samples and information. Fred Ottoboni, Sydney Smith, and Robert Graul, Department of Public Health, State of California, kindly shared samples, experience, and ideas.

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Continuous Analysis of Reactive Organics by Selective Combustion

William B. Innes
Purad Inc., Upland, Calif. 91786

■ The selective combustion method for analysis of hydrocarbons involving thermocatalytic oxidation effects in a vanadia–alumina catalyst bed can be used for rapid continuous analysis of a wide range of organics providing the ratio of catalyst volume to flow rate is low, and proper steps are taken to prevent condensation and sorption effects in the inlet system. Under such conditions, response increases and selectivity decreases with temperature up to 400°C on a variety of organics. Response passes through a maximum with flow rate, the flow rate maximum decreasing with ease of oxidation. Reversible deactivation from aromatics can be neglected above 350°C, but is significant at lower temperatures. Idle exhaust derived from leaded fuels does not noticeably deactivate the catalyst over prolonged periods under 400°C. Liquids containing organics including exhaust condensate can be analyzed after evaporation in dry air. A substantial fraction of the total response to vehicle exhaust is associated with the condensible fraction. Responses at optimum conditions (365°C, 1.0 SCFH, 0.013-cc catalyst) on gasoline vehicle sources would be expected to be essentially additive, linear, and give good correspondence with photochemical reactivity. Actual comparisons of smog effects vs. instrument responses are needed to prove the correspondence.

Selective response to photochemical smog-forming organics designated by us as reactive organics is believed essential for effective evaluation of exhaust control systems since there is wide variation in exhaust composition from various systems, as well as in the smog-producing properties of individual components.

The objective of the current work was to develop a continuous reactive organic instrument having fast response and high sensitivity with negligible inlet system losses. A discrete sample version has previously been described and commercialized (Innes, 1969).

Earlier work (Innes, 1970) indicated that the primary factor in achieving fast response on a continuous basis by the selective combustion method was use of a small bore reactor. Work reported herein involves 0.1-in. bore reactors and is primarily concerned with effect of operating parameters, such as flow rate, temperature, and air/sample ratio on response, linearity, and additivity; possible decrease in response with usage due to poisoning from coking and lead deposition; interferences; vehicle exhaust testing; response to individual organics vs. their smog effects in comparison with other instrumentation; and theoretical considerations.

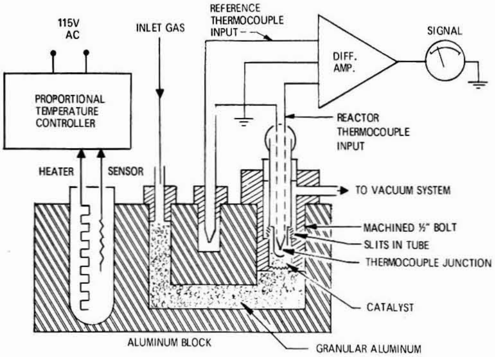

Figure 1. Flow diagram showing reactor element

Experimental

A flow diagram of the system used as well as some detail on a reactor element is shown in Figure 1, and a sampling probe is shown in Figure 2. Atmospheric air normally flows through the instrument by suction. It passes through a heated line and then into a preheater and reactor system contained in an aluminum block. The removable reactor housed in $^1/_8$-in. stainless steel tubing, contains high-surface-area vanadia–alumina catalyst and a thermocouple temperature sensor. The gas exits from the reactor into a silica gel trap, a rotameter, and passes out through a diaphragm pump. If measurement of other combustibles, primarily CO, is wanted, a second larger vanadia–alumina catalyst bed followed by a platinum catalyst reactor detector can be used, but this option is best considered separately.

In testing gas samples, the sample leg of the probe shown in Figure 2 is inserted in the gas source, and the steady-state response caused by catalyst bed temperature rise due to heat of combustion gives a measure of reactive organic content as illustrated in Figure 3.

The procedure used for testing liquid samples involves injecting measured amounts of the liquid with a 0–10 μl Hamilton syringe into a gallon glass bottle of dry air containing aluminum rivets, capping off with an aluminum foil–covered stopper, shaking to effect mixing, and then testing the vapor

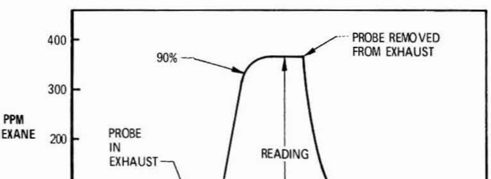

Figure 2. Sample probe

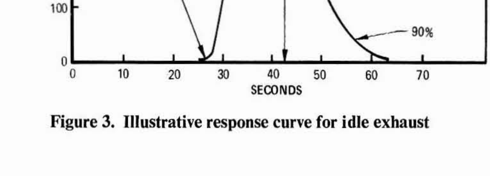

Figure 3. Illustrative response curve for idle exhaust

sample as described above. In the case of high-boiling liquids—e.g., organics in water—the bottle is warmed to minimize adsorption on the bottle walls. The vapor carbon content of organics is calculated from the known carbon content of the liquid, the volume of the bottle, and volume injected assuming vaporization to a perfect gas. In the case of fuels, it is necessary to estimate the C/H ratio to make the computation, but the uncertainty is less than 5%.

In the case of exhaust water condensate derived from combustion, response for organics in the water phase vs. that in the gas is computed from data on measurement of both and assumption of a stoichiometric amount of water vapor in exhaust gas (16% less about 2% for water content of the saturated gas at condensation temperature). That is:

$$\frac{\text{Total R.O. in condensate}}{\text{Total R.O. in ``dry'' gas}} = \frac{14}{86}\left[\frac{(\text{Response for condensate})^*}{\text{Response for ``dry'' gas}}\right]$$

$$^*\text{Response for condensate} = \left[\begin{array}{c}\text{Response to mixture}\\ \text{of condensate + air}\\ \text{in glass container}\end{array}\right]\left[\frac{\text{Volume of glass container}}{\begin{array}{c}\text{Volume of condensate}\\ \text{assuming vaporization}\end{array}}\right]$$

R.O. = total reactive organics based on instrument response

Data and Discussion

Effect of Operating Parameters. Major parameters that can affect results include: nature of sampling system; ratio of combustion-supporting gas (normally air) to sample gas; total flow rate; reactor temperature; nature of catalyst; nature of probe; reactor geometry and design particularly reactor bore diameter; and catalyst temperature. Their effects are complex and this work is limited to a 0.013-cc, 0.25-cm diam bed of high-surface-area vanadia–alumina catalyst ahead of the temperature sensor.

Reactor Temperature. The effect of temperature on steady-state response at indicated conditions is shown in Figure 4 and Table I for various organics and for a standard mixture. In general, the more reactive organics have a lower temperature coefficient so that more selective response is observed at low temperatures.

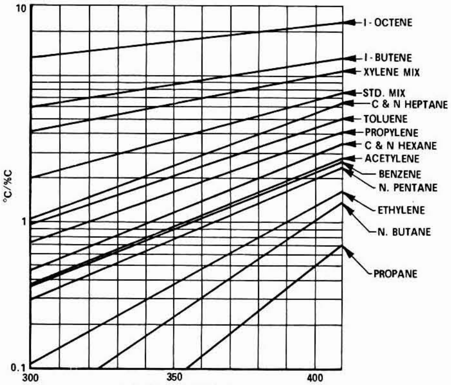

Figure 4. Response vs. temperature for hydrocarbons

Flow Rate. Response generally decreases with flow rate for less reactive organics in the range 0.75–1.5 SCFH as shown by the data in Table II. However, the effect is small or in the opposite direction for reactive organics.

Linearity, Additivity, and Air/Sample Ratio. From a theoretical standpoint as discussed below, results like those for discrete sample testing (Innes, 1970) would be expected to be substantially linear and additive, if oxygen is well in excess of combustibles. This seems to be the case as illustrated by the data in Table III. Changing air/sample ratio is simply one way of changing the level of reactive organics, and results are predictable on the basis of response proportional to overall reactive organic concentration providing there is a substantial excess of oxygen. With lesser amounts of oxygen, response may increase less than linearly with reactive organic content, and reproducibility may be affected as discussed below.

Possible Decrease in Response with Usage. SHORT TERM EFFECTS. It is well-known that oxidation intermediates are

Table I. Response in °C/% C vs. Temperature for Miscellaneous Components

	Temp, °C			
	300	350	365	400
Phenol	6.0	9.5	11	15
Ethanol				
Methanol				
Acetone				
Formaldehyde	5.1	7.0	7.7	9.4
Benzaldehyde	1.4	7.0	9.7	
Acetic acid	1.1	2.3	3.9	
Auto exhaust[a]	4.5 ± 1.2			8.5 ± 1.5
Gasolines[a]	2.1 ± 0.5			8.5 ± 1.5
Standard mix[b]	2.1	3.0	3.8	7.3

[a] Based on numerous tests with 10 fuels. Most exhaust from Idle Mode.
[b] See Table II.

Table II. Illustrative Effect of Flow Rate on Response

Compound nature	% Organic carbon after air dilution	Flow rate, SCFH 0.5	1.0	1.5
		Response in °C/%C		
n-Butane	0.77	0.43	0.39	0.27
Propylene	0.10	2.50	2.30	1.65
Standard mix[a]	0.12	5.2	5.0	4.6

[a] 0.65% *n*-butane, 0.65% 1-butene, 0.65% propylene, 25% CO, and 73% nitrogen.

Table III. Linearity and Additivity

	Av additivity	Av linearity	
Flow rate, SCFH	1.5	0.5	1.5
Catalyst temp, °C	Theoretical response,[a] %		
329		96	90[b]
343	100[c]	100[c]	
357	100[c]	100[c]	
399	95[c]	95[c]	

[a] Theoretical response = $V_1R_1 + V_2R_2$ where V_i = volume of *i*th component, and R_i is the response per unit volume of *i*th component.
[b] Values ranged from 0.75 to 0.95 for the nine organics tested; temperature rise up to 8 °C.
[c] Equal to 100% within reproducibility of test (5%) for various mixtures of butene, butane, propene, and toluene up to at least 8 °C temperature rise. Block temperature between 625–750°F.

Table IV. Reversible Deactivation From Heavy Dosage HC Exposure[a]

Catalyst temp, °C	Time required for response recovery, min.		
	Toluene[b]	Xylene[c]	Butene[d]
330	3	40	<1
345	1	3	<1
365	<1	<1	<1

[a] Expressed as time required for response to standard mix to return to initial level.

[b] 150 cc 2.3% C toluene.

[c] 150 cc 1.5% C xylene.

[d] 150 cc 0.35% C butene.

Table V. Permanent Effects from Prolonged Continuous Exposure to Idle Exhaust from Leaded Fuel[a]

Reactor temp, °C	329	343	371	398
Air/sample ratio	0.6	1.0	2	3
Exposure time, hr	5	2.5	10	5
	% Decrease in response on standard mix			
	<5	<5	<5	<5

[a] Total flow rate through instrument = 1.5 SCFH.

produced at low temperatures (Dixon and Longfield, 1960). If they are refractory toward further oxidation and strongly sorbed, they might have short-term effects on catalytic activity and thereby affect response, response time, and recovery time. Such effects were noted in the case of aromatic hydrocarbons particularly at low temperatures as shown by the data in Table IV, but at the chosen operating temperature, 365°C, and high air/sample, effects with exhaust gas normally containing about one-third aromatics are slight. It is believed that the intermediates in question are primarily aromatic aldehydes since these compounds give slow response and recovery when directly injected. At air/vehicle exhaust ratios below one third, there is significant evidence of organic matter buildup on the catalyst since rapid brief temperature rise phenomena is noted on replacing sample with air.

LONG TERM EFFECTS. Lead products in exhaust gas derived from lead additives in the fuel can irreversibly poison oxidation catalysts by lead compound deposition in the outer pore structure. In view of the small amount of catalyst prior to the probe this might be expected to be a serious problem. It was studied at four temperature levels by continuous flow of sample plus air through the catalyst bed and results are shown in Table V.

Table VII. Calculated Minimum Line Temperature To Be Above the Dewpoint

Air/sample ratio	Ambient air r.h., %	Ambient temp, °C	Minimum sample line temp, °C[a]
1	50	30	41
2	50	30	36
2	0	30	31
2	50	35	42
4	50	30	31
7.7	90	30	33
7.7	50	10	18

[a] Calculated for typical exhaust using the relationship:

$$P_m = [(P_a x \mathrm{r.h.} x \; A/S)/(A/S + 1)] + [P_{H_2O}/(A/S + 1)]$$

where P_a = vapor pressure of water at ambient temperature, r.h. = relative humidity, A/S = ratio of combustion air to sample, P_{H_2O} = water vapor pressure in raw exhaust gas for which a value of 100 mm Hg is assumed, P_m = dewpoint water vapor pressure, and Min. sample line temp = temp where liquid water has a vapor pressure of P_m.

The data show no evidence of such poisoning at temperatures up to 400°C. Above this, some slow permanent loss in response with prolonged usage would be expected. That is, it is speculated that only when the lead compounds are molten or in the vapor form do they deposit out on the catalyst and, thereby, act as a poison, and some of the lead may be in the form of halides melting at about 400°C with a vapor pressure of 1 mm Hg at about 525°C. Experience in normal usage on vehicle exhaust over several months has not shown significant decrease in response at 365°C.

Interferences. Carbon monoxide and hydrogen might be expected to interfere in view of their relatively high concentration in exhaust and high heats of combustion. The degree of interference at levels in normal vehicle exhaust is negligible as judged from Table VI. Hydrogen response per molecule increases with concentration on a greater-than-linear basis.

Tests on noncombustibles such as carbon dioxide showed no effects. Water vapor presented a problem in the case of discrete sample analysis because of transient heat of sorption and so it was necessary to water-saturate the gas stream to eliminate error owing to gas stream water content. However, sorption heat effects, because of their rapidity and transient nature do not appear to significantly affect continuous analysis which measures steady-state values.

Vehicle Exhaust Testing. Application of this analyzer to vehicle exhaust appears to require operation under conditions that eliminate liquid condensation or sorption in the inlet

Table VI. Relative Response for Various Organics vs. 1-Butene on a Carbon Basis at Optimum Conditions[a]

Carbon No.	Highly branched paraffins	Alkyl benzenes	Normal and cyclo paraffins, %	Multialkyl benzenes, %	Benzyl aldehydes, %	1 and 2 Olefins	Dienes	Aliphatic aldehydes	Branched internal olefins
1			0.0					82	
2			0.2			5		100	
3			1.0			21		105	
4			3.5			100	125		
5			8						250
6	3[b]	10	17			150			
7		25	31		100	180			
8	10[c]	44		70		230			
9			74						

[a] 365°C, 470 cc/min, 0.013 cc catalyst. Under these conditions relative response to H_2 and CO is less than 0.1% on a mol basis.

[b] 2,2-dimethyl butane.

[c] 2,2,4-trimethyl pentane.

system to achieve rapid response and recovery. The relatively high response to water-soluble aldehydes and higher aromatics which tend to condense out with the water and be adsorbed on the wall is believed responsible since tests on condensate indicated that this fraction accounted for about 15% of the total response at the Idle Mode.

Two methods have been combined to prevent water condensation; adding the combustion-supporting air at the sample probe and heating of the line. The calculated degree of heating required to keep above the dewpoint is given in Table VII vs. relative humidity and sample dilution.

Table VIII. Smog Effects, Causes, and Role of Various Hydrocarbons

Smog effect	Direct cause	HC Contributors
Eye irritation	Aldehydes (some in raw exhaust)	Olefins
	PAN[b]	C_3+ olefins
	PBN[c]	Benzylic hydrocarbons, aromatic olefins
Reduced visibility	photochemical aerosols	C_3+ olefins
	NO_2	C_4+ paraffins and monoalkyl benzenes, 0.6–1.3[a] Dialkyl benzenes and terminal olefins, 1.6–3.5[a] Di- and internal olefins, and aromatic olefins, 4–40[a]
Oxidant	ozone	same as for NO_2
Biological cell damage and polymer degradation	ozone (major) NO_2 (minor)	same as above

[a] Numbers refer to average rate of NO conversion to 50% level in ppb/min for 1 ppm hydrocarbon + 0.4 ppm NO in clean air when exposed to standard radiation (Glasson and Tuesday, 1970).

[b] PAN = peroxyacyl nitrates.

[c] PBN = peroxybenzoyl nitrates.

The sampling probe of choice, Figure 2, incorporates a 20-gage syringe needle for the sampling leg vs. a 0.05-in. bore air leg giving a 7/1 air/sample ratio. Caps with replaceable glass wool filtering material (sample leg) are provided to keep out particulate matter that might accumulate in the line since it has been found that accumulation of such matter can give slow response and recovery owing to their sorption of organics as evidenced by restoration of rapid response on cleaning the line. The combination of the filter and the 20-gage restrictor also serves to eliminate velocity effects that might affect flow of sample/air.

The sample probe is designed in such a way that it can be conveniently clipped to a tailpipe with the air leg outside and the sample leg inside. If hydrocarbons are present at the air leg, they will be measured to an even greater degree than those in the sample leg. However, it appears that this does not normally present significant error. It is believed that the low HC content of air next to exhaust pipe results from fresh air being drawn along the tailpipe by the exhaust stream. Error from this cause would need consideration under windy conditions.

Instrument Response vs. Smog Effects. Ideally, instrument response should correspond with smog production if the objective is to control smog. The smog effects and their cause based on extensive literature (Faith, 1966; Altshuller, 1966; Huess and Glasson, 1968; Glasson and Tuesday, 1970; Levy and Miller, 1970; Stephens and Scott, 1962, 1969; Altshuller et al., 1969) are given in Table VIII.

Selective combustion instrument discrimination between reactive and nonreactive hydrocarbons decreases with increasing temperature and decreasing flow rate. A temperature of 365°C and flow of 1.0 SCFH has been chosen as optimum considering response correlation with smog effects, response time, recovery time, possible lead poisoning at higher temperatures, etc. Response data for various organic classes under these conditions are given in Table VI.

Table IX. Composition, Reactivity, and Instrument Responses on an Organic Carbon Basis

	Composition										
	% Present in sources below on a carbon basis										
		Vehicle exhaust				Normalized values, % (see Table X)					
Compound class	Evaporative losses	Non-device 1958–65[b,c]	Engine modification systems[d]	Catalytic device[e]	Raw fuel typical[f]	Reactivity scale[g]	NDIR response	CSC response	FI response	FI response ex CH_4	Subtractive FI
C_1 + C_2 paraffins	0	6	7	32	0	0	50	0	55	0	0
Acetylene	0	5	6	2	0	0	2	15	49	49	98
Benzene	2	4	4	7	1	0	2	15	49	49	0
C_4+ paraffins	74	26	16	36	59	12	100	20	49	49	0
C_7+ aromatics	4	35	31	13	31	37	18	50	49	49	98
Ethylene	0	5	8	7	0	100	8	6	49	49	98
C_3+ olefins	20	15	22	2	9	100	50	100	49	49	98
C_2+ aldehydes[h]	0	4	6	1	0	100	0	100	0	0	0

[a] Based on Rose (1968).

[b] From 86-vehicle gas chromatography data in California Air Resources Laboratory (1968) except for methane and aldehydes which were estimated from other source information (Hughes and Hurn, 1960; Oberdorfer, 1967; Innes and Tsu, 1963).

[c] Using basin mix fuel.

[d] Estimated from data (Bonamassa and Wong-Woo, 1966; Wodkowski and Weaver, 1970; Rose, 1968).

[e] Estimated from data on a catalytic muffler system (Innes, 1964).

[f] Primarily based on Sanders and Maynard (1969).

[g] See text.

[h] See Fracchia et al. (1967).

Consideration of the various smog effects led the California Air Resources Board in 1968 (California Air Resources Laboratory, 1968) to adopt the scale given in Table IX. Aldehydes are also included since it has been indicated elsewhere (Altshuller et al., 1969) that they are at least as important as olefins and tests on exhaust condensate, as described above, confirmed that the water fraction was responsible for about 20% of the response. Values have been put on a carbon basis and rounded off. A similar mass rating scale has been used in federal work (Rose, 1968). Differences between isomers as shown in part in Table VI, although important in respect to reaction rate factors, are less important from a dosage point of view and presumably are neglected in the CARB rating to simplify matters. Selective combustion response shows similar differences with structure as shown in Table VIII. That is, for the same C number, branched internally bonded olefins give higher response than terminal olefins, *n* paraffins give higher response than highly branched paraffins, and multialkyl benzenes give higher responses than alkyl benzenes.

Assuming additivity, and listed values for reactivity, response, and composition in Table IX, a comparison has been made between available test methods with respect to agreement with the reactivity values given in Table X. This shows that the selective combustion method should give good correspondence for all gasoline engine sources of current interest which is not true of other methods. Raw fuel is included because tailpipe exhaust from present day cars can be considered roughly as mixtures of cracked products from normal combustion and raw fuel resulting from misfires. Of course, fuels vary appreciably depending on octane, feedstocks, and refining process. Gasoline reactivity ratings by CSC would be expected to give a relative measure of smog contribution for a given fuel for cars with misfires.

The grouping of compounds is an approximate approach dictated primarily by lack of detailed source composition data. The detailed CSC data in Table VI permits more precise computation of CSC response when composition detail is available. It is expected that CSC response will agree even better with a reactivity scale on such a basis. In particular, CSC response to evaporative losses would be lower and in better agreement with reactivity since the paraffinic components are primarily C_4s and C_5s with low CSC response.

Table X. Computed Relative Reactivity of the Organic Carbon in Various Sources vs. Normalized Instrument Response on an Organic Carbon Basis Based on Data in Table IX

	Source				
		Vehicle exhaust			
Reactivity or response on an organic carbon basis[a]	Evaporative losses	Non-device 1958–65	Engine modification systems	Catalytic device	Raw fuel typical
Reactivity	30	40	49	19	28
CSC resp.[b]	37	43	49	18	36
NDIR resp.[c]	85	43	37	56	69
FI resp.[d]	49	47	47	50	49
FI resp. ex CH_4[e]	49	42	43	33	49
Subtractive FI[f]	24	59	66	24	39

[a] Value $= 0.01 \sum_{C_1 + C_2 \text{ paraffin}}^{C_2 + \text{aldehyde}}$ (Reactivity or response) (% present)

[b] Values normalized so that olefins are rated at 100.

[c] Values normalized so that *n*-hexane is rated at 100.

[d] Values normalized so that hydrocarbons other than methane are rated at 49.

[e] Same as FI response except methane contribution neglected.

[f] Corresponds to differential between total hydrocarbon and hydrocarbon with unsaturates (except benzene) scrubbed out.

Theoretical Considerations

While precise analysis of continuous selective combustion response is complex because it involves heat transfer to probe, walls and catalyst, as well as kinetic information, a simple expression can be derived if certain assumptions are made:

- first-order kinetics [justified by earlier studies (Innes and Duffy, 1961)]
- a negligible degree of conversion ahead of the probe (applicable at 1 SCFH where $K < 1000$ min^{-1}, conversion less than 3%)
- heat transfer from bed to walls can be neglected as an approximation since it is less than 10% of heat transfer to gas—i.e., the fraction is 0.11 $(DG)^{-0.2}$ per empirical heat transfer relationships (McAdams, 1942) (it amounts to about 9% of the heat transferred to the gas under listed conditions)
- gas temperature equal to probe temperature (believed to be a valid approximation for a very small thermocouple probe)
- steady-state temperature conditions prevail

With such assumptions, the following approximate expressions are valid:

$$\text{heat transfer from catalyst to gas} = FC_a\Delta T_e$$

$$\text{heat generated in bed} = Q_mVKC_m$$

Since steady-state conditions prevail, heat generated = heat transfer to gas since heat transfer to walls can be neglected, so that

$$FC_a\Delta T_e = Q_mVC_mK$$

and

$$\Delta T_e = Q_mC_mVK/FC_a \tag{1}$$

Substituting values of 470 scc/min, 365°C, and 1% carbon in Equation 1:

$$\Delta T_{1\%} = 7.3 \times 0.01 \times 0.0127\, K/470 \times 0.000314 = 0.0063\, K$$

and

$$K = 159\, \Delta T_{1\%}$$

Rate constants, *K*, below 1000 obtained by applying this expression appear to be in line with other work (Innes and Duffy, 1961). The equation also predicts linear response with organic concentration and decrease in response with flow rates over 1.0 SCFH when *K* is less than 1000 in line with data in Table II.

Recovery and Response Times

The transient conditions which determine response and recovery times involve catalyst heat capacity as well as heat generation and heat transfer. During temperature rise

$$\frac{d\Delta T}{dt} = \frac{\text{rate of heat generation} - \text{rate of heat transfer}}{\text{heat capacity of catalyst bed}}$$

Substituting in relationships above

$$d\Delta T/dt = (Q_mC_mVK - FC\Delta T)/VC_c$$

Integrating from 0 to *t* and ΔT and substituting values for the integration constant

$$t = (VC_c/FC) \ln (1 - \Delta T/\Delta T_e) \qquad (2)$$

During recovery, $d\Delta T/dt$ = rate of heat loss/heat capacity of bed. Integrating from $T = \Delta T_e$ to T and $t = 0$ to t

$$t = (VC_c/FC_a) \ln \Delta T/\Delta T_e \qquad (3)$$

For both 90% of equilibrium ($\Delta T = 0.9\ \Delta T_e$) and 90% of recovery ($\Delta T = 0.1\ \Delta T_e$), the equations predict equal t values of 2.45 sec. These compare with observations on hydrocarbons with low reaction rate constants of about 3.5 sec for response and 7 sec for recovery, but are reasonable considering the neglected effects such as gas diffusion and probe heat transfer time as well as sorption phenomena.

Response and recovery times according to Equations 2 and 3 depend primarily on catalyst volume. They predict an inverse relationship between response time and flow rate.

Nomenclature

C_a = air heat capacity, cal/scc,°C = 0.000314
C_c = catalyst heat capacity, cal/cc = 0.216
C_m = fractional concentration of organic, scc C/total scc
D = catalyst bed diameter, 0.25 cm
F = flow rate, scc/min = 470 (1.0 SCFH)
G = mass velocity, g/cm^2, min = 12.2 (1.0 SCFH)
K = first-order rate constant, min^{-1}
Q_m = heat of combustion, cal/scc C = 7.3 (varies ±0.3 for diff hydrocarbons)
scc = volume of gas at standard conditions, cc at 0°, 1 atm
SCFH = flow rate, std ft^3/hr
ΔT = temperature rise, °C
ΔT_e = equilibrium temperature rise, °C
$\Delta T_{1\%}$ = equilibrium temperature rise for 1% C, °C
t = elapsed time, min
V = volume of catalyst ahead of probe, 0.0127 cc

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Production of Fungal Protein from Cellulose and Waste Cellulosics

Charles J. Rogers,[1] Emile Coleman, Donald F. Spino, and Thomas C. Purcell[2]
U.S. Environmental Protection Agency, Cincinnati, Ohio 45268

Pasquale V. Scarpino
Department of Civil Engineering, University of Cincinnati, Cincinnati, Ohio 45221

Technology developed to utilize waste cellulose as a fermentation substrate to produce edible protein could serve a dual purpose: reduce the amount of waste to be disposed of and help alleviate food problems throughout the world. Since 1.4 to 2.0 billion tons per year of the waste discarded in the United States is cellulosic in nature, the need for this technology is intimately associated with the solid waste disposal problem. Cellulose fiber is potentially the most valuable component of refuse, and research efforts are being directed toward recovering and recycling this material back into products of commercial value. In this recycling concept, there is a genuine need to develop uses for this recovered cellulose other than that of its potential fiber value. Efforts were made, therefore, to develop a cellulose fermentation process for the production of a high-quality protein with the use of fungi as the agents of biosynthesis.

Producing protein through mass cultivation of fungal mycelium is a relatively recent development, and using waste

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[1] To whom correspondence should be addressed.

[2] Present address, PEDCO, Environmental Specialists, Inc., Cincinnati, Ohio 45246.

■ Fungal protein, comparable to cereal grain in chemical composition, containing all of the essential amino acids, was produced by fermentation of waste cellulosic substrates. Besides its high-quality protein content, *Aspergillus fumigatus* readily degraded cellulose. Various processes to increase the susceptibility of cellulose to biodegradation, such as alkali treatment, electron irradiation, photochemical treatment, and hydrolysis, were investigated. Only the photochemical treatment process proved significant.

cellulose as a substrate for fungal cultivation appeared to be a feasible approach because of the high cellulase activity of some fungal species. The results from early studies of fungal growth carried out in static cultures (Litchfield, 1968) were variable because of nonuniform conditions of aeration and poor contact of the mycelium with the substrates. With the use later of submerged culture techniques, more uniform growth and improved yields of fungal proteins were achieved (Litchfield, 1968). The research carried out in laboratories of the Office of Solid Waste Management Programs is directed toward the development of technology to handle the wide varieties of cellulosic waste (Rogers et al., 1969). Several molds have been isolated and tested with native (untreated) and modified cellulose. Selected, truly cellulolytic molds that would attack native cellulose as well as treated cellulose have been used.

In developing a fermentation process employing waste cellulose to produce high-quality fungal protein, both physical and chemical treatments were evaluated to attempt to speed up the waste recycling process. Submerged culturing techniques were also used to improve the yields of fungal protein.

Experimental Methods and Materials

Several different cellulosic materials were tested in this biodegradation study. Substrates with and without lignin contents were used: the two pure cellulosic substrates were filter paper and Solka Floc 200 mesh (Brown Co., New York, N.Y.); the waste cellulosic substrates were ground refuse, wood pulp, and cellulosic fractions of water-pulped refuse ground to particle sizes of approximately 60 mesh.

Microbiological Procedures. The fungi used in this study were obtained from the exposure of agar plates to air; from fungal growth on and within a potato and on a pepper; from the Quartermaster Research and Engineering Center, Natick, Mass.; and from the Federal Water Quality Administration, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio.

A special medium containing finely divided cellulose in mineral agar (Sanborn, 1928) was prepared to determine if the fungi were cellulolytic. When fungi were inoculated on this medium, those fungi with cellulolytic activity formed a halo around the colonies. The clear zone aided in recognizing and isolating the cellulose degraders.

The degradation of untreated pure and waste cellulosic substrates was compared with that of cellulosic substrates previously treated by alkali oxidation, high-temperature hydrolysis, electron radiation, and the nitrite photochemical process. The medium for these studies contained 1 gram each of NH_4Cl, K_2HPO_4, KH_2PO_4, $MgSO_4$, $CaCl_2$, and yeast extract and 40 mg of thiamine combined with sterile water to a final volume of 1 liter. This mineral salt medium was adjusted to pH 5, and 100-ml portions were placed in 500-ml shaker flasks each containing 1 gram of cellulose. The flasks were autoclaved at 121°C for 15 min. After cooling, the medium was inoculated with selected fungi, incubated at 35°C in an environmental room on a reciprocal shaker, and observed for the disappearance of cellulose and the growth of the fungal mass. The inocula for these experiments were obtained from 48-hr fungal cultures grown in a mineral salt medium containing glucose, cellobiose, and cellulose in 0.1% concentrations. The dry weight of each inoculum was approximately 10% of the weight of the substrate. After the biodegradation rates were established in 100 ml of medium, the process was scaled up and similar rates reproduced in a 25-l. fermenter (Brunswick Scientific Co., New Brunswick, N. J.).

Treatment of Cellulose (Rogers, 1969, pp 40, 43, 45, and 56). ALKALI. Cellulosic substrates were subjected to an alkali-oxidation treatment (Dunlap, 1969). The treatment sequence was designed to swell the cellulose structure, break up the lignin physical structure, and modify the cellulose into a shorter molecular chain (Stone et al., 1965). One gram of each alkali-treated substrate was tested to determine the biodegradation rate and compare it with that of untreated cellulose.

HIGH-TEMPERATURE HYDROLYSIS. A high-temperature, stirred chemical reactor constructed of Type 316 stainless steel was used to study the effects of high-temperature hydrolysis on the biodegradation rates of cellulose (Autoclave Engineers, Inc., Erie, Pa.). This treatment process was designed to remove some crystallinity and to provide some readily fermentable sugars so the initial growth of the molds will be accelerated. Theoretically 10% fermentable sugars could be liberated under the conditions used (Saeman, 1945). The 1% cellulose suspension in the reactor was removed and adjusted to pH 5. Biodegradation rates were then compared with that of untreated cellulose.

ELECTRON IRRADIATION. In an experiment designed to determine if irradiated cellulose was more susceptible to degradation than untreated cellulose, two polyethylene bags, one containing 10.0 grams of 40-mesh ground cellulose and the other containing 10.0 grams of 100-mesh ground cellulose, were irradiated for 1 and 2 hr, respectively. A dynamic electron source (Dynamatron, NASA Lewis Laboratory, Cleveland, Ohio), provided an exposure of 10^8 rad/hr. The irradiated samples were then used in biodegradation studies and compared with nonirradiated cellulose samples of the same mesh sizes.

NITRITE PHOTOCHEMICAL TREATMENT. The nitrite photochemical process was another method used to modify cellulose to increase its susceptibility to biodegradation. This process, described in U.S. Patent 3,352,773 by the Gillette Co. (Schwartz and Rader, 1967), involves the use of uv light and sodium nitrite. Aqueous solutions of sodium nitrite from 0.1 to 0.8% were prepared, and 100-ml aliquots of these various concentrations were added to 10–40 grams of cellulose. The cellulose-nitrite slurries were poured $^1/_4$ in. deep in aluminum trays and irradiated at 3650Å from one to five days. One-gram samples were removed daily, and biodegradation rates of these samples were compared with that of untreated cellulose.

Amino Acid Analysis. When all the cellulose had been utilized, the fungal mycelium was removed from the media and washed several times with distilled water. After this material was dried in a hot-air oven at 75°C for 24 hr and then cooled, the samples were prepared for amino acid analysis. Ion exchange chromatographic techniques (Spackman et al., 1958) and a bioanalyzer (Phoenix Precision Instrument Co., Philadelphia, Pa.) were employed to determine the amino acids.

Twenty milligrams of the mycelium was weighed on a microanalytical balance and transferred into a reusable vacuum hydrolysis tube. Ten milliliters of 6*N* HCl was pipetted into the tube. The ground joint and the stopcock of the tube were lightly greased with Dow Corning high-vacuum stopcock grease and then pressure-clamped. The contents were frozen in a Dry Ice–acetone bath, and the air was evacuated at pressures of 50 to 100 μ of Hg. The tube was then filled and flushed with nitrogen. After the third flush with nitrogen, the tube gases were evacuated at pressures of 50 to 100 μ of Hg and the stopcock was firmly closed. The closed tube was placed in a 110°C oven for 22 hr. After hydrolysis was complete, the tube was removed from the oven and cooled to room temperature. The stopcock was gently opened to release the pressure, and the bottom was separated after the clamp was removed. The content of the tube was filtered through a sintered glass filter under vacuum, and the filtrate reduced to dryness by freeze-drying. After the sample was completely dried, it was diluted volumetrically to 5.0 ml with 0.20*M* sodium citrate buffer, pH 2.2. One half milliliter of this solution was pipetted onto the chromatographic column of the bioanalyzer for amino acid determination.

Results and Discussion

This study comparing the biodegradation rates of untreated and treated cellulose provides a way to select those highly cellulolytic fungi capable of degrading cellulose without pretreatment. Because large quantities of cellulose are involved, a process with no pretreatment would save time and money.

When the degradability of untreated and alkali-treated cellulose was compared, the degradation rates of alkali-treated cellulose equaled or surpassed that of the untreated. Four of the 12 fungi samples completely degraded both untreated and alkali-treated cellulose in four days. With each of the other fungi studied, some degradation of treated cellulose occurred in four days; the untreated cellulose was not biodegraded, however. This finding compares with that of Norkrans (1950) who reported that cellulolytic fungi usually degrade the more readily accessible, amorphous portions of cellulose. The cellulose was completely utilized when the medium solution cleared and fungal masses developed; when the solution remained turbid from the suspended cellulose, it was evident that the cellulose was not utilized.

When the degradability of untreated and high-temperature-treated cellulose was compared, the untreated was obviously more biodegradable. It is not clear whether the high-temperature hydrolysis yields products that inhibit growth or whether structural modification of the substrate accounts for this result. Gilligan and Reese's work (1954) possibly explains the result of this high-temperature hydrolysis process: when the degree of polymerization of cellulose is reduced during acid hydrolysis, the disaggregated cellulose chains in the amorphous regions tend to recrystallize and make the substrate more resistant to enzymatic hydrolysis. Apparently, then, high-temperature-treated cellulose is an inferior substrate compared with untreated cellulose.

Earlier reports that irradiation modifies cellulose prompted evaluation of the effect of radiation on biodegradation rates. King et al. (1964) found that when organic molecules are irradiated, the covalent bonds are ruptured, and Reese (1956) found that gamma rays in low doses decreased the susceptibility of cellulose to degradation, and high doses produced the opposite effect.

When the degradability of untreated and electron-irradiated cellulose was compared, only the untreated was found to be degraded. Blouin and Arthur (1958) and Arthur (1958) may have explained why this modification of cellulose is a nonbiodegradable form: the presence of carbonyl and car

Table I. Amino Acid Content of Selected Fungi, Peanut Meal, and Soybean Meal (gram amino acid/100 grams protein)

Amino acid	*A. fumigatus* No. 3	*A. fumigatus* No. 6	*Penicillium* sp. No. 7	*Trichoderma viride* No. 9	*Chaetomium* sp. No. 10	*Geotrichium candidum* No. 11	Peanut meal[a]	Soybean meal[a]	FAO ref.[b,c]
Alanine	5.90	5.60	5.90	5.10	6.60	6.00	4.2	3.30	...
Arginine	3.70	3.80	7.80	4.00	8.20	6.70	10.6	7.30	...
Aspartic acid	8.80	8.30	8.90	7.70	10.70	6.40	15.1	3.70	...
Cystine, half	...	0.40	...	...	...	...	1.60	1.9	1.2
Glutamic acid	11.00	11.30	13.30	9.90	11.70	11.30	17.40	18.40	...
Glycine	5.30	3.80	5.70	5.90	5.60	4.20	5.00	4.00	...
Histidine	2.20	1.90	3.30	1.60	4.70	3.20	2.10	2.90	...
Isoleucine	7.30	7.20	4.50	4.00	5.60	3.90	4.00	6.00	4.2
Leucine	8.80	10.90	5.70	5.10	6.60	6.70	6.70	8.00	4.8
Lysine	4.40	5.60	5.70	4.40	5.60	5.30	3.00	6.80	4.2
Methionine	7.30	6.50	1.10	2.00	...	2.70	1.00	1.70	2.2
Phenylalanine	6.10	5.30	4.70	5.50	6.10	7.40	5.10	5.30	2.8
Proline	2.90	3.40	3.60	3.70	2.80	3.20	5.20	5.00	...
Serine	5.50	4.10	4.50	2.60	4.20	5.00	6.60	4.20	...
Threonine	7.00	4.40	5.60	4.40	4.80	7.40	1.60	3.90	2.8
Tryptophan	...	...	...	...	...	...	...	...	1.4
Tyrosine	3.90	3.00	6.10	3.70	4.20	4.20	4.40	4.0	2.8
Valine	2.60	5.30	6.10	4.80	6.60	12.40	4.40	5.3	4.2

[a] Block and Bolling (1951).
[b] *Chemical and Engineering News* (1967).
[c] Food and Agriculture Organization (1957).

boxyl group formations, in addition to the chain cleavage, may have accounted for the loss of enzyme specificity for this modified substrate.

Of the cellulose treatment processes evaluated, the nitrite photochemical treatment was superior to other processes. The time required for the biodegradation of 1.0 gram of untreated cellulose by fungus no. 6 decreased from four to one–two days. For this preliminary photochemical study, 100 ml of a 0.2% nitrite solution containing 40 grams of cellulose was considered suitable, and the irradiation period was finally limited to 24 hr. The nitrite concentration and the period selected for irradiation are not considered optimum, however. Additional studies of this treatment process may further increase the biodegradation rate of cellulose.

The use of fungi as food is not new. Pringsheim and Litchtenstein (1920) reported feeding animals with *Aspergillus fumigatus* grown on straw supplemented with inorganic nitrogen. The experiments reported here were designed to optimize the growth of cellulolytic fungi, and the results provide some of the parameters needed to develop continuous processes for producing fungal proteins for animal feed.

In our laboratory, the individual amino acids liberated during the protein hydrolysis reaction are totaled to determine the amount of protein in fungal mycelium. To determine the percent of the protein content, this total plus the amount of liberated ammonia is divided by the weight of the sample, and the quotient is multiplied by 100 (Coleman, 1972). The amino acid content of cellulolytic fungi grown on cellulosic substrates as determined in our laboratory and the content of peanuts and soybean meal reported by Block and Bolling (1951) can be compared (Table I). Later work by Wolf (1970) is also in agreement with the soybean values given in Table I.

Usually the amount of protein is determined by first analyzing for total nitrogen (Kjeldahl nitrogen analysis) and then converting to protein by multiplying by a factor of 6.25 (based on the fact that a nominal protein material contains 16% nitrogen). Litchfield (1968) used this method in his compilation of data about fungal protein. Because nonprotein nitrogen materials can occur in single-cell organisms and can contribute to the total nitrogen content, we believe the method used in this study to determine protein is more realistic because it does not include nonprotein nitrogen compounds.

The weight of the fungal mycelium produced from a gram of cellulose ranged from 0.5 to 0.68 gram. The percent protein composition of fungi tested was: no. 3, 6.8; no. 6, 13.3; no. 9, 6.8; no. 10, 4.9; no. 11, 7.1. Protein grains such as corn, wheat, and rye range from 10 to 15% (Block and Bolling, 1951). Fungus no. 6 is well within this range.

The amino acid composition of fungus no. 6 in this study compared favorably with that found by Block and Bolling for the peanut and soybean meal (Table I), and contained in a number of cases more essential amino acids than that of the fungi reported on by Litchfield (Rogers, 1969, p 17). Anderson and Jackson (1958) reported that the amino acid profile of most microorganisms is quite similar and, in general, is deficient in the sulfur-containing amino acids. The amino acid composition of the fungi reported in Table I had the sulfur-containing amino acid methionine and, in one case, cystine. The essential amino acids histidine, isoleucine, leucine, lysine, phenylalanine, threonine, valine, and methionine were all present in the protein composition of the fungi. The other essential amino acid, tryptophan, may have been present in the fungal mycelium; acid hydrolysis, however, decomposes this compound.

Litchfield (1968) reported typical protein and fat-content values of fruiting bodies and mycelia for a wide variety of fungi. In general, the protein content of the fruiting body phase of the fungi is greater than that of the mycelium. Since *Aspergillus niger* was reported to have a high protein content, its biodegradation properties were evaluated. Preliminary experiments with *A. niger*, fungus no. 12, showed that substrates such as Solka Floc, hydropulped refuse, and cellulosic waste from a wood-pump mill were not utilized by this organism. When this fungus utilizes agricultural starch waste, however, its protein content is 36% and it contains all the essential amino acids (Rogers et al., 1970).

Conclusions

The data reported here indicate that fungi can be used as a biosynthetic agent to produce high-quality protein from cellulose wastes such as kraft paper, agricultural waste, and urban refuse after a process such as hydropulping first separates the cellulosic fibers in the refuse from noncellulosic materials.

Without an effective pretreatment process, recycling cellulose cannot become an economically feasible reality. We hope that this study might promote additional investigations of the pretreatment processes that increase the biodegradation rates of cellulose. In our evaluation of several of these processes, only the photochemical treatment proved to be significant. This process reduced the cellulose fermentation time by one fourth to one half the time required for untreated cellulose. The percent of protein content of the fungi grown from cellulosic wastes ranged from 4.5 to 13.3%. Fungi no. 6, the one with the highest protein content, contained all of the essential amino acids, and in most cases, the amino acid content exceeded FAO requirements (*Chem. Eng. News*, 1967).

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Relationships Between Lake Trophic State and Nitrogen and Phosphorus Loading Rates

Earl E. Shannon[1] **and Patrick L. Brezonik**[2]
Department of Environmental Engineering, University of Florida, Gainesville, Fla. 32601

■ Nitrogen and phosphorus budgets were calculated for 55 north-central Florida lakes by considering watershed land use patterns and population characteristics. Nitrogen and phosphorus contributions to the lakes from the various land use areas, the residences within the watershed, and point sources, such as sewage treatment plants, were estimated, totaled, and expressed as annual loadings per unit lake volume. Significant multiple regression relationships between a quantitative index of trophic state (TSI) and the nitrogen and phosphorus loadings indicate that lake trophic state is largely dependent on the gross supply of nitrogen and phosphorus to the lake. Furthermore, it appears that phosphorus loading is more significant (or the limiting factor). Graphical relationships between the TSI and nitrogen and phosphorus loadings were devised, and these may be useful in predicting lake response to a particular nitrogen or phosphorus loading. Sources of uncertainty in relating lake trophic state to nutrient supply are discussed in light of the results.

Although nitrogen and phosphorus are not the only nutrients required for algal growth, it is generally agreed that they are the two main nutrients involved in the lake eutrophication process. In spite of current controversy over the role of carbon (Bowen, 1970; Legge and Dingeldein, 1970; Kerr et al., 1970), researchers as a whole regard phosphorus as the most frequent limiting nutrient in lakes. Ryther and Dunstan (1971) recently concluded that nitrogen is the critical limiting factor to algal growth and eutrophication in coastal marine waters. Numerous algal assays have shown either nitrogen or phosphorus or both to be limiting algal productivity in lakes.

Several factors have complicated attempts to quantify the seemingly obvious correlations between lake trophic state and measured nitrogen and phosphorus concentrations of the lake waters. For example, measured inorganic nutrient concentrations do not necessarily denote nutrient availability to the plant, but merely represent what is left over by the lake production processes. In addition, numerous morphometric, physical, and chemical factors affect the availability of nutrients in lakes (Brezonik et al., 1969). Although relationships between nutrient concentrations and plant production are of interest in specific studies, it is often more desirable from management and eutrophication control standpoints to quantify the dependence of lake water quality on nutrient supply. Thus Vollenweider (1968) and others have emphasized the importance of nutrient (particularly nitrogen and phosphorus) supply in determining a lake's trophic state. Although various lake factors, such as mean depth, detention time, basin shape, and sedimentation rate, affect the amounts of nutrients a lake can assimilate, nutrient budget calculations represent a first step in quantifying this dependence.

A few lacustrine nitrogen and phosphorus budgets have been reported in the literature—e.g., Rohlich and Lea (1949) for Lake Mendota, McGauhey et al. (1963) for Lake Tahoe, and Edmondson (1961) for Lake Washington. Vollenweider (1968, 1969) has summarized most of the budget calculations for American and European lakes. Comprehensive evaluation of the nutrient balance for a lake requires measurement of all potential nutrient sources and sinks (Table I) over an extended period to assess seasonal and other effects. Some sources and sinks—e.g., groundwater, nitrogen fixation, and denitrification—require elaborate sampling and experi-

Table I. Potential Nitrogen and Phosphorus Sources and Sinks for Lakes

Natural	Cultural
Precipitation on lake surface	Domestic and industrial waste waters
Swamp runoff	Agricultural runoff
Virginal meadowland runoff	Managed forest runoff
Forest runoff	Urban runoff
Soil erosion	Septic tanks
Aquatic bird and animal wastes	Landfill drainage
Leaf and pollen deposition	
Groundwater influxes	
Nitrogen fixation[a]	
Sediment recycling	
Sinks	
Outlet losses	Denitrification[a]
Fish catches	Volatilization[a]
Aquatic plant removal	Groundwater recharge
	Sediment losses

[a] Applies to nitrogen alone.

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[1] Present address, Public Health Engineering Division Environmental Health Center, Ottawa 3, Canada.
[2] To whom correspondence should be addressed.

mental procedure to be adequately evaluated. Consequently, manpower and time constraints have resulted in very few complete nutrient balances being attempted. An alternative and simpler method is to use literature estimates for nutrient exports from various sources and information on the various land use and population characteristics of the lake watershed. This approach was used by Lee et al. (1966) for nitrogen and phosphorus budget calculations for Lake Mendota. While perhaps not as accurate as actual measurement, there is no other realistic alternative when evaluating budgets for a large number of small lakes.

This paper presents partial nitrogen and phosphorus budget data for 55 lakes in north-central Florida. The budgets are referred to as partial budgets since no attempt was made to account for such sources of nitrogen and phosphorus as nitrogen fixation, leaves and pollen, and groundwater. Adequate data were not available to evaluate most sinks, and consequently none was considered. The partial budget calculations therefore estimate gross supply or loading. The statistical relationships between the budgets and lake trophic state are described, and the problems of relating trophic state and nitrogen and phosphorus supply are discussed.

Methods

Nitrogen and Phosphorus Supply Calculations. Watershed areas for each of the 55 lakes were outlined and measured using USGS 1/24,000 topographic maps. For each watershed recent aerial photographs were obtained, and five categories of land use were delineated and measured using photogrammetric techniques. The land use categories were forest, urban, fertilized cropland, pasture, and cleared unproductive areas. The population characteristics of each watershed were also evaluated in three categories. Residences on a lake shoreline were classified as immediate cultural units. Residences remote from a lake shoreline, but within the watershed, were categorized as remote cultural units. The immediate and remote cultural units were enumerated from the aerial photographs, and each unit was assumed to utilize a septic tank. Residences served by sanitary sewer facilities and sewage treatment plants comprised the third category. Recent population figures were obtained for municipalities served by sewage treatment plants within each of the lake watersheds. Complete morphometric, land use, and population figures for these lakes have been reported elsewhere (Shannon, 1970). Data pertinent to the present study have been deposited with the ACS Microfilm Depository Service.

Table II. Expected Quantities of Nitrogen and Phosphorus from Various Sources

Source	Ref.	Quantity of nitrogen	Quantity of phosphorus
Domestic sewage	Vollenweider (1968)	3940^a	795^a
Fertilized area			
Citrus farms	. . .	2.24^b	0.018^b
Muck farms	. . .	0.11^b	0.135^b
Pastured area	Milar (1965)	0.85^b	0.018^b
Unproductive cleared area	Brink (1964)	0.18^b	0.006^b
Forested area	Sylvester (1961)	0.24^b	0.008^b
Urban area	Weibel (1969)	0.88^b	0.110^b
Rainfall	Brezonik et al. (1969)	0.58^c	0.044^c
Septic tanks			
Immediate	. . .	2420^d	138^d
Remote	. . .	970^d	13.8^d
Domestic ducks	Paloumpis and Starret (1960)	480^e	90^e

[a] Grams/capita/year
[b] Grams/m^2 of land use area/year
[c] Grams/m^2 of lake area/year
[d] Grams/septic tank/year
[e] Grams/duck/year

Literature figures for the expected contributions of nitrogen and phosphorus from the various sources were compiled, and the values used in this study are summarized in Table II. Where applicable, each value is accompanied by the literature reference. Literature estimates were not available for two sources. Muck (recovered marshland) and citrus farm contributions were calculated from average fertilizer composition and application rates, assuming that 10% of the applied nitrogen and 1% of the applied phosphorus was exported from the soil to the lake. The figures for percentage fertilizer losses were reported by Vollenweider (1968) and, although approximate, probably represent lower limits. Septic tank contributions were estimated using a similar procedure. An average septic tank was assumed to have a daily effluent volume of 475 liters with total nitrogen and phosphorus concentrations of 35 mg/l. and 8 mg/l., respectively (Polta, 1969). For septic tanks associated with immediate cultural units, it was estimated that 25% of the nitrogen and 10% of the phosphorus in the effluent were exported to the lake. For remote cultural unit septic tanks it was estimated that 10% of the nitrogen and 1% of the phosphorus discharged eventually reached the lake.

Contributions from domestic sewage are expressed in Table II as the amount per capita per year. These sewage figures were used only when effluent records for the individual plants were not available. One lake (Mize) harbors a colony of 50 domestic ducks; estimated nitrogen and phosphorus contributions from ducks are thus listed in Table II. Several large lakes—e.g., Griffin and Apopka—receive nitrogen and phosphorus via citrus processing plant effluents. The magnitude of the contributions was determined from average plant flow rates and concentrations (Environmental Engineering Inc., 1970).

Formulation of a Trophic State Index. Lake trophic state—the condition demonstrated by a lake in response to nutrient enrichment—is a multidimensional and hybrid concept as suggested by Margalef (1958). Adequate description of the concept requires the consideration of several physical, biological, and chemical characteristics of the lake—i.e., trophic state indicators. In this study, seven indicators were combined to form a trophic state index (TSI) capable of expressing the concept quantitatively on a numerical scale (Shannon and Brezonik, 1972). The index was derived by extracting the first principal component from the correlation matrix of the seven indicators. In effect, the technique reduces the concept of trophic state from seven dimensions to a single one yielding a new component variable, which can then be treated mathematically as a conventional parameter. In general, principal component analysis reduces the dimensionality of a concept or phenomenon—e.g., trophic state—by expressing original observation—e.g., trophic state indicators—in terms of fewer component variables, which are linear functions of the observation variables. The first principal component of a set of variables is the linear combination of the variables which explains the maximum variance in the original data. The seven indicators included in the index were primary production, chlorophyll *a*, total phosphorus, total organic nitrogen, Secchi disc, specific conductivity, and Pearsall's (1922) cation ratio (Na + K)/(Ca + Mg). So that all variables would contribute to the index in a positive sense—i.e., increasing value of the variable being associated with increasing eutrophy—inverse values for Secchi disc transparency and for Pearsall's cation ratio were used. The data matrix for computation of the principal component consisted of mean values over a one-year period for the seven variables on each lake, and the resulting first principal component explained about 70% of the variance in the original data. The resulting trophic state index gave a range of values from 1.3 for four ultraoligotrophic lakes to 22.1 for a hypereutrophic lake (Table III). Obviously no exact physical meaning can be placed on the absolute magnitude of the index values, but the values are felt to be a relative, quantitative expression of trophic state conditions in the lakes. This contention is supported at least in part by the fact that the rank of the lakes according to TSI values is in substantial agreement with rankings based on qualitative inspection of trophic indicator data.

The 55 lakes were also subjected to a cluster analysis considering the seven indicators to obtain five distinct trophic groups of lakes—i.e., ultraoligotrophic, oligotrophic, mesotrophic, eutrophic, and hypereutrophic. Additional details on the development of the TSI and its usefulness and on the cluster analysis have been presented elsewhere (Shannon, 1970; Shannon and Brezonik, 1972).

Statistical Methods. The statistical relationships between lake trophic state, as expressed by the TSI, and nitrogen and phosphorus loadings were investigated using stepwise multiple regression and canonical correlation techniques. In stepwise regression, independent variables (in this case, nitrogen and phosphorus loadings) are added to the regression equation in decreasing order of their partial correlation with the dependent variable (TSI), or synonymously in decreasing order of their statistical significance. The program BMD02R (Dixon, 1968) was used with the zero-intercept option. This option was specified since it was desirable, at least in a theoretical sense, to have a TSI value of zero when there were no nitrogen and phosphorus loadings.

The canonical correlation technique is commonly used to analyze the statistical relationships—i.e., the nature and extent of covariation—between two sets of variables considered in vector form. This method has the advantage of not requiring the selection of one parameter as the dependent variable. Furthermore, it does not assume orthogonality (independence) among variables, which assumption is made (but often violated) in regression analysis. In this study one set of variables consisted of the seven trophic state indicators included in the TSI, and the other set was composed of the nitrogen and phosphorus loadings. The method determines the linear combination of variables—i.e., the canonical variate—for each set which yields a maximum correlation between the two sets. The absolute value of the coefficient associated with each variable within the canonical variates expresses the relative weight or importance of that variable in determining the canonical correlation. The BMD06M (Dixon, 1968) program was used for canonical correlation analyses.

Results and Discussion

Nitrogen and Phosphorus Budgets. The calculated nitrogen and phosphorus loading rates for each of the 55 lakes are

Table III. Calculated Nitrogen and Phosphorus Supplies for 55 Florida Lakes

	Lake	Type[a]	TSI[b]	N[c]	P[c]
1	Santa Fe	O	2.5	0.28	0.015
2	Little Santa Fe	O	2.3	0.32	0.014
3	Hickory Pond	O	2.5	2.25	0.051
4	Altho	O	2.5	0.53	0.031
5	Cooter Pond	M	5.3	3.72	0.101
6	Elizabeth	M	3.2	1.45	0.064
7	Clearwater	O	2.6	1.01	0.051
8	Hawthorne	E	9.1	1.62	0.130
9	Little Orange	M	3.4	2.58	0.082
10	Unnamed	M	3.2	0.54	0.021
11	Moss Lee	O	2.8	0.39	0.020
12	Jeggord	O	2.8	0.57	0.027
13	Still Pond	U	1.9	1.73	0.072
14	Lochloosa	M	5.2	1.15	0.044
15	Orange	M	4.3	1.85	0.071
16	Palatka Pond	M	3.2	2.70	0.121
17	Newnan's	E	7.1	2.61	0.118
18	Mize	M	4.2	2.05	0.183
19	Calf Pond	M	4.6	2.42	0.132
20	Unnamed	H	18.5	3.99	0.335
21	Meta	M	3.1	3.00	0.250
22	Alice	H	10.7	106.00	18.000
23	Bivin's Arm	H	14.7	6.86	0.424
24	Clear	E	8.8	4.31	0.405
25	Unnamed	M	6.4	2.07	0.113
26	Beville's Pond	M	3.1	2.89	0.187
27	Unnamed	M	5.8	0.77	0.032
28	Kanapaha	H	13.5	48.30	2.950
29	Watermelon Pond	M	3.6	1.45	0.062
30	Long Pond	O	2.8	5.94	0.183
31	Burnt Pond	E	8.3	2.27	0.092
32	Wauberg	E	7.4	0.63	0.028
33	Tuscawilla	M	4.8	2.60	0.124
34	Apoka	H	22.1	2.23	0.161
35	Dora	H	18.5	3.00	0.127
36	Harris	M	6.3	1.10	0.029
37	Eustis	H	10.5	1.46	0.077
38	Griffin	H	13.7	3.69	0.183
39	Weir	M	3.3	0.29	0.010
40	Kingsley	U	1.9	0.18	0.015
41	Sandhill	U	1.3	0.29	0.015
42	Magnolia	U	1.3	0.25	0.011
43	Brooklyn	U	1.5	0.26	0.016
44	Geneva	U	1.8	0.31	0.022
45	Swan	U	1.5	0.26	0.015
46	Wall	O	2.1	3.27	0.124
47	Santa Rosa	U	1.3	0.18	0.009
48	Adaho	U	2.2	1.03	0.039
49	McCloud	U	1.5	1.35	0.058
50	Anderson-Cue	U	1.5	3.10	0.187
51	Suggs	O	2.3	2.24	0.071
52	Long	U	1.3	0.55	0.026
53	Winnott	M	2.0	0.41	0.016
54	Cowpen	U	1.5	0.42	0.021
55	Gallilee	U	1.6	0.86	0.036

[a] U = ultraoligotrophic, O = oligotrophic, M = mesotrophic, E = eutrophic, H = hypereutrophic.

[b] Trophic State Index

[c] In g/m^3/year

presented in Table III expressed as grams per cubic meter of lake volume per year. Loadings expressed per unit lake surface may be obtained by simply multiplying the volumetric loading by lake mean depth. Nutrient loadings are often expressed on a unit surface area basis and in turn related to lake mean depth to predict lake response; for example, see Vollenweider (1968). In Florida lakes, mean depths rarely exceed 5 meters, and most lakes are completely mixed year round. Consequently, the analyses reported here pertain to the volumetric loading data of Table III. Analyses performed on surface loading data gave similar results. Table III also gives the numerical value of the TSI for each lake along with its trophic group from Shannon and Brezonik (1972).

In general, the results indicate a positive correlation between nitrogen and phosphorus supply and trophic state as quantified by the TSI, but several discrepancies are evident. Lakes Alice and Kanapaha, although demonstrating hypereutrophic characteristics, have nitrogen and phosphorus loadings at least an order of magnitude higher than any of the other hypereutrophic lakes. This can be attributed to the fact that both lakes have had their natural watersheds increased by cultural activities, which have resulted in very short detention times for the lakes. Lake Alice receives 1 to 2 million gallons per day (gpd) of sewage effluent and 10–12 million gpd of cooling water from University of Florida facilities. Lake Kanapaha, which is connected with a sinkhole draining an urbanized stream, has had its watershed enlarged two- to threefold by drainage diversion schemes. Thus the hydraulic characteristics of these two lakes separate them from the remainder of the study lakes, which receive runoff from natural watersheds. To prevent severe bias in the statistical analyses, these two lakes were excluded from the sample group.

Anderson-Cue Lake (No. 50) has a nitrogen and phosphorus loading comparable to hypereutrophic Lake Dora (35) but a TSI typical of ultraoligotrophic lakes. Two reasons for this discrepancy are the lake has not had sufficient time to equilibrate with its nutrient supply and the TSI has not been sensitive to the lake response. This lake has been artificially enriched with nitrogen and phosphorus at approximately the present loading rates since 1967 as part of a study of eutrophication factors in Florida lakes (Brezonik and Putnam, 1968; Brezonik et al., 1969). Prior to 1967, the lake was ultraoligotrophic and similar in most aspects to the control, McCloud Lake (49). The enriched and control lakes are still ultraoligotrophic according to their TSI's although some increased growths of attached algae have recently been noted in Anderson-Cue Lake. Since the TSI accounts for phytoplankton production and biomass alone, this response is not reflected in the TSI. Perhaps if total plant biomass and primary production (macrophytes, attached algae, and phytoplankton) in the lake were incorporated into the TSI, Anderson-Cue Lake may have a higher TSI value than the control lake.

Relative Importance of Various Nutrient Sources. Six representative lakes were selected (Table IV) for the purpose of comparing the percentage contributions of the various nutrient sources to the overall nitrogen and phosphorus budgets. To illustrate general trends occurring in the transition from ultraoligotrophic to culturally hypereutrophic conditions, one lake from each of the five trophic groups is included in the comparison. In addition, Newnan's Lake is included as an example of a naturally eutrophic lake. For the ultraoligotrophic and oligotrophic lakes, the natural nutrient sources of rainfall and runoff from forested regions are dominant, although Lake Santa Fe receives a small portion of its nitrogen and phosphorus supply (21%) from cultural sources. Orange Lake could perhaps be classified as naturally mesotrophic since most of its nitrogen and phosphorus supply is derived from natural sources.

Lakes Hawthorne and Dora have obviously been influenced by the cultural activities in these watersheds. The former receives the major portion of its nitrogen and phosphorus supply from urban runoff and septic tanks while sewage effluent and agricultural runoff have played a significant role in the deterioration of Lake Dora. Newnan's Lake has a large, heavily forested watershed, and the associated runoff appears to be the predominant factor in the eutrophication of this shallow lake. Eutrophication of this sort is virtually impossible to control, whereas measures can be taken to control the cultural sources degrading lakes like Hawthorne and Dora.

Statistical Analyses. Results of the statistical analyses are summarized in Table V. Several regression relationships were tested using both additive and multiplicative models. All the regression results presented in Table V were significant at the 99% confidence level. Using the magnitude of the multiple correlation coefficient, *R*, as a criterion for choosing

Table IV. Percentage Contributions from Various Cultural and Natural Sources for Selected Lakes

Lake and type[a]	Nutrient	Sewage	Urban runoff	Fertilized area	Pasture area	Unproductive cleared area	Forest area	Septic tanks	Rainfall on lake surface	% Cultural
Santa Rosa (U)	N	0	0	0	0	0	47	13	40	13
	P	0	0	0	0	0	30	11	59	11
Santa Fe (O)	N	0	7	5	7	1	41	2	37	22
	P	0	15	1	3	N.S.	25	2	54	21
Orange (M)	N	0	1	10	11	4	57	N.S.	17	21
	P	0	5	2	6	3	49	N.S.	35	13
Newnan's (E)	N	0	8	2	14	4	56	1	15	25
	P	0	22	N.S.[b]	7	3	41	1	26	30
Hawthorne (E)	N	0	36	N.S.	N.S.	5	14	32	13	68
	P	0	57	N.S.	N.S.	2	6	23	12	80
Dora (H)	N	13	4	74	N.S.	N.S.	1	2	6	93
	P	60	12	14	N.S.	N.S.	1	1	12	87

[a] See Table III for key to symbols.
[b] Not significant (less than 1%).

Table V. Statistical Analyses of Relationships Between TSI and N and P Loading Rates[a]

Correlation matrix:

	TSI	N	P
TSI	1.000	0.773	0.786
N		1.000	0.935
P			1.000

Stepwise Regression Analyses:

Regression model	Equation	*R*
	(1) $\mathrm{TSI} = 26.11\,(P) + 0.90\,(N)$	0.793[b]
	(2) $\mathrm{TSI} = 48.86\,(P) - 5.26\,(N)(P) + 0.83\,(N)$	0.811[b]
Additive	(3) $\mathrm{TSI} = 26.10\,(P) - 242.36\,(P)^2 + 1.12\,(N)^2 + 28.68\,(N)(P) + 2.37\,(N)$	0.830[b]
	(4) $\mathrm{TSI} = 0.19\,(N/P)$	0.643[b]
Multiplicative	(5) $\mathrm{TSI} = 1.08\,(P)^{0.92} \times (N)^{0.04}$	0.620[b]

Canonical Correlation Analysis:

Canonical variate of trophic state indicators	Canonical variate of N and P loadings	Canonical correlation coefficient
$0.69\,(\mathrm{TP}) + 0.64\,(1/\mathrm{SD}) + 0.48\,(\mathrm{CL}) - 0.36\,(\mathrm{TN}) + 0.34\,(\mathrm{PP}) + 0.33\,(\mathrm{CD}) + 0.17\,(1/\mathrm{CR})$	$1.19\,(P) - 0.23\,(N)$	0.723

[a] Key to symbols. 1/SD = inverse Secchi Disc, m^{-1}; CD = Specific Conductance, μmho cm^{-1}; TN = Total Organic Nitrogen, mg/l.; TP = Total Phosphorus, mg/l.; PP = Primary Production, mg C/m^3-hr; CL = Chlorophyll *a*, mg/m^3; 1/CR = Inverse Pearsall (1921) cation ratio ([Ca] + [Mg]/[Na] + [K]); N = Nitrogen Loadings (g/m^3-year); and P = Phosphorus Loadings (g/m^3-year).

[b] Significance at 99% confidence level

among the regression equations, an additive equation (3) in Table V, including simple, interaction, and quadratic terms, explains the largest percentage of variation in TSI ($R = 0.830$). However, Equation 1 incorporating only the simple loadings gives comparable significance ($R = 0.793$), and inclusion of the interaction terms thus provides only marginal increases in *R*. The multiplicative model (Equation 5) is the least significant and comparison of the additive and multiplicative equations suggests that the functional relationship between TSI and nitrogen and phosphorus loadings may itself be additive with one nutrient being more significant—i.e., limiting. In Florida lakes it appears that phosphorus loading is the limiting factor since it is the first independent variable incorporated by the stepwise procedure into the regression equations, and it has the highest simple correlation (0.786, Table V) with the TSI. Although nitrogen loading is also highly correlated with the TSI (0.773), it is of secondary significance in the regression equations. It is interesting to note that the TSI is significantly correlated with the ratio of nitrogen to phosphorus; however, the *R* values obtained are lower than those for the additive regression equations. These results imply that trophic state is primarily dependent on phosphorus and nitrogen supplies, with phosphorus being the overall limiting factor, and the ratio of the loadings of secondary significance.

Canonical correlation analysis (Table V) derived a canonical variate of the seven trophic indicators that was significantly correlated (0.723) with the canonical variate of nitrogen and phosphorus loadings. In general, the analysis corroborates the regression results. For instance, phosphorus loading is the more significant of the two loadings based on the weighting factors in the canonical variate (1.19 for P vs. −0.23 for N). The most heavily weighted trophic indicator in the indicator canonical variate is total phosphorus concentration (TP). Thus, the larger weightings associated with P and TP illustrate the dependence of average total phosphorus concentration on the phosphorus loading. Vollenweider (1968) observed a similar correlation between spring total phosphorus concentration and phosphorus supply for a group of European lakes. A canonical correlation analysis of the land use and population patterns vs. the trophic state indicators (Shannon and Brezonik, 1972) resulted in a higher correlation coefficient and assigned the highest weighting to primary production. This is perhaps more appropriate, at least in a theoretical sense, since primary production is often considered the fundamental trophic state indicator. There is some inherent error in using literature values of the expected nitrogen and phosphorus contributions from land use patterns to obtain nutrient loadings, and this quite likely explains the lower correlation coefficient for the analysis in Table V. In other words, the land use and population characteristics in their raw form contain more significant information than the calculated nitrogen and phosphorus loadings.

Although the regression and canonical correlation analyses resulted in statistically significant relationships, there was considerable disagreement between the predicted and observed values of TSI. For example, Lake Griffin has an experimental TSI of 13.7 and a predicted TSI, using Equation 3 of Table V, of 9.6, a 30% error. Similar discrepancies exist for some of the other lakes with the average error being about ±25%. Thus, in spite of the strong trends demonstrated by the significant regression relationships, there is substantial scatter of the experimental data about the fitted regression surfaces. Several possible sources of uncertainty will be discussed later.

Of great interest in control of cultural eutrophication is the development of critical loading rates, above which eutrophic conditions might be expected to ensue. Recently, Vollenweider (1968) analyzed the available nutrient budget and trophic condition data for several lakes and proposed permissible and critical loading rates for nitrogen and phosphorus as a function of mean depth. For lakes with a mean depth up to 5 meters, the permissible nitrogen and phosphorus loadings were 1.0 and 0.07 gram/m^2/year, respectively. Critical loadings were 2.0 and 0.12 gram/m^2/year.

Critical loading rates for nitrogen and phosphorus can be estimated for Florida lakes from regression equations in Table V and similar ones where TSI is expressed as a function of areal nitrogen and phosphorus loadings. Comparison of TSI values and trophic conditions in the 55 Florida lakes (Shannon and Brezonik, 1972) indicates that eutrophic conditions can be expected when TSI values are greater than 7.0 and oligotrophic conditions when the TSI is less than about 4.0. Assum-

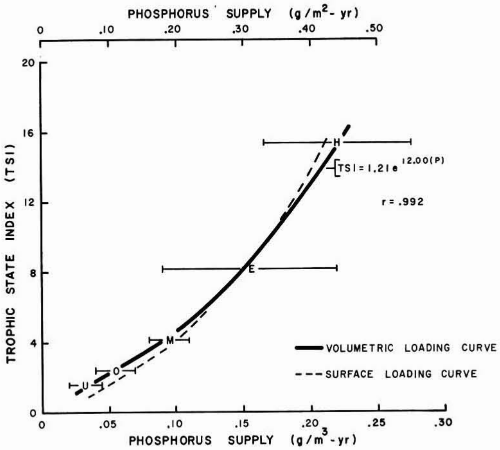

Figure 1. Mean TSI values for five trophic groups vs. annual phosphorus loading in g/m³-year and g/m²-year

Brackets indicate range for one standard error. Symbols of trophic groups are: ultraoligotrophic (U), oligotrophic (O), mesotrophic (M), eutrophic (E), hypereutrophic (H)

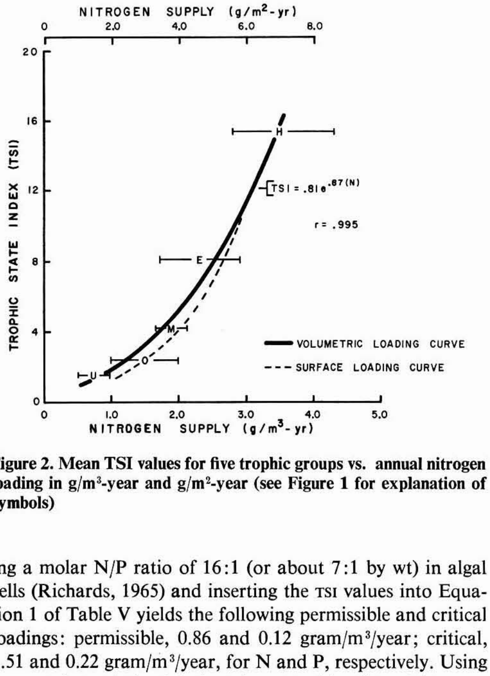

Figure 2. Mean TSI values for five trophic groups vs. annual nitrogen loading in g/m³-year and g/m²-year (see Figure 1 for explanation of symbols)

ing a molar N/P ratio of 16:1 (or about 7:1 by wt) in algal cells (Richards, 1965) and inserting the TSI values into Equation 1 of Table V yields the following permissible and critical loadings: permissible, 0.86 and 0.12 gram/m³/year; critical, 1.51 and 0.22 gram/m³/year, for N and P, respectively. Using a regression relationship based on areal loadings (Shannon, 1970) analogous permissible and critical areal loading rates can be derived. These are: permissible, 2.0 and 0.28 gram/m²/-year; critical, 3.4 and 0.49 gram/m²/year, for N and P, respectively. These values are somewhat larger than Vollenweider's permissible and critical rates but are in the same general range. Florida lakes appear capable of assimilating somewhat greater quantities of nutrients before becoming mesotrophic or eutrophic than suggested by Vollenweider's analysis.

Some interesting results were obtained through graphical presentation of the relationships between the TSI and phosphorus and nitrogen supplies, respectively. In Figure 1, the mean TSI for each trophic group (Shannon and Brezonik, 1972) is plotted against the corresponding mean phosphorus loading. Figure 2 represents a similar treatment considering mean nitrogen loadings. The horizontal bounded lines represent ±1 std error of the group loading mean. In both graphs the dependence of TSI on nitrogen or phosphorus loading can be adequately described by an exponential function similar to the classical logarithmic growth curve. The least squares equation and correlation coefficients are shown for each figure. That both curves are similarly shaped is to be expected since the nitrogen and phosphorus loadings are themselves highly correlated (Table V). The within-group deviation of loadings is considerably more pronounced for the phosphorus relationships, particularly for the hypereutrophic groups of lakes. Such deviations are to be expected when representing the complex process of trophic state change in terms of a single nutrient input. In addition, the hypereutrophic group is essentially unbounded at the upper end and therefore not subjected to artificial boundary constraints as are the other four groups. Quite likely, changes in the limiting nutrient will occur over any extended range of trophic state response. Thus, the relationships of Figures 1 and 2 reflect only an average situation, and their major utility probably lies in the area of lake management. For example, given knowledge that either nitrogen or phosphorus is limiting and a known or proposed nutrient loading, potential lake response can be determined by consulting the appropriate relationship.

The aforementioned graphical relationships are most applicable for determining the response of shallow, subtropical lakes. For deeper lakes, loadings could possibly be expressed on an areal basis and the surface loading curve (dashed lines in Figures 1 and 2) used for predictive purposes. However, the graphical relationships derived by Vollenweider (1968) seem more appropriate when dealing with lakes of mean depth greater than 10 meters.

Sources of Uncertainty. The concept of trophic state response may be idealized in functional form as:

$$\text{TS} = f(\text{P},\text{N},M,S,T\ldots) \tag{1}$$

where TS represents trophic state; P, specific phosphorus loading; N, specific nitrogen loading; *M*, morphometric and hydrological characteristics of the lake such as mean depth and shoreline development which influence lake mixing; *S*, a sedimentation factor; and *T*, time. Other factors, including the loading of other growth-essential nutrients, might conceivably enter into the functional relationships. Vollenweider (1969) used a similar general relationship as the basis of a proposed lake typology system where the trophic state of a lake could be determined using a multidimensional approach.

In this study an attempt has been made to approximate Equation 1 considering TSI, and nitrogen and phosphorus loadings as follows:

$$\text{TSI} = g(\text{N},\text{P}) + C \tag{2}$$

where *C* is an uncertainty term representing the discrepancy between values of TSI predicted by the function *g*(N,P) and the values that might be obtained from the true causal relationship of Equation 1, (if it were known). Individual components of the uncertainty term may include the following: *g* is an approximation of *f*, the nitrogen and phosphorus supply calculations are in error, and the TSI does not represent the concept of trophic state (TS) completely. Approximations of *f* were obtained here by using multiple regression techniques.

These approximations included only two of a number of potentially important variables—i.e., nitrogen and phosphorus loadings.

Furthermore, the relationship is based on gross loading rates of N and P, whereas the impact of nutrient enrichment on lake trophic state is perhaps more closely related to net enrichment—i.e., the difference between the summed sources and the summed sinks. However, the error resulting from this treatment is probably negligible in the present context since the hydraulic detention times of the lakes are large in comparison with the turnover times for N and P in the lakes. Hence the rate of gross nutrient loading can reasonably be assumed to relate directly to the productivity or trophic state of the lake. The loadings were estimated using land use and population characteristics and literature values of individual source contributions, a procedure that contains some inherent uncertainty. The TSI may not completely describe the concept of trophic state in spite of the fact that it incorporates seven of the more significant trophic state indicators. As previously discussed in reference to Anderson-Cue Lake, it does not account for macrophyte and periphyton biomass or primary production, which in some lakes may constitute a significant proportion of total lake primary production.

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Concentration of Mercury in the Manufacture of Fish Protein Concentrate by Isopropyl Alcohol Extraction of Sheepshead and Carp

Thomas A. Gasiewicz and Frank J. Dinan[1]

Department of Chemistry, Canisius College, Buffalo, N.Y. 14208

■ Levels of mercury in bottom feeding freshwater fish and their corresponding fish protein concentrates have been determined and found to correlate with a fish:fish protein concentrate enrichment factor of approximately 5. This finding indicates that no mercury is extracted from the fish used in this study during the concentrate manufacture via isopropyl alcohol extraction, and further suggests that only fish of low initial mercury concentration may be used as starting material in this process if the resultant fish protein concentrate (FPC) is not to exceed the maximum allowable mercury concentration level.

Production of FPC from scavenger fish affords a route by which these fish can be converted to a form of protein which can be used as a dietary supplement (Sidwell et al., 1970). This process is of potentially great importance in the Great Lakes. In recent years, whereas the game fish population of these lakes has gradually depleted, there has been a noted increase in the population of bottom feeding or scavenger fish which have a significantly lower demand for dissolved oxygen (DO) (Beeton, 1971). These fish generally have much higher oil and amine contents than game fish and are therefore little used for human consumption. However, bottom feeding fish offer a potentially large source of material for conversion to FPC, which is a nearly tasteless and odorless material.

It is well-known that the lower Great Lakes, particularly Lakes Erie and Ontario, have been extensively polluted by industrial and municipal wastes (Beeton, 1971). Since fish from these lakes would be susceptible to the ingestion and concentration of such heavy metals as mercury, this study has attempted to correlate quantitatively the level of mercury concentration in individual scavenger fish with the concentration of mercury in the FPC made from these fish.

Two types of bottom feeding fish commonly found in the Great Lakes, sheepshead (*Archosargus probatocephalus*) and carp (*Cyprinus carpio*) were used in this study. These fish were caught in the eastern end of Lake Erie and the mouth of the Niagara River, and immediately frozen. (One sample used in this study was obtained from a stream in Hershey, Pa.) Each individual fish was finely ground without evisceration, and a representative sample taken for mercury determination. The remaining ground fish was subsequently converted to FPC using isopropyl alcohol as the extracting solvent. The procedure followed for FPC preparation was exactly that recommended by the Bureau of Commercial Fisheries (1966). In each case, a representative sample of the resulting FPC was taken for analysis. The wt % FPC obtained from the fish was carefully determined. In this way, it was possible to correlate the mercury concentration in a given fish with that of the FPC obtained from that fish and to obtain an accurate enrichment factor for the FPC process.

Mercury determinations were carried out using flameless atomic absorption (Hatch and Ott, 1968). Both whole fish and FPC samples were digested in concentrated sulfuric acid for 2 hr prior to their determination. All analyses were conducted in duplicate.

Table I shows the results obtained in this study. All of the figures in this table have been adjusted for an average value of 97% recovery of known amounts of mercuric chloride run through the digestion-analysis procedure.

The quality of the FPC prepared during this study was assessed by comparing the ash (23%), protein (72%), and lipid (0.23%) content of this material with the published values obtained for the same fish species (Great Lakes Laboratory, 1970). In each case, standard methods were used for the determination of these values (Association of Official Agricultural Chemists, 1965).

Inspection of the data in Table I discloses that the mercury originally present in each whole fish is not removed by the extraction process. In fact, there is an observed five- to sixfold concentration factor in going from whole fish to FPC via the isopropyl alcohol process. This figure compares favorably

Table I. Mercury Enrichment Factors for FPC Preparation

Sample	Catch location	Hg concn in whole fish,[a] μg Hg/g	Hg concn in FPC,[a] μg Hg/g	Wt % FPC obtained	Theoretical enrichment factor[b]	Obsd enrichment factor[c]
Sheepshead (*A. probatocephalus*)	Niagara River	0.20 ± 0.03	1.21 ± 0.18	19.5	5.1	5.5
	Eastern Lake Erie	0.15 ± 0.01	0.79 ± 0.07	19.5	5.1	5.2
Carp (*C. carpio*)	Eastern Lake Erie	0.58 ± 0.01	3.12 ± 0.14	20.9	4.9	5.4
	Hershey Park, Hershey, Pa.	0.11 ± 0.01	0.62 ± 0.02	18.0	5.5	5.6

[a] Each value listed is the average of two determinations with the calculated standard deviation.
[b] Determined as follows: 100/wt % FPC
[c] Determined as follows: [Hg] in FPC/[Hg] in whole fish

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[1] To whom correspondence should be addressed.

Table II. Mercury Levels in Fish and Fish Protein Concentrate

Whole fish [Hg], μg/g	Corresponding FPC [Hg],[a] μg/g	Max. safe consumption of FPC, g/day
0.10	0.5	80
0.20	1.0	40
0.30	1.5	26.7
0.40	2.0	20.0
0.50	2.5	16.0
0.60	3.0	13.3
0.70	3.5	11.4

[a] Assuming a 5:1 enrichment factor.

with a theoretical concentration factor of approximately 5. This factor is based on the wt % FPC obtained from the fish, assuming that all of the mercury originally present remains in the concentrate. The observed enrichment factors are generally slightly higher than the theoretical factor, but within the experimental error of the method. The reason for this consistently higher factor is not clear at present.

The presence of mercury at levels in the range 0.3–0.9 μg Hg/g in FPC obtained from the National Center for Fish Protein Concentrate has been previously reported by Beasley (1971) who speculated that this level of mercury results from the sum of concentration processes occurring in both the environment and in FPC manufacture. However, the level of mercury concentration in the whole fish used to prepare this FPC was not determined. Therefore, the exact extent of mercury loss or concentration during the FPC manufacturing process could not be known.

The approximately fivefold enhancement of mercury concentration which has been found to occur during the FPC process suggests that a definite limitation exists on the mercury concentration in fish used as starting material for the manufacture of FPC via isopropyl alcohol extraction. Table II shows the theoretical relationship which exists between the mercury concentration of whole fish converted to FPC and the amount of FPC which can be safely consumed. These figures are based on a recommended maximum daily consumption of 60 μg of Hg (Berglund and Berlin, 1969) and an estimated current consumption of approximately 20 μg Hg/day (Bowen, 1966). It is further assumed that fish protein concentrate is approximately 80% protein (Ayres, 1966).

Inspection of these data discloses that only 32 grams of FPC prepared from whole fish having a mercury concentration of 0.25 μg/g, which is only one half the Food and Drug Administration (FDA) recommended maximum, and not an unreasonable figure for lower Great Lakes scavenger fish, could be safely consumed. This level drops to 16 grams of FPC for material prepared from fish at the 0.5 μg Hg/g level. It is important to note, however, that the FDA guideline for mercury concentration is 0.5 μg/g and that FPC exceeding this limit cannot be sold in this country. In view of these limitations, scavenger fish taken from polluted waterways would seem to be of limited value for conversion to FPC. Furthermore, the observed concentration effect demonstrates that the heavy metals content of any FPC must be considered carefully before this material is used for human consumption.

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Critical Evaluation of Rate-Controlling Processes in Manual Determination of Nitrogen Oxides in Flue Gases

Geoffrey Margolis
Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass. 02139

John N. Driscoll[1]
Walden Research Corp., Cambridge, Mass. 02139

The most common wet chemical method for the determination of high concentrations of nitrogen oxides in the presence of sulfur dioxide is the phenol disulfonic acid (PDS) technique. Although reliable results are obtained, a serious drawback is the exceptionally long time required for analysis. This results from the long standing time and the tedious (4–6 hr) evaporation step required by the procedure. The incentive for reducing the time required is obvious. The objective of this paper was, therefore, to evaluate critically the entire procedure, identify any rate-controlling steps and make changes to substantially reduce the time required.

Consideration of the equilibrium constants of Stull (1965) for the nitrogen oxides at typical combustion temperatures indicates that the two most stable oxides are NO and NO_2 with the former species being predominant. This is also borne

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[1] To whom correspondence should be addressed.

■ The phenol disulfonic acid procedure for NO_x analysis requires considerable standing time (about 24 hr) for completion. A theoretical evaluation of the procedure has indicated that the rate-controlling step is the gas phase oxidation of nitric oxide which produces a species that is more easily absorbed. This conclusion was verified experimentally. Strategies for reducing the analysis time are discussed. These strategies were based on increasing oxidation rates by mixing with pure oxygen and operation at elevated pressures. Use of rapid chemical analysis methods were also considered. Analysis showed that for operation at atmospheric pressure, mixing with oxygen resulted in a maximum reduction in oxidation time of about fivefold. Oxidation time at other pressures was inversely proportional to the square of the total pressure. For a sample containing 400 ppm nitric oxide, use of the above procedures can reduce overall analysis time to 5 hr for atmospheric operation and to about 10 min for operation at 10 atm.

out in the free energy minimization calculations of James (1971). As the combustion gases are cooled, equilibrium considerations predict an increase in the NO_2 concentration but the NO concentration remains high because of kinetic limitations (short residence time). Thus, the major nitrogen oxide component in flue gases is nitric oxide.

Wet chemical techniques for nitric oxide involve three basic steps: first, the conversion of nitric oxide to a product which is more easily absorbed [since nitric oxide has a low solubility in aqueous solutions, and no wet chemical techniques are available which are specific for nitric oxide (Driscoll et al., 1972)]; second, the actual absorption; and third, the chemical analysis of the nitrate or nitrite concentration in the aqueous solution. The first two steps proceed simultaneously while the third step is started only after the absorption is complete.

The time, T_A, required for completion of the analysis is directly determined by the rate at which each of the above steps proceeds. If, however, one of the steps is considerably slower than any of the others, then this will effectively govern the overall analysis time, T_A—i.e., it will be rate controlling. Identification of this slow step greatly simplifies the process of modifying experimental conditions to decrease the time for completion of the analysis.

The approach taken was to attempt to define the rate-determining step by computing first the time required for the conversion of NO to a soluble product, and then the time for absorption of these species. This was then followed by experimental verification of the theoretical conclusions.

Determination of Rate-Controlling Step

Estimation of Time Required for the Production of the Absorbed Species: In the PDS method, the absorbable species (NO_2 and/or N_2O_3) are produced from the oxidation of the nitric oxide by molecular oxygen present in the sample. The time required for the production of each of these species will be discussed in the following sections.

NITROGEN DIOXIDE. NO_2 is produced by the gas phase oxidation of NO. This is a third-order reaction that has been widely discussed in the literature (Bodenstein, 1935). The consumption rate of NO is given by:

$$-\frac{dP_{NO}}{dt} = k(P_{NO})^2(P_{O_2}) \qquad (1)$$

where P_{NO} = partial pressure of NO, atm; P_{O_2} = partial pressure of O_2, atm; and k = reaction rate constant = 23.2 $atm^{-2}\,sec^{-1}$ at 86°F taken from Sherwood and Pigford (1952).

The overall oxidation can be represented by:

$$2NO + O_2 \rightarrow 2NO_2 \qquad (2)$$

if immediate removal of NO_2 by absorption is assumed. Provided that the total number of moles in the reaction system remains approximately constant (a good assumption at the low NO concentrations generally encountered in an effluent sample) then Equation 1 can be integrated to give:

$$\frac{1}{P_{NO}} - \frac{1}{(P_{NO})_{init}} + \frac{1}{[2(P_{O_2})_{init} - (P_{NO})_{init}]} \times \ln\left\{\frac{(2P_{O_2})_{init}(P_{NO})}{(P_{NO})_{init}[2(P_{O_2})_{init} - (P_{NO})_{init} + P_{NO}]}\right\} = \frac{k}{2}[(2P_{O_2})_{init} - (P_{NO})_{init}]t \qquad (3)$$

where the subscript init refers to the initial value.

Use of Equation 3 permits computation of the oxidation times for NO_x production.

DINITROGEN TRIOXIDE. N_2O_3 is highly soluble in water and is produced by reaction between NO and NO_2. Thus:

$$NO + NO_2 \rightleftharpoons N_2O_3 \qquad (4)$$

As such it too must be considered as a possible absorbable species.

Data of Peters and Koval (1959) indicate that Reaction 4 is fast relative to the oxidation of NO (Reaction 2). However, calculation of the time to complete the production of N_2O_3 is complicated by the fact that both NO_2 and N_2O_3 can be absorbed. If it is assumed that the absorption rates of both NO_2 and N_2O_3 are infinitely rapid, it is clear that no N_2O_3 will be produced since the NO_2 will be immediately absorbed. In this case, the time will be the same as the oxidation time calculated earlier for NO_2. If, on the other hand, it is assumed that only the N_2O_3 absorption is infinitely rapid, then the production of N_2O_3 can be described as follows:

$$2NO + O_2 \rightarrow 2NO_2 \text{ (slow)} \qquad (2)$$

$$2NO_2 + 2NO \rightarrow 2N_2O_3 \text{ (fast)} \qquad (5)$$

$$(N_2O_3 + H_2O \rightarrow \text{products infinitely rapid})$$

Overall gas stoichiometry $\quad 4NO + O_2 \rightarrow 2N_2O_3 \qquad (6)$

Clearly, the kinetics of Reaction 2 once again control the rate of formation of N_2O_3, but the overall stoichiometry is represented by Equation 6. Integration similar to those performed previously results in Equation 7 from which it is possible to calculate the oxidation times for N_2O_3 production.

$$\frac{1}{P_{NO}} - \frac{1}{(P_{NO})_{init}} + \frac{1}{[4(P_{O_2})_{init} - (P_{NO})_{init}]} \times \ln\left\{\frac{4(P_{O_2})_{init}(P_{NO})}{(P_{NO})_{init}[(4P_{O_2})_{init} - (P_{NO})_{init} + P_{NO}]}\right\} = \frac{k}{4}[(4P_{O_2})_{init} - (P_{NO})_{init}]t \qquad (7)$$

Since the concentration of oxygen and nitric oxide encountered in air pollution studies are such that

$$(P_{O_2})_{init} \gg (P_{NO})_{init}$$

it is evident that both Equations 3 and 7 reduce to:

$$\frac{1}{P_{\mathrm{NO}}} - \frac{1}{(P_{\mathrm{NO}})_{\mathrm{init}}} = k(P_{\mathrm{O_2}})_{\mathrm{init}}t \qquad (8)$$

Equation 8 can be rewritten:

$$\frac{\dfrac{(P_{\mathrm{NO}})_{\mathrm{init}}}{(P_{\mathrm{NO}})} - 1}{k(P_{\mathrm{O_2}})_{\mathrm{init}}t} = (P_{\mathrm{NO}})_{\mathrm{init}} \qquad (9)$$

If it is assumed that $(P_{\mathrm{O_2}})_{\mathrm{init}}$ is 0.05 atm (a typical combustion effluent oxygen concentration), the time for oxidation of a given fraction of the initial NO can be plotted against the initial NO. Such a plot is shown in Figure 1, with

$$\frac{P_{\mathrm{NO}}}{(P_{\mathrm{NO}})_{\mathrm{init}}}$$

as a parameter. It is interesting to note that the time required for 97.5% conversion of 400 ppm NO (typical flue gas concentration) is 28.5 hours. This compares favorably to the recommended overnight (24 hr) standing time of ASTM (1970).

Times for Absorption of NO_2 or N_2O_3. Mechanisms for the absorption of nitrogen oxides in aqueous solutions are complex. Wendel and Pigford (1958), writing on the kinetics of nitrogen tetroxide absorption in water, state: "Despite the large quantities of nitric acid made by the absorption of nitrogen oxides in water, the kinetics and reactions involved are not yet fully explained . . . " A simple reason for the confusion that still exists in the analysis of the absorption is the large number of possible reactions that can occur in the liquid absorbent and the complex interaction between these reactions and the transport processes.

The absorption of equilibrium mixtures of NO_2 and N_2O_4 in N_2 (or air) into aqueous solutions has been extensively studied usually in wetted-wall columns. The results of Bolshakoff (1934) and Chambers and Sherwood (1937) obtained in long wetted-wall columns indicated that the absorption of nitrogen dioxide into both aqueous and sodium hydroxide solutions was gas film–controlled.

However, it now appears that the absorption rate may be controlled by chemical reactions occurring in the liquid phase and/or possibly the gas phase. Denbigh and Prince (1937) and Wendel and Pigford (1958) using short wetted-wall columns reported that chemical reaction between nitrogen dioxide and water controlled the absorption rate. Similarly, both Eagleton et al. (1948), and Peters and Holman (1955) working with long wetted-wall columns, concluded that the absorption rates were chemically controlled.

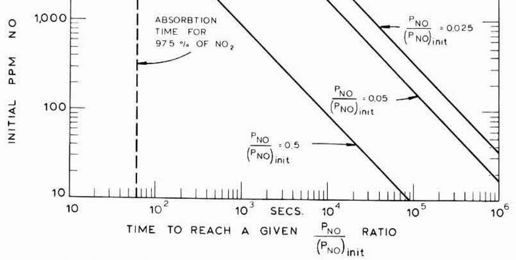

Figure 1. Plot of time to reach a given $P_{\mathrm{NO}}/P(_{\mathrm{NO}})_{\mathrm{init}}$ ratio vs. initial NO in sample

Nevertheless, there have also been reports of the possible existence of a homogeneous gas phase reaction between NO_2–N_2O_4 and water that occurs during absorption, and that may affect the absorption rates. The evidence in favor of a gas phase reaction results mainly from the absorption of NO_2–N_2O_4 in alkaline solutions in which nitric oxide and mist were observed in the off gases by Chambers and Sherwood (1937) and Eagleton et al. (1948). Since sodium nitrite does not decompose in alkaline solution, it is postulated that NO_2 must have reacted with water vapor in the gas phase, producing NO and acid mist. On the other hand, the absence of mist and NO in many similar experiments by Denbigh and Prince (1937) and Caudle and Denbigh (1953) has been cited as opposing evidence. The enhancement of the absorption rate of NO_2 was first reported in Eagleton et al. (1948) who showed that the presence of NO in the feed gas stream to a wetted-wall column resulted in absorption rates as much as 10 times faster than those reported for NO_2 absorption under similar conditions. Recently, Peters and Koval (1959) have suggested that even in the absence of nitric oxide in the feed, the absorption rates of NO_2 are affected by the NO produced during absorption. Subsequently, Koval and Peters (1960) concluded that a critical factor in analyzing absorption data, particularly from a short residence time contactor, is the nitrous acid concentration.

In calculating absorption times, it will be assumed that the rate of absorption of NO_2 is kinetically controlled with its rate of absorption being given by

$$-\frac{dn_{\mathrm{N_2O_4}}}{dt} = kC_{\mathrm{N_2O_4}} \qquad (10)$$

This mechanism, although by no means completely proved, appears to be fairly generally accepted particularly in situations where HNO_2 concentrations are low. It would be expected that such conditions would prevail since the nitrous acid would be rapidly removed by reaction in the absorbing media to produce HNO_3 in the PDS method.

Admittedly, as discussed above, there is evidence that in the presence of NO, the absorption rate of NO_2 is enhanced. However, owing to the sparse data available, quantitative estimation of this enhancement is not possible and so absorption rates will be calculated using the above equation with the realization that the answer may be conservative.

The data from Wendel and Pigford (1958) and Denbigh and Prince (1937) can be approximated by the following equation for 25°C:

$$N_A = 50 \times 10^{-6} P_{\mathrm{N_2O_4}} \qquad (11)$$

where N_A = flux of absorbing species in g-mol N_2O_4/cm^2 sec, and $P_{\mathrm{N_2O_4}}$ = bulk partial pressure N_2O_4, atm.

If it is assumed that an NO_2–N_2O_4–inert gas mixture is contained in a well-mixed volume of V liters, at 1 atm pressure and 25°C, a material balance on the N_2O_4 in the gas volume gives:

$$\frac{dn_{\mathrm{N_2O_4}}}{dt} = -50 \times 10^{-6} A P_{\mathrm{N_2O_4}} \qquad (12)$$

where $n_{\mathrm{N_2O_4}}$ = moles N_2O_4, and A = area for absorption, cm^2

$$\therefore \ \frac{V}{RT}\frac{dP_{\mathrm{N_2O_4}}}{dt} = -50 \times 10^{-6} A P_{\mathrm{N_2O_4}} \qquad (13)$$

Equation 13 is readily integrated to give:

$$\ln \frac{(P_{\mathrm{N_2O_4}})_{\mathrm{init}}}{(P_{\mathrm{N_2O_4}})_{\mathrm{final}}} = 50 \times 10^{-6} RT \frac{A}{V} t \qquad (14)$$

Since it can be assumed that NO_2 and N_2O_4 are in equilibrium, the following relationship holds:

$$K = \frac{P_{N_2O_4}}{(P_{NO_2})^2} \tag{15}$$

Equation 15 can therefore be substituted into Equation 14 to give:

$$2 \ln \frac{(P_{NO_2})_{init}}{(P_{NO_2})_{final}} = 50 \times 10^{-6} RT \frac{A}{V} t \tag{16}$$

For a typical analytical absorption system, we may take: $V = 1$ liter and $A = 100$ cm^2. The time then to reduce the NO_2 ppm to 2.5% of its initial value is given by:

$$t = \frac{2 \ln 40}{50 \times 10^{-6} \times 0.082 \times 298 \times 100} = 60 \text{ sec}$$

It must be emphasized that it has been assumed in the material balance, Equation 12, that the gas phase is well mixed—i.e., that no N_2O_4 or NO_2 concentration gradients exist. In actual practice, this will not be the case unless stirrers are placed in the gas space. Furthermore, it is also assumed that the liquid is well mixed and of such a volume that the acid concentrations are negligible. Once again, this is probably not quite correct.

Finally, it should be pointed out that the absorption of the nitrogen oxides is followed immediately by oxidation of the nitrous acid produced to nitric acid for the PDS method. The kinetics of this reaction are not well documented but the oxidation is considered to be rapid.

Time for Chemical Determination of the Nitrate Concentration: On completion of the absorption, the PDS procedure calls for determination of the nitrate ion concentration in the solution by nitration of phenol disulfonic acid and subsequent colorimetric measurements. This is done by making the solution basic and evaporating to dryness. The overall determination takes about 4–6 hr to complete with the major portion of this time being the evaporation step.

Driscoll et al. (1972) have shown that the nitrate electrode can be used in place of PDS to determine the nitrate concentration. The readout is rapid (minutes) and this eliminates the tedious and time-consuming evaporation step. Good agreement was obtained between NO_x values determined by both PDS and the nitrate electrode.

Summary. The obvious conclusion which can be drawn from the times calculated in the previous section is that the production of an absorbable species controls the rate at which nitrogen oxides can be absorbed.

Experimental Verification of Theory

Methods and Procedures. Mixtures of nitric oxide in room air or tank air containing 4% oxygen in nitrogen were prepared using flowmeters. The nitric oxide flowmeter was calibrated with a soap film buret. The flowmeter calibration for air was that supplied by the manufacturer. The nitric oxide mixtures in room air or in tank air were passed into a 5-liter mixing vessel. Samples were collected downstream of the mixing vessel in 2-liter evacuated flasks containing 25 ml of either 0.005*N* sodium hydroxide or $3 \times 10^{-3}N$ H_2SO_4–0.03% H_2O_2 absorbing solution. The samples were shaken periodically in an effort to provide good gas-liquid contact during the appropriate standing time. Following the absorption period, the solution was poured out, the flasks were quantitatively rinsed, and the nitrate concentration in the solutions was determined. Measurements of the nitrate concentration in the absorbing solution were made with an Orion Research nitrate ion selective electrode with a fiber tip saturated calomel as a reference. The potential was read out on an Orion Research Model 701 digital pH meter. The nitrate electrode procedure is described in detail by Driscoll et al. (1972). The stoichiometric factor used for the caustic absorption calculations was 0.5 since the electrode does not respond to nitrite. In acidic solution, all the nitrite is immediately oxidized, and the corresponding stoichiometric factor was 1.0.

Results. Concentrations of nitrate were determined for a series of mixtures of nitric oxide in air where the oxygen level, contact time with the absorbing solution, and concentration of nitric oxide were varied. The results are reported as NO_2 measured in Table I. Previously, it was shown that the rate-determining step in the oxidation-absorption process was the gas phase oxidation of nitric oxide to soluble species. The nitrogen dioxide concentrations were calculated by Equation 8. Computed nitrogen dioxide values are compared with the measured NO_2 concentrations in Table I. The agreement is excellent. The correlation coefficient for the measured vs. calculated results is 0.99. Regression analysis of the data gives NO_2 (calcd) $= -2.46 + (1.07)(NO_2$ meas). Based on the agreement between calculated results and measured NO_2 in Table I, it appears that the gas phase oxidation is, as predicted, the rate-determining step in the oxidation-absorption process for determining nitrogen oxides.

Methods for Reducing Analysis Time of Nitrogen Oxides

It has been shown earlier that the gas phase oxidation of nitric oxide is the longest step in the process for determining NO_x. An additional time-consuming step involves analysis of the nitrate content of the aqueous solution after absorption. Methods for reducing the required times for both these processes are considered in this section.

A simple and obvious method of reducing the oxidation time is to increase the oxygen partial pressure and, if necessary, the total pressure to greater than 1 atm. To illustrate this concept, consider the mixing in a vessel of a flue gas composed of *Y* ppm nitric oxide and *Z* ppm oxygen with *X* atm of pure oxygen, such that the final pressure in the vessel is always kept at *A* atm. The partial pressure of the components after mixing will be:

$$(P_{O_2})_{init,anal} = X + (A - X) \frac{Z}{10^6}$$

Table I. Comparison of Measured and Calculated NO_x Concentrations

Init NO concn, ppm	O_2, %	Contact time, min	NO_2 meas,[a] ppm	NO_2 calcd,[b] ppm	Remarks
217	6.5	15	118	50	NaOH absorption
217	20.0	30	140	140	NaOH absorption
217	20.0	60	148	170	NaOH absorption
447	9.0	30	293	287	H_2O_2 absorption
533	6.5	60	282	396	NaOH absorption
533	20.0	60	448	479	NaOH absorption
533	20.0	60	468	479	NaOH absorption
1009	6.5	70	752	873	NaOH absorption
1009	20.0	90	932	969	NaOH absorption
1174	9.0	60	1028	1066	H_2O_2 absorption

[a] Nitrate analysis by nitrate electrode.

[b] Calcd from:

$$\frac{1}{(P_{NO})} - \frac{1}{(P_{NO})_{init}} = k(P_{O_2})_{init} t$$

$$(P_{\mathrm{NO}})_{\mathrm{init,anal}} = (A - X)\frac{Y}{10^6}$$

Substituting into Equation 8 gives:

$$\frac{\dfrac{(P_{\mathrm{NO}})_{\mathrm{init,anal}}}{(P_{\mathrm{NO}})_{\mathrm{anal}}} - 1}{kt\left[X + (A - X)\dfrac{Z}{10^6}\right]} = (A - X)\frac{Y}{10^6} \qquad (17)$$

Equation 17 indicates that the time to reach a given fractional conversion in the analytical sample (after dilution) passes through a minimum as X is varied. This minimum is the result of two opposing effects—the increase in rate caused by increased oxygen partial pressure and the decrease in rate resulting from a simultaneous reduction in NO concentration (since the final pressure A is constant). It is easily demonstrated that the minimum time results when the *total* oxygen partial pressure $[(P_{\mathrm{O_2}})_{\mathrm{init,anal}}]$ is 0.5 A atm. This result was pointed out by Fine (1971). Thus, to attain the maximum reduction in oxidation times, a sample containing 5% O_2 should be diluted with 0.475 atm of O_2 for a final pressure of 1 atm. Using such a dilution and Equation 17, the time to reach a given fractional conversion of the NO in the mixture can be calculated for different initial NO concentrations—i.e., Y. This is shown in Figure 2. Comparison of times from Figures 1 and 2 clearly indicate that the oxygen dilution will result in about a fivefold reduction in oxidation times. Thus, this technique provides a simple but effective means for reducing the time required for analysis.

However, even at 100 ppm NO, the time required for 95% conversion to NO_2 is still 9 hr. Further reduction in the oxidation time can be achieved by increasing the pressure to above 1 atm. Equation 18 obtained by the substitution of $(P_{\mathrm{O_2}})_{\mathrm{init,anal}} = 0.5\,A$ atm in Equation 17 shows this effect:

$$\frac{t_{A\ \mathrm{atm}}}{t_{1\ \mathrm{atm}}} = \frac{1}{A^2} \qquad (18)$$

Thus, operation at 10 atm will result in a further hundredfold reduction in the oxidation time.

This principle has been used by Dupont in their Model 460 NO_x analyzer. The nitric oxide is converted to NO_2 by oxygen at high pressures. The oxidation time here is about 5 min.

Other oxidants such as ozone or dichromate paper have been used for rapid oxidation of nitric oxide at low concentrations by DiMartini (1970) and Singh et al. (1968). The reaction of nitric oxide with ozone is about 10^5 times as fast as oxidation with molecular oxygen. Thus, the NO is oxidized within seconds. One major problem is that oxidation to nitrogen pentoxide cannot be prevented. When the gaseous species are absorbed into an aqueous medium, the N_2O_5 as well as NO_2 will be absorbed producing nitrate. The ozone technique should provide a more rapid method for reducing the absorption time.

The second step which requires reduction in time is the determination of nitrate in aqueous solutions. Earlier in this paper, results are described with the nitrate electrode as a rapid readout for nitrate. DiMartini (1970) used the nitrate electrode coupled with ozone oxidation of nitric oxide to achieve continuous and rapid readout of nitric oxide concentrations at low levels. Coulehan and Lang (1971) have modified the phenol disulfonic acid procedure in an effort to reduce the analysis time. Their procedure involves mimimizing the volume of the absorbing solution and performing the nitration of PDS in 50% H_2SO_4 instead of in fuming H_2SO_4. They obtain excellent agreement between their modified procedure and the original PDS method. The analysis time is, therefore, reduced substantially.

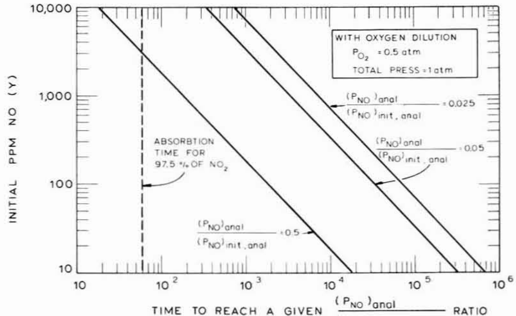

Figure 2. Plot of time to reach a given $(P_{\mathrm{NO}})_{\mathrm{anal}}/P(_{\mathrm{NO}})_{\mathrm{init,\ anal}}$ ratio vs. initial NO in sample

In summary, it has been shown that time required for NO_x analysis can be reduced substantially and it should be possible to complete the absorption and analysis steps within a few hours instead of the 30 hr presently required for the PDS method.

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Effect of Chemical Structure on Microbial Degradation of Methyl-Substituted Aliphatic Acids

Max W. Hammond and Martin Alexander[1]

Laboratory of Soil Microbiology, Department of Agronomy, Cornell University, Ithaca, N.Y. 14850

■ Soil microorganisms rapidly degraded unsubstituted mono- and dicarboxylic acids, but all dimethyl-substituted compounds tested were relatively resistant to microbial attack. An *Arthrobacter* formed a single product in large amounts from 2,2-dimethylglutaric acid. Gas chromatography–mass spectrometry suggested that the metabolite was 2,2-dimethyl-3-oxopropanoic or 2,2-dimethyl-3-oxobutanoic acid. Only a single product was detected in cultures of a gram-negative bacterium grown on 4,4-dimethylvaleric acid, and this was identified as trimethylacetic acid. It is suggested that dimethyl substitution renders fatty acids refractory to microbial degradation by posing a hindrance to β-oxidation.

A variety of pesticides, detergents, and industrial organic wastes persist for reasonably long periods in environments supporting heterogeneous and metabolically active microbial communities. This suggests that the chemicals may be intrinsically resistant to microbial attack. In some instances, the resistance appears to be associated with the presence in the molecule of substituents that prevent microorganisms from attacking the particular compound (Alexander, 1965; Alexander and Lustigman, 1966; Focht and Alexander, 1970).

The addition of a single methyl substituent to certain types of aliphatic compounds frequently makes them more resistant to microbial degradation than the corresponding unsubstituted molecules (Thijsse and Zwilling-deVries, 1959; Alexander, 1965; Van der Linden and Thijsse, 1965). Nevertheless, the degradation of aliphatic compounds having a single methyl substituent is carried out by microorganisms (Van der Linden and Thijsse, 1965) and mammalian tissues (Kennedy, 1957; Stokke, 1968). On the other hand, dimethyl-substituted aliphatic compounds are notably resistant to degradation (Mohanrao and McKinney, 1962; Alexander and Dias, 1971; Stokke, 1968).

The present study was designed to investigate the susceptibility of a variety of substituted aliphatic acids to degradation by soil microorganisms and to provide a basis for understanding why these molecules are refractory to biological degradation.

Materials and Methods

Survey of Degradability. The rate of degradation was determined by measuring dissolved oxygen (DO) utilization in a solution containing 1.6 grams K_2HPO_4, 0.4 gram KH_2PO_4, 0.2 gram $MgSO_4 \cdot 7H_2O$, 0.025 gram $CaCl_2 \cdot 2H_2O$, 2.3 mg $FeCl_3 \cdot 6H_2O$, 0.82 gram $(NH_4)_2SO_4$, and 1.0 liter air-saturated distilled water. Each organic acid was neutralized and added to the solution in an amount sufficient to provide for a DO utilization of 8.3 mg/l. Standard 300-ml bottles used for determination of biochemical oxygen demand (BOD) in water analysis (American Public Health Association, 1965) were filled with the solution, each bottle also receiving 30 mg of soil to provide the microbial inoculum.

For calibration of the oxygen electrode, the inoculated salts solution containing 0.1% KCN was employed. For measurement of DO utilization resulting from oxidation of soil organic matter and nitrification, the inoculated salts solution receiving no organic acid was used. After the bottles were equilibrated at 25°C, the initial DO level was determined by the Alsterberg modification of the Winkler method (American Public Health Association, 1965). The initial nitrite and nitrate concentrations were estimated by the procedures of Montgomery and Dymock (1961, 1962) after removal of soil particles by centrifugation. The BOD bottles were covered to prevent algal development, and they were incubated at 25°C with a water seal maintained constantly at their tops.

An oxygen monitor with a Clark-type polarographic electrode (Yellow Springs Instrument Co., Yellow Springs, Ohio) was used for DO determination. The oxygen probe was fitted with a rubber stopper so it could be held in the neck of the bottles. Three bottles were tested at regular intervals for DO utilization in solutions both with and without the test compounds. The values reported have been corrected for oxygen utilization resulting from nitrification and the oxidation of organic matter in the soil inoculum.

Isolation of Microorganisms. The solution used for enrichment contained 12.5 grams K_2HPO_4, 3.89 grams KH_2PO_4, 0.20 gram $MgSO_4 \cdot 7H_2O$, 0.10 gram $CaCl_2 \cdot 2H_2O$, 0.01 gram $FeCl_3 \cdot 6H_2O$, 0.82 gram $(NH_4)_2SO_4$, 1.0 gram organic acid, and 1.0 liter distilled water. The 2,2-dimethylglutaric acid was obtained from Aldrich Chemical Co. (Cedar Knolls, N.J.), and 4,4-dimethylvaleric acid was furnished by G. M. Whitesides. The solutions were adjusted to pH 7.2, and the media were sterilized by filtration. To prepare solid media, the agar was autoclaved separately and mixed with the liquid medium. The media (100 ml) were inoculated with 1.0 gram of soil, and the enrichments were incubated at 30°C in 500-ml Erlenmeyer flasks on a rotary shaker operating at 200 rpm. After three serial subcultures, plates of the appropriate acid-containing medium were streaked with the enrichment, and the isolates were purified by repeated restreaking. The cultures were characterized by standard techniques (Society of American Bacteriologists, 1957).

Metabolic Studies. The isolates were grown at 30°C on a rotary shaker in 900 ml of the same medium used for enrichments, except that it was supplemented with 50 ppm yeast extract. After three days of growth, the supernatant was separated from the cells by centrifugation. The supernatant was diluted to 1800 ml with distilled water, and concentrated HCl was added to adjust the pH to 2.0. Approximately 20 grams of NaCl was then added, and the solution was extracted with anhydrous ethyl ether for 3 hr. The ether extracts were dried using anhydrous Na_2SO_4 and allowed to evaporate at room temperature to approximately 20 ml. Uninoculated medium was extracted in the same manner.

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[1] To whom correspondence should be addressed.

The extracts and authentic compounds were silylated and chromatographed using a gas-liquid chromatograph (Varian Aerograph, Walnut Creek, Calif.) fitted with a flame ionization detector. For the silylation, 1.0 ml of extract was mixed with 1.0 ml of chloroform, and to this was added 0.2 ml of trimethylchlorosilane and 0.1 ml of hexamethyldisilazane. The mixture was agitated vigorously for 30 sec and then allowed to stand for 5 min before samples were injected into a 5 ft × $^1/_8$ in. stainless steel column packed with 100/120 mesh Chromosorb W as the solid support and 10% DC 200 as the stationary phase. The temperatures of the column, injector, and detector were 160°, 210°, and 190°C for cultures grown on 2,2-dimethylglutaric acid and 110°, 210°, and 195°C for bacteria cultured on 4,4-dimethylvaleric acid. The flow rate of the carrier gas, N_2, was 42 ml/min. The solvent and solvent plus silylating agents were also examined by gas chromatography.

Esterification of extracts and authentic organic acids was accomplished using a modification of the diazomethane procedure described by Schlenk and Gellerman (1960). Five milliliters of extract was evaporated to 1.0 ml under a stream of dry N_2. The sample was then treated with 0.1 ml absolute methanol, and ether-saturated N_2 was allowed to pass through the sample after it had first gone through a tube containing 3 ml of 2-(2-ethoxy-ethoxy)ethanol, 2 ml of 60% KOH, and 1.5 ml of a saturated solution of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in ether. When the bubbling in this tube ceased, another 1.5 ml of the *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide solution was added, and this process was repeated until about 1 min after the sample turned yellow. The tube containing the sample was then removed, and its contents were concentrated by evaporation under a stream of dry N_2. Methyl esters of the authentic organic acids were prepared by this procedure using 5 mg of each compound in 1.0 ml of ethyl ether.

Gas chromatography of methyl esters was accomplished by injecting the compounds into a 5 ft × $^1/_8$ in. stainless steel column having 100/120 mesh Aeropak 30 (Varian Aerograph) as the solid support and 3% SE-30 (Varian Aerograph) as the stationary phase. The temperatures of the column, injector, and detector were 90°, 160°, and 145°C for products in cultures grown on 4,4-dimethylvaleric acid and also for authentic compounds and uninoculated media, and the temperatures in studies of 2,2-dimethylglutaric acid metabolism were 100°, 170°, and 150°C, respectively. The flow rates of the carrier gas, N_2, were 12 and 32 ml/min in studies of 4,4-dimethylvaleric acid and 2,2-dimethylglutaric acid degradation, respectively. Samples of ethyl ether and ethyl ether treated with methanol and diazomethane in the esterification process were also examined by gas chromatography.

Mass spectrometric analysis was accomplished using a Perkin-Elmer (Wilton, Conn.) mass spectrometer, Model 270, with a gas-liquid chromatograph injection system. The gas chromatograph contained a 6 ft × $^1/_8$ in. stainless steel column packed with Chromosorb W (100/120 mesh) as the solid support and SE-30 (1-52) as the stationary phase. The carrier gas was helium, the ionization voltage was 70 eV, and the column temperature was 80°C.

Results

The extent and rate of degradation of the substituted and unsubstituted aliphatic acids differed appreciably (Table I). The nonmethylated mono- and dicarboxylic acids were all readily attacked microbiologically, as shown by the disappearance of oxygen from the reaction mixtures. The effect of a single methyl group on the rate of valeric acid degradation depended on its position; the 2- and 4-methylvaleric acids were destroyed almost as readily as the unsubstituted acid, but the attack on 3-methylvaleric acid was somewhat delayed. On the other hand, the dimethyl-substituted acids were invariably resistant, regardless of whether the methyl groups were on the α-, β-, or γ-carbon atoms. Only by the 20th day was there appreciable decomposition of any of the compounds containing quaternary carbons, and even then only two seem to have been largely degraded. Little nitrification occurred in the test period.

Table I. Oxygen Utilization by Soil Microorganisms Metabolizing Aliphatic Acids

Organic acid	Substrate concn, mg/l.	Days			
		2	5	10	20
		Oxygen uptake, mg/l.			
Trimethylacetic	4.1	0.1	0.0	1.2	7.2
Valeric	4.1	6.4	7.0	7.5	...
2-Methylvaleric	3.5	3.6	7.3	7.5	...
2,2-Dimethylvaleric	3.3	0.0	0.3	0.1	...
3-Methylvaleric	3.5	0.0	3.9	6.6	...
4-Methylvaleric	3.5	3.4	5.4	7.3	...
4,4-Dimethylvaleric	3.3	0.2	0.1	0.3	...
Hexanoic	3.5	6.2	7.4	7.4	...
Octanoic	2.9	3.1	3.7	5.2	7.2
2,2-Dimethyloctanoic	3.5	0.3	0.2	0.4	0.9
Malonic	13.5	4.2	4.9	7.0	7.2
Dimethylmalonic	6.6	0.1	0.0	0.3	0.7
Succinic acid	8.3	3.7	5.2	7.1	7.1
2,2-Dimethylsuccinic	5.9	0.0	0.0	0.0	0.5
Glutaric	6.6	0.3	4.6	6.0	7.1
2,2-Dimethylglutaric	4.9	0.3	0.3	0.6	2.7
3,3-Dimethylglutaric	4.9	0.2	0.1	4.2	7.2

The data thus show that monomethyl substitution delays somewhat and dimethyl substitution appreciably retards microbial destruction of aliphatic acids, presumably by slowing or preventing β-oxidation. Yet, since some of these compounds were attacked, as indicated by changes in the DO concentration, individual populations must have the capacity to overcome this hindrance to β-oxidation or possess a different mechanism for fatty acid degradation. To establish how compounds which are refractory to attack are indeed metabolized, isolates able to grow on media containing 2,2-dimethylglutaric acid or 4,4-dimethylvaleric acid as carbon sources were obtained. These isolates all required growth factors, but this need could be satisfied by adding yeast extract to the media. By comparing the extent of growth in solutions containing inorganic salts and 50 ppm yeast extract with and without the appropriate organic acid at a concentration of 0.1%, it became clear that the organisms were proliferating at the expense of the organic acids rather than using the yeast extract as a significant carbon source.

The microorganism isolated on 2,2-dimethylglutaric acid appears to be a member of the genus *Arthrobacter*. It exists as chains of rods which fragment into large, almost coccoidal rods in old cultures. The smaller cells are gram-negative while the larger cells are gram-positive. The bacteria do not form endospores, and they are not acid fast. The microorganism utilizing 4,4-dimethylvaleric acid, also a bacterium, was a short, nonmotile, gram-negative rod.

Products in the culture fluid were examined after a three-day incubation period. The chloroform used contained no contaminating chemicals which might yield spurious results.

Table II. Gas-Liquid Chromatography of Derivatives of Organic Acids and Compounds in Uninoculated Media and in Three-Day Cultures

	Retention time, sec		
Substrate	Authentic acid	Compounds in uninoculated medium	Compounds in bacterial culture
	Trimethylsilyl derivatives		
2,2-Dimethylglutaric	387	385	65, 70
4,4-Dimethylvaleric	308	305	75
	Methyl esters		
2,2-Dimethylglutaric	538	535	87[a]
4,4-Dimethylvaleric	285	290	88

[a] Also compounds with retention times of 97, 123, 155, 225, 502, and 535 sec.

However, analysis of the combination of chloroform and silylating reagents revealed the presence of substances which gave peaks in the gas chromatograms, but these peaks were neglected when they appeared in the chromatograms of the media and culture extracts.

The retention times of peaks in gas chromatograms of the trimethylsilyl derivatives of the authentic organic acids and of extracts of the uninoculated medium and the three-day cultures are shown in Table II. The retention times of metabolites in the two cultures are not directly comparable because of the differences in temperatures used for chromatography. The data show that at least two products were excreted in media containing the two test substrates.

Methyl esters of the authentic organic acids and of components in the uninoculated medium and supernatants of three-day cultures were prepared. The retention times of the various compounds are shown in Table II. Six products were detected in cultures grown on 2,2-dimethylglutaric acid, but only the one with the shortest retention time was formed in appreciable amounts. A single metabolite was noted in cultures of the bacteria grown on 4,4-dimethylvaleric acid, and this compound was chromatographically identical with the methyl ester of trimethylacetic acid, both having retention times of 88 sec. No peaks were observed in chromatograms of either the ether used or the ether treated in the esterification procedures.

In analyzing for the product formed from 4,4-dimethylvaleric acid by combined gas chromatography–mass spectrometry, it was again found that the methyl ester of the product obtained from three-day cultures had the same retention time as authentic methyl trimethylacetate, about 97 sec under the conditions employed. Furthermore, the mass spectra of both the authentic compound and the bacterial metabolite showed the same parent ion at *m/e* 116, and the two spectra were essentially identical (Figure 1). Hence, the bacterium apparently has indeed converted the substituted valeric acid to trimethylacetic acid, a process involving the loss of two carbon atoms.

Only the compound corresponding to the first peak in extracts of the culture grown on 2,2-dimethylglutaric acid was analyzed by combined gas chromatography–mass spectrometry. The other compounds were present in only trace amounts. The mass spectrum of the methyl ester of this metabolite is shown in Figure 2. Prominent are *m/e* values of 28, 29, 31, 43, 59, 85, and 102.

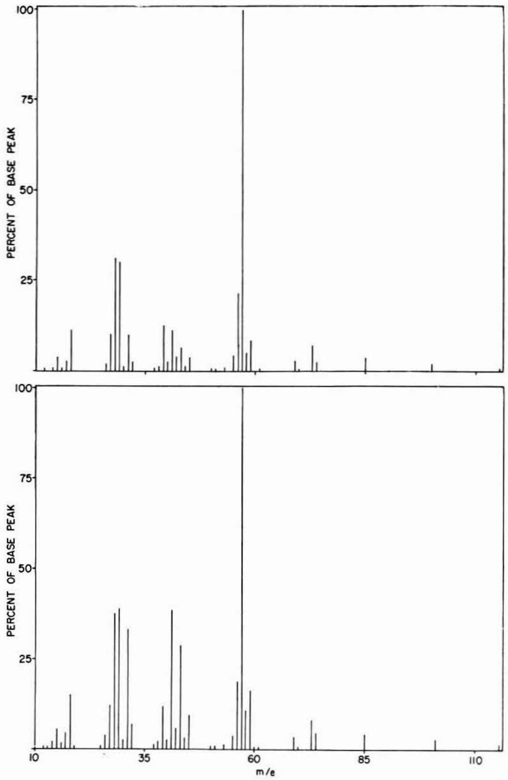

Figure 1. Mass spectra of the methyl esters of authentic trimethylacetic acid (top) and of the metabolite in cultures provided with 4,4-dimethylvaleric acid (bottom)

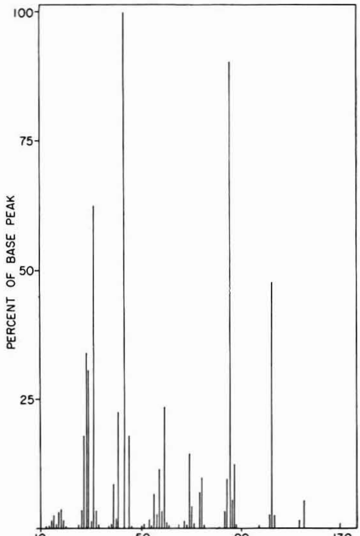

Figure 2. Mass spectrum of the methyl ester of the bacterial product in cultures metabolizing 2,2-dimethylglutaric acid

A highly likely structure for the ester is methyl-2,2-dimethyl-3-oxobutanoic acid. Although the parent ion for this proposed structure did not appear in the mass spectrum, the peaks observed are those to be expected when similar compounds are analyzed by mass spectrometry. The fragments may then represent $CH_3C(O)C(CH_3)_2$ (*m/e*, 85), $CH_3OC{=}O$ (*m/e*, 59), $CH_3C{=}O$ (*m/e*, 43), CH_3O (*m/e*, 31), and the parent ion minus $CH_2{=}C{=}O$ (*m/e*, 102), and the minor fragments at *m/e* 101, 113, and 129 may be the parent ion minus CH_3CO, CH_3O, and CH_3, respectively. The parent ion minus $CH_2{-}C{=}O$ is a characteristic fragment ion of methyl ketones, such as is the proposed structure. The actual metabolite excreted by the bacterium grown on 2,2-dimethylglutaric acid might then be either 2,2-dimethyl-3-oxopropanoic acid or 2,2-dimethyl-3-oxobutanoic acid since both form methyl-2,2-dimethyl-3-oxobutanoic acid when reacted with diazomethane.

Discussion

If the microbial attack on simple fatty acids proceeds by a β-oxidation sequence involving the sequential formation of the α,β-unsaturated acid, the β-hydroxy-, and the β-keto compound, and the β-keto acid is cleaved to yield acetic acid and a fatty acid with two carbon atoms less than the original substrate, then the normal functioning of the sequence requires two protons on both the α- and the β-carbons. Substituents on these two carbons would prevent β-oxidation, although the blockage could be overcome if the substituent is removed. Alternatively, the organism may be able to degrade an α-substituted compound if the acetic acid moiety cleaved from the molecule contains the substituent; since the β-carbon is converted to a carboxyl group, a hindrance on this carbon would have to be removed prior to its conversion to a carboxyl.

Such an hypothesis that resistance is associated with a hindrance to β-oxidation is consistent with the findings reported herein. The observation that 3-methylvaleric acid is more slowly degraded than 2-methylvaleric acid is in agreement with the finding that β-substitution of aliphatic acids prevents β-oxidation (Stokke, 1968), at least until the substituent is removed enzymatically. The hindrance unquestionably is more severe in dimethyl-substituted acids. Removal of both methyl groups would require more enzymes than cleavage of one, which likely would reduce the number of organisms able to degrade these molecules. The data clearly show how effectively such disubstitution retards the decomposition of mono- and dicarboxylic acids.

Nevertheless, the isolation of bacteria capable of utilizing 4,4-dimethylvaleric and 2,2-dimethylglutaric acids indicates that these compounds are biodegradable, to some extent at least. However, the reaction catalyzed by the active organisms provides further evidence in support of, rather than against, the hypothesis of an obstruction created by dimethyl substitution. The demonstration that 4,4-dimethylvaleric acid disappearance is accompanied by trimethylacetic acid accumulation suggests that β-oxidation readily removes the first two carbons from the carboxyl end, but then the organism is unable to degrade rapidly, if at all, the dimethylsubstituted product that is excreted.

Similarly, regardless of whether the product formed from 2,2-dimethylglutaric acid is 2,2-dimethyl-3-oxopropionic or 2,2-dimethyl-3-oxobutanoic acid, the data clearly show the marked obstruction imposed by the dimethyl substitution. The bacterium derives energy from the decomposition of the molecules, but it does so by a metabolic sequence that leaves a product still containing the two methyl groups. The sequence may involve an oxidation of the dimethylglutaric acid and a subsequent decarboxylation to give dimethylsuccinic acid, which in turn is converted to 2,2-dimethyl-3-oxopropanoic acid; such aldehydes are products of β-oxidation by higher plants (Stumpf, 1969). Alternatively, the reaction might involve an incomplete β-oxidation starting at the terminal end to yield a carbonyl compound which, if the ω-carboxyl is removed, would give rise to 2,2-dimethyl-3-oxobutanoic acid; microorganisms are known to form methyl ketones by pathways such as this (Gehrig and Knight, 1963; Johnson et al., 1933).

These refractory products containing a quaternary carbon may be very slowly degraded microbiologically, as shown by the changes in DO when trimethylacetic acid was incubated with a soil inoculum. Goodhue and Schaeffer (1969) showed, too, that pentaerythritol, a compound containing a quaternary carbon, was oxidized by a *Flavobacterium*. In addition, we have isolated a strain of *Arthrobacter* which, when provided with traces of yeast extract, will grow on and degrade trimethylacetic acid. How these bacteria metabolize these recalcitrant molecules awaits further study.

Acknowledgment

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Relationship Between Atmospheric Carbon Dioxide Amount and Properties of the Sea

Gilbert N. Plass

Department of Physics, Texas A&M University, College Station, Tex. 77843

■ The variation of the atmospheric CO_2 amount with the properties of the sea is obtained from numerical solution of the equilibrium equations. Solutions are given when: there is insufficient time for equilibrium with either $CaCO_3$ deposits or the clay sediments; there is sufficient time for equilibrium with the $CaCO_3$ deposits, but not with the clay sediments; and the time is sufficiently long for equilibrium with both $CaCO_3$ deposits and the clay sediments. The variation of the partial pressure of the atmospheric CO_2 is shown as a function of the total CO_2 in the sea and atmosphere, the mean temperature of the sea, and the volume of the sea. The implications for theories of climatic change are discussed.

There is a continual interchange between CO_2 in the atmosphere and the oceans. If the amount of CO_2 is changed in one of these systems, it must eventually change in the other. The time constant for equilibration depends on many factors such as the rate of oceanic circulation, the time required to come to equilibrium with $CaCO_3$ deposits, the rate at which positive ions interact with various forms of clay, the rate at which the average temperature of the seas change, and even on the influence of the atmospheric CO_2 on the climate and rate of formation of glaciers. Nevertheless, equilibrium calculations of the amount of CO_2 in the atmosphere and oceans probably have validity over certain time scales. Calculations which neglect the $CaCO_3$ equilibria are valid for the shortest time period, perhaps a few hundred years. Over longer time periods the $CaCO_3$ equilibrium must also be taken into account; under some conditions the equilibrium with various clays must be considered as well.

Some calculations of the variation of the atmospheric CO_2 amount with the total CO_2 in the atmosphere–ocean system were made by Plass (1956b). More recently Bolin and Eriksson (1959) and Eriksson (1963) have made more extensive calculations. However, because of the nonlinear nature of the equations, all of their results are based on solutions valid only for first-order deviations of the quantities from their original values. Solutions are often desired for the present problem when the first-order deviations are not small; in this event their results are not valid. The purpose of this paper is to present solutions which are valid over a wide range of the parameters and thus can be used to study long-term climatic changes on the earth. Average values are used for the oceanic parameters and no attempt is made to take account of the important variations of these quantities with depth and latitude. A model that allows for these variations would be much more complex and probably is not necessary for the present purpose of studying the large-scale variations which occur over long time periods.

Calculation of Carbon Dioxide Equilibrium

The equations which govern the CO_2 equilibrium are written here in the form used by Buch (1951) and Harvey (1955). The pertinent equations are:

$$\alpha P_{CO_2} = [CO_2] \tag{1}$$

$$[HCO_3] = K_1[CO_2]/[H] \tag{2}$$

$$[CO_3] = K_2[HCO_3]/[H] \tag{3}$$

$$\Sigma[CO_2] = [CO_2] + [HCO_3] + [CO_3] \tag{4}$$

$$[A] = [HCO_3] + 2\,[CO_3] \tag{5}$$

$$S = 0.674\, b\, \Sigma[CO_2] + 82.3\, P_{CO_2} \tag{6}$$

where the following symbols have been used: P_{CO_2}, partial pressure of CO_2 in the atmosphere; α, absorption coefficient for CO_2 in seawater, in mM l.$^{-1}$ atm^{-1}; $[CO_2]$, sum of concn of CO_2 and H_2CO_3 in seawater, in mM l.$^{-1}$; $[HCO_3]$, concn of bicarbonate ion in seawater, in mM l.$^{-1}$; $[CO_3]$, concn of carbonate ion in seawater, in mM l.$^{-1}$; [H], hydrogen ion concn in seawater, in M l.$^{-1}$; k_1, first apparent dissociation coefficient of H_2CO_3 in seawater; k_2, second apparent dissociation coefficient of H_2CO_3 in seawater; $\Sigma[CO_2]$, total CO_2 in seawater, in mM l.$^{-1}$; $[A]$, carbonate alkalinity in seawater, in M equiv l.$^{-1}$; S, total CO_2 amount in ocean–atmosphere system in units of 10^{20} grams; $b = V/V_o$ where V is the volume of the oceans and V_o is their present volume.

The first three equations determine the chemical equilibriums, while the next two equations are the definitions of the total CO_2 in seawater and the carbonate alkalinity. These equations apply when there is insufficient time for the system to come to equilibrium with the $CaCO_3$ in the oceans. The total CO_2 amount in the ocean–atmosphere system can be obtained from the total CO_2 in the seawater plus the amount in the atmosphere from Equation 6, which agrees with the data given by Eriksson (1963).

Over longer time intervals the $CaCO_3$ equilibrium must also be taken into account; the appropriate set of equations is Equations 1–4 plus the following:

$$[A] = [HCO_3] + 2\,[CO_3] = [A_o] + 2\,\Delta[Ca] \tag{7}$$

$$S = 0.674\, b\Sigma[CO_2] + 82.3\, P_{CO_2} = S_o + 0.674\, b\Delta[Ca] \tag{8}$$

$$L = [Ca][CO_3] \tag{9}$$

where the following symbols have been used: $[A_o]$, carbonate alkalinity in seawater at the present time, in mM l.$^{-1}$; $\Delta[Ca] = [Ca] - [Ca]_o$, change in concn of calcium ion in seawater, in mM l.$^{-1}$, where $[Ca]_o$ is the concn at the present time; S, total CO_2 amount in ocean–atmosphere system in units of 10^{20} grams; S_o, total CO_2 amount in ocean–atmosphere system before $CaCO_3$ equilibrium in units of 10^{20} grams, as defined by Equation 8; L, solubility product of $CaCO_3$ in mM^2 l.$^{-2}$.

Over extremely long time periods MacIntyre (1970) has stated that the clay sediments on the sea floor control the hydrogen ion concentration by absorption of these ions while releasing sodium ions. In this case it may be assumed that [H] remains constant while $[A]$ varies. Equations 1–4 and 7–9 also describe this equilibrium.

To study large variations in the atmosphere–ocean system it is essential to have accurate solutions of these equations.

The set of Equations 1–6 can be reduced to a single quadratic equation for the quantity $[HCO_3]$:

$$\{(0.674\, b + 82.3\, \alpha^{-1})\, 2\, K_2 - 0.337\, bK_1\}\, [HCO_3]^2 + S_oK_1\, [HCO_3] + K_1[A](0.337\, b[A] - S_o) = 0 \quad (10)$$

Once $[HCO_3]$ is obtained from the solution of this equation, all of the other variables may be obtained from simple substitutions in the remaining equations. Thus the exact equilibrium values for the complete atmosphere–ocean system may be calculated when the time intervals are relatively short (perhaps a few hundred years).

For longer time intervals, $CaCO_3$ equilibrium must also be considered. There is no closed solution to the set of nonlinear equations (1–4 and 7–9). However, a computer code was written which used the half interval search method to obtain the solution of the equations accurate to eight significant figures. If equilibrium occurs with the clay sediments, the appropriate equations become linear and can be solved easily, if it is assumed that [H] is constant.

Calculated CO_2 Variation

The variation of the partial pressure of CO_2 with the total CO_2 in the sea and atmosphere is shown in Figure 1. The dashed curves apply when $CaCO_3$ reactions are neglected and represent the solutions of Equations 1–6. The solid curves apply when $CaCO_3$ equilibrium has been established and represent the exact solutions of Equations 1–4 and 7–9. Results are shown for five different average temperatures for the sea, 0°, 4°, 12°, 20°, and 28°C. The equilibrium constants in the equations for each of these temperatures were taken from the tables and data in Harvey (1955). It was assumed from Eriksson (1963) that the total CO_2 amount in the sea and atmosphere is 1.4175×10^{17} kg today and that $[A] = 0.00221$ with an average temperature of the sea at 4°C at the present time. The results shown here are insensitive to minor variations in the numerical values assumed for these quantities and for the equilibrium constants. The curves for $CaCO_3$ equilibrium are plotted with S_o (the total CO_2 amount before $CaCO_3$ equilibrium) as defined by Equation 8 as the abscissa. The connection between S and S_o is discussed later.

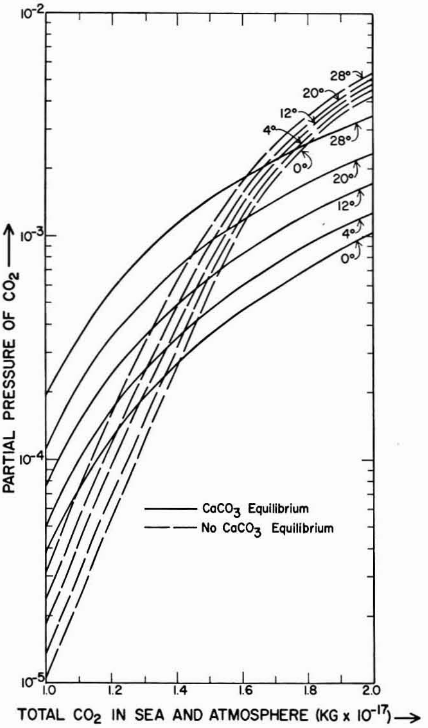

Figure 1. Partial pressure of atmospheric CO_2 as a function of the total CO_2 amount in the sea and atmosphere in units of kg $\times$ 10^{-17}

Curves are given for average sea temperatures of 0°, 4°, 12°, 20°, and 28°C and when there is insufficient time for $CaCO_3$ equilibrium and when there is $CaCO_3$ equilibrium. The total CO_2 amount for the case of $CaCO_3$ equilibrium refers to the amount present before additional CO_2 is deposited or dissolved from the $CaCO_3$ sediments. The present oceanic volume is assumed.

When there is insufficient time for $CaCO_3$ equilibrium the partial pressure of CO_2 varies rapidly with the total CO_2 amount in the sea and atmosphere from a value of 1.35×10^{-5} to 4.39×10^{-2} when $S = 1$ and 2, respectively, and the average temperature T of the sea is 4°C. The CO_2 partial pressure increases as the temperature increases as shown in Figure 1. The variation of the CO_2 partial pressure with S_o is more moderate when equilibrium is established with $CaCO_3$; the partial pressure is 5.12×10^{-5} and 1.295×10^{-3} when $S_o = 1$ and 2, respectively, and $T = 4$°C. It is interesting that the CO_2 partial pressure is more sensitive to the sea temperature when there is $CaCO_3$ equilibrium than when there is insufficient time for this equilibrium to be established.

The volume of the seas has changed appreciably during the geologic history of the earth as water has been removed and added by glaciation and other processes. The CO_2 partial pressure as a function of the total CO_2 in the sea and atmosphere is shown in Figure 2 for various values of b =

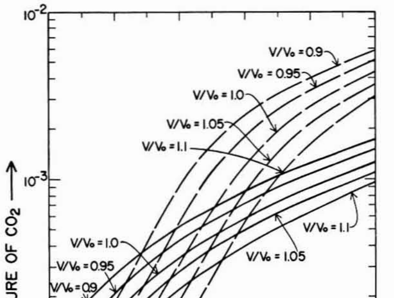

Figure 2. Partial pressure of atmospheric CO_2 as a function of the total CO_2 amount in the sea and atmosphere before $CaCO_3$ equilibrium in units of kg $\times$ 10^{-17}

Curves are given for various ratios of V/V_o where V is the volume of the sea, and V_o is the present volume. The average temperature of the seas is assumed to be 4°C.

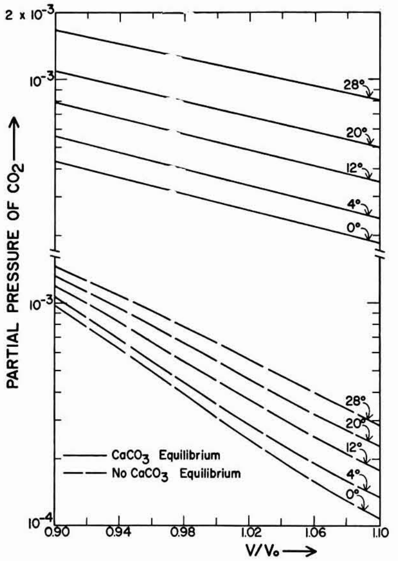

Figure 3. Partial pressure of atmospheric CO_2 as a function of the ratio V/V_o, where V is the volume of the sea and V_o is the present volume

The total CO_2 amount in the sea and atmosphere is assumed to be 1.4175 $\times$ 10^{17} kg. Curves are given for various average temperatures of the sea.

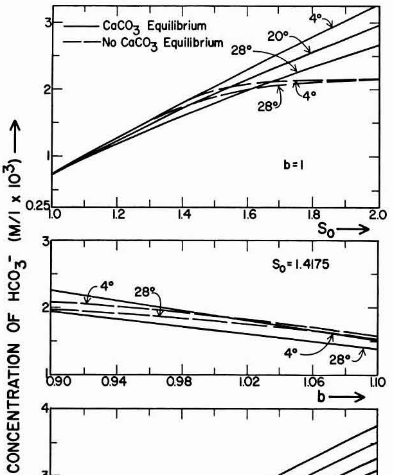

Figure 4. $[HCO_3]$ in M/l. $\times$ 10^3 for various values of S_o (total CO_2 amount in ocean–atmosphere system before $CaCO_3$ equilibrium in units of 10^{17} kg), b (ratio of volume of sea to present volume), T (average temperature of sea), and with and without $CaCO_3$ equilibrium

V/V_o. When b is less than unity, water has been withdrawn from the seas and extra CO_2 must enter the atmosphere.

The variation of the CO_2 partial pressure as a function of $b = V/V_o$ is shown in Figure 3. All of these curves are for $S = 1.4175$. The variations of the CO_2 partial pressure with b are larger when there is no $CaCO_3$ equilibrium; the variation with temperature is greater when there is $CaCO_3$ equilibrium.

The variation of some of the other components of the system is also shown in order to understand the CO_2 variations better. In Figure 4 $[HCO_3]$ is shown as a function of both S_o and b. When the $CaCO_3$ equilibrium is neglected, $[HCO_3]$ tends to approach a limiting value as the total CO_2 amount in the sea and atmosphere becomes large ($S_o > 1.8$). The variation of these quantities with both temperature and sea volume is shown in this figure.

Similarly the variation of $[CO_3]$ with temperature, sea volume, and total CO_2 amount is shown in Figure 5. The value of $[CO_3]$ tends to become quite small when $S > 1.8$ and there is no $CaCO_3$ equilibrium. When there is $CaCO_3$ equilibrium, the variations are relatively small compared to those when there is no $CaCO_3$ equilibrium.

The pH of the sea is shown in Figure 6 as a function of the temperature, sea volume, and total CO_2 amount. The variation of the pH with b and S_o is less when there is $CaCO_3$ equilibrium than without it; however, the variation with the sea temperature is greater when there is $CaCO_3$ equilibrium.

All of the results when there is $CaCO_3$ equilibrium have been plotted against S_o, the total CO_2 amount in the sea and atmosphere before additional carbonate ions are dissolved from the carbonate sediments or are precipitated. The total final amount of CO_2 in the sea and atmosphere after $CaCO_3$ equilibrium, S, is shown in Figure 7 for various values of b, T, and S_o.

Clay sediments on the sea floor are believed by MacIntyre (1970) to maintain the pH at nearly a constant value when

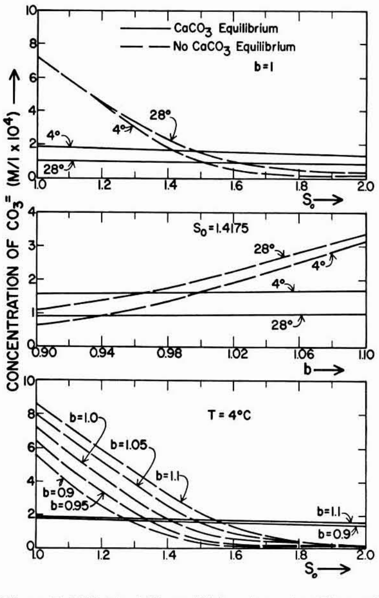

Figure 5. $[CO_3]$ in M/l. $\times$ 10^4 (see legend to Figure 4)

there has been an extremely long time period for equilibrium. Hydrogen ions are exchanged with sodium ions in these sediments. In general, the variations of the partial pressure of CO_2 with the relevant parameters are smaller when the pH is kept constant. As an example, Equations 1–4 and 7–9 were solved with this requirement. When $b = 1$ and $T = 4°C$, the partial pressure of CO_2 is 1.43×10^{-4} and 6.90×10^{-4} when $S_o = 1$ and 2, respectively. Although this variation is somewhat smaller than that shown in Figure 1 for $CaCO_3$ equilibrium, considerable changes are still possible. When $b = 1$ and $S_o = 1.4175$, the partial pressure of CO_2 is 3.52×10^{-4} and 4.91×10^{-4} when $T = 0°C$ and 28°C, respectively. When $T = 4°C$ and $S_o = 1.4175$, the partial pressure of CO_2 is 4.56×10^{-4} and 0.302×10^{-4} when $b = 0.9$ and 1.1, respectively.

Theories of Climatic Change

The atmospheric carbon dioxide variations can be estimated from the curves presented here as changes occur in the average temperature of the seas, the volume of the seas, and the total amount of CO_2 in the atmosphere and sea. Large variations in the atmospheric CO_2 amount must have some effect on the climate through its influence on the atmospheric infrared flux. Plass (1956a, b) has calculated that for a reasonable average cloud distribution over the earth that the average surface temperature should increase 2.5°C or decrease 2.7°C when the carbon dioxide amount in the atmosphere is doubled or halved. These results assume that no other factors in the atmosphere change as a result of the CO_2 variations. Later calculations by Kaplan (1960, 1961) and Moller (1963) obtained results for the temperature change from CO_2 variations which are in essential agreement with these considering the different methods used and the complexity of the calculations. Moller's conclusions about the effect of water vapor are based on approximate equations which have been criticized by Plass (1964).

More recently, Manabe and Strickler (1964) and Manabe and Wetherald (1967) have discussed models which include for the first time some of the complex interactions that occur within the atmosphere. They have calculated from one of their models that the equilibrium temperature of the earth's surface increases 2.92°C for clear sky conditions and 2.36°C for average cloudiness conditions when the CO_2 content of the atmosphere is doubled. These results are remarkably close to those obtained earlier by Plass (1956a, b), when one considers both the more reliable laboratory data available to Manabe and co-workers together with the more complex model used which preserves a reasonable lapse rate in the atmosphere.

Plass (1956b) suggested that a realistic theory of climatic change should consider the effect of CO_2-induced temperature variations on the equilibrium between the sea and the atmosphere. This is now possible on the basis of the curves given here. For example, an increase in the total CO_2 amount increases the partial pressure of CO_2. This in turn is expected to increase the mean temperature of the earth's surface and eventually the mean temperature of the seas. This causes further increases in the atmospheric amount, since the warmer seas cannot hold as much carbonate.

The sequence of events in a glacial epoch can be interpreted from Figure 2. If there is a decrease in the total CO_2 in the sea and atmosphere from some external cause (such as decreased volcanic activity and deposition of carbonates or increased weathering of igneous rocks), the atmospheric CO_2 amount also decreases. This brings about lower temperatures according to the CO_2 theory; the eventual lower temperatures of the seas in turn further decrease the atmospheric amount. If these temperatures are sufficiently

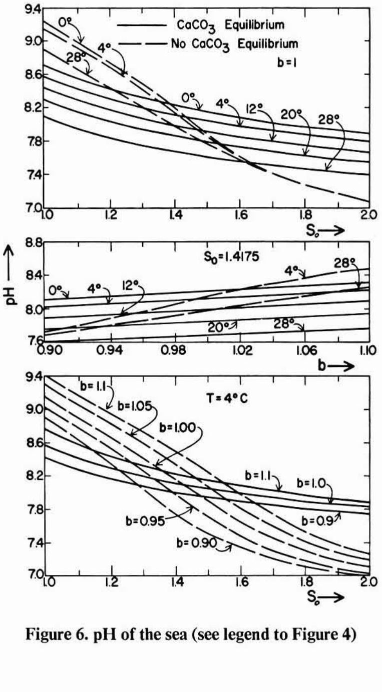

Figure 6. pH of the sea (see legend to Figure 4)

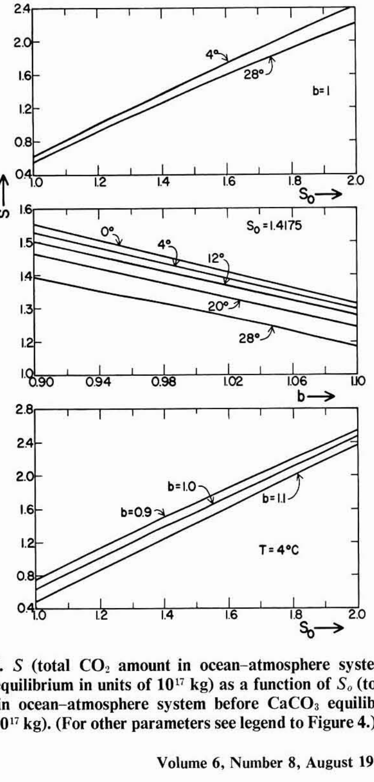

Figure 7. ***S*** **(total CO_2 amount in ocean–atmosphere system after $CaCO_3$ equilibrium in units of 10^{17} kg) as a function of** ***S_o*** **(total CO_2 amount in ocean–atmosphere system before $CaCO_3$ equilibrium in units of 10^{17} kg). (For other parameters see legend to Figure 4.)**

low, appreciable glaciation begins to form on the earth's surface; as a consequence of the volume of water frozen in the glaciers, the volume of the oceans is reduced. As the ocean volume decreases, more CO_2 is released into the atmosphere according to Figure 2. Eventually, enough CO_2 will accumulate in the atmosphere to warm the surface sufficiently to start melting the glaciers. This in turn increases the volume of the seas so that they can absorb excess CO_2 from the atmosphere. The decrease in atmospheric CO_2 amount leads to lower surface temperatures and the cycle of glaciation starts over once again. Such a cycle would probably repeat a number of times before reaching an equilibrium state because of the long time constants involved in the processes (the time for glaciers to form and melt, the turnover time of the seas, the time for the average sea temperature to change appreciably).

Discussion

The equilibrium equations for the interaction of CO_2 between the sea and the atmosphere are solved for three different assumptions: there is insufficient time for equilibrium with either the $CaCO_3$ deposits or the clay sediments; $CaCO_3$ equilibrium occurs, but not with the clay sediments; equilibrium occurs with both the $CaCO_3$ deposits and the clay sediments. Various theories of climatic change may be tested from these results by the calculation of the partial pressure of the atmospheric CO_2 as a function of variations in the total CO_2 in the sea and atmosphere, the average temperature of the sea, and the volume of the sea.

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Isolation of Metal-Binding Fractions from Tobacco Smoke Condensate

Vincent N. Finelli, Edward E. Menden, and Harold G. Petering[1]

Department of Environmental Health, College of Medicine, The University of Cincinnati, Cincinnati, Ohio 45219

■ Tobacco smoke condensate (TSC) from nonfilter research cigarettes was fractionated on a weak cation exchange column [carboxymethyl cellulose in the Cu(II) form], yielding three fractions: noncomplexing substances, protonated copper-binding ligands, and nonprotonated copper-binding ligands. Analysis for copper was done by atomic absorption spectrometry and showed the amount of complexed copper in the protonated ligand fraction to be 271 ± 42 μg/cigarette and in the nonprotonated ligand fraction to be 720 ± 59 μg/cigarette. Several known protonated and nonprotonated ligands were also fractionated on the cation exchanger, and their behavior was compared to that of the TSC fractions. The cation exchanger was also used in the zinc, cadmium, iron(III), and lead forms to determine the binding activity of whole TSC solutions toward these metals. Results, expressed in μmol of metal/cigarette, were copper, 14.6; zinc, 12.8; cadmium, 8.3; iron, 0.5; and lead, 0.5.

A previous paper (Michael et al., 1971) reported the copper-binding activity of tobacco smoke condensate (TSC) by measuring copper chelates extractable in the organic phase in a two-phase system.

The health effects of cigarette smoke and the role that trace metals may have in chemical carcinogenesis (Dixon et al., 1970), atherosclerosis (Kannel, 1971) and other chronic diseases stimulated us to study the activity of TSC constituents on trace metals metabolism. To study the biological effects of TSC constituents on the metabolism of zinc, copper, and iron, it seemed necessary to isolate from the total tobacco tar those agents which most likely bind transition metals. Our goal was not to isolate and identify any one specific ligand, but to group in a few fractions all those TSC constituents which have metal-binding activity.

Sorption of ligands from solutions by cation exchangers containing a complexing metal ion has been reported by several investigators (Stokes and Walton, 1954; Helfferich, 1961, 1962; Carunchio and Grassini Strazza, 1966). Preparation in situ and isolation of zero-charge complexes passing complexing anions through a cation exchanger in the metal form have also been reported (Mitrofanova et al., 1964; Muzzarelli et al., 1969). Furthermore, Walton and others have done extensive work on the fractionation of amines and other nitrogen-containing compounds using the ligand exchange chromatography technique (Cockerell and Walton, 1962; Suryaraman and Walton, 1962; Shimomura and Walton, 1968).

To separate the metal-binding constituents from whole TSC, we have used a weak cation exchanger, carboxymethyl cellulose in the Cu(II) form. This method permitted us to fractionate TSC into three distinct fractions: noncomplexing fraction (F_1) containing TSC constituents which do not bind Cu(II); protonated ligands (F_2) containing those constituents able to form zero-charge chelates with Cu(II); nonprotonated ligands

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[1] To whom correspondence should be addressed.

(F_3) containing those compounds which form charged complexes with Cu(II).

Experimental

Material. APPARATUS. A Perkin-Elmer Model 303 atomic absorption spectrophotometer with recorder readout was used for the determination of copper. A Mason Mark III rotary 24-port cigarette smoker (R. W. Mason, Clevedon, England) was used for smoking the cigarettes mechanically (Michael et al., 1971).

REAGENTS. Acetone (Amsco C.P.), 4-methyl-2-pentanone (MIBK) (Matheson, Coleman and Bell, bp 114–116°C), and ethanol (U.S. Industrial Chemicals Co.) were used as received. The cation exchanger carboxymethyl cellulose was obtained in the sodium form from Bio-Rad Laboratories. Metal standards for atomic absorption spectrophotometric analysis were prepared by diluting stock solutions of 1000 ppm (Fisher Scientific Co.) with 10% nitric acid or 95% ethanol. The 2-amino-2-(hydroxymethyl)-1,3-propanediol (TRIS) (Fisher, Analyzed) was used to stabilize the aqueous copper solutions in the two-phase extraction experiments. Ammoniacal ethanol solutions, 2 and 5% (w/v), were prepared by diluting, respectively, 7.7 and 19.3 ml of 29% (w/v) aqueous NH_3 (sp gr 0.90) to 100 ml with 95% ethanol.

Methods. PREPARATION OF TOBACCO SMOKE CONDENSATE. TSC was prepared from 85-mm nonfilter research cigarettes obtained from the Tobacco and Health Research Institute of the University of Kentucky. The method used was that reported by Michael et al. (1971). The final solution of TSC in MIBK contained 1 cigarette equiv of TSC/ml.

PREPARATION OF CARBOXYMETHYL CELLULOSE IN Cu(II) FORM. Carboxymethyl cellulose (Cellex CM) was obtained from the manufacturer in the sodium form. It was washed with 0.1*N* HCl, left to settle for a period of 2 hr, and the cloudy supernatant was discarded; this procedure was repeated several times. Subsequently deionized H_2O was used for washing out excess acid; three washings were usually sufficient. To transform the exchanger back into the sodium form, it was equilibrated with a solution of 5*M* NaCl. After filtration through a Buchner funnel, a solution of 5*M* $CuCl_2$ was used to impregnate the Cellex CM. This mixture was filtered again through a Buchner funnel and washed exhaustively with 95% ethanol (until washings were free of copper). The amount of copper retained by Cellex CM was found to be equal to the rated capacity of the exchanger.

Results

Fractionation of TSC on Cellex CM–Cu(II) Column. A column was packed with Cellex CM–Cu(II) form (1 × 10 cm) and equilibrated with MIBK. A sample of TSC dissolved in MIBK, 0.5-ml volume equivalent to 0.5 cigarette, was put on the column, and elution with MIBK was performed. The first volume of effluent, a deep brown solution, was collected together with more volume of colorless MIBK effluent (F_1); the total volume was 35 ml. After having collected the first fraction, 95% ethanol was used as eluent. A dark-colored band was displaced from the column and collected in 10 ml volume (F_2). Subsequently, a third band was eluted and collected in 10 ml volume when 2% (w/v) ammoniacal ethanol was used as eluent (F_3). The collected fractions were then analyzed for copper, evaporated, and measured gravimetrically for total organic material. A similar column without TSC sample, eluted simultaneously with the same volumes of solvents, provided the blanks necessary for the mentioned analyses. The data collected are summarized in Table I.

The fractions obtained were tested with a biphasic extraction technique (Michael et al., 1971) for the ability of forming neutral complexes with Cu(II). A 10-ml volume of an aqueous solution of 0.01*M* $CuCl_2$ in 0.1*M* TRIS at pH 5.7 was equilibrated with an equal volume of the MIBK solution of each fraction obtained from the fractionation of five cigarettes equivalent of TSC. The amount of copper extracted into the organic phase, as determined by atomic absorption spectrophotometric analysis, was found to be 40, 190, and 6 μg/cigarette equiv for F_1, F_2, and F_3, respectively. The unfractionated TSC extracted 250 μg of copper/cigarette equiv into the organic phase.

By substituting Cu(II) with other metals, such as Zn(II), Cd(II), Fe(III), and Pb(II), in preparing the Cellex CM in the metal form, using the above procedure, we have been able to determine the binding activity of TSC toward each metal. In Table II we report the amounts of complexed metal per cigarette.

Preparation of Copper-Free TSC Ligands. To obtain the ligands free of copper from both F_2 and F_3 fractions, the copper-containing effluents from Cellex CM–Cu(II) column were evaporated to dryness under reduced pressure and redissolved with 5% (w/v) ammoniacal ethanol. Each solution was then passed through a column of Cellex CM (H^+ form) which had been equilibrated with ethanol. Ammonia competes with TSC ligands for copper to form charged cupric-ammonia complexes of the type $[(NH_3)_nCu]^{2+}$ ($n = 1 \rightarrow 4$) and ($\beta_4 = 10^{15}$). On eluting with 5% ammoniacal ethanol, the cupric-ammonia complexes remained sorbed on the cation exchanger as a blue band on top of the column, while the copper-free TSC ligands were eluted. The effluents were checked and found to be free of copper.

Cellex CM–Cu(II) Column Studies. For comparative purposes, known Cu(II)-complexing ligands and mixtures of these compounds have been chromatographed through a Cellex CM–Cu(II) column. Protonated ligands such as 3-

Table I. Fractionation of TSC on Cellex CM–Cu(II) Column

(Figures corrected for the column blank)

Fraction	Eluent	Organic material, mg/cig ± S.D.	Complexed Cu[a], μg/cig ± S.D.
TSC (unfractionated		36.0 ± 3.0	. . .
F_1	MIBK	29.4 ± 1.0	0
F_2	95% ETOH	6.6[b]	271 ± 42
F_3	2% NH_3 in ETOH		720 ± 59

[a] The amount of copper found in the effluents of the column blank averaged 0 μg for F_1 and F_2 and 100 μg for F_3.

[b] By difference: TSC − F_1.

Table II. Binding Activity of TSC Toward M^{n+} on Cellex CM–M^{n+} Form

Metal	Amount of metal complexed by TSC[a] μg/cig	μmol/cig
Cu(II)	951	14.6
Zn(II)	833	12.8
Cd(II)	925	8.3
Fe(III)	28	0.5
Pb(II)	108	0.5

[a] Values reported represent total amount of metal found in the effluents F_2 and F_3.

ethoxy-2-oxobutyraldehyde-bis(thiosemicarbazone) (KTS), diethyldithiocarbamic acid diethylammonium salt, and 2,4-pentandione were separated from nonprotonated ligands such as *N,N*-dimethyl-*p*-phenylenediamine; 2,2′,2″-tripyridine; *N,-N,N′,N′*-tetramethylethylenediamine; and cyclohexylamine on Cellex CM–Cu(II) column. The behavior of these ligands on the column followed the expectation: the protonated ligands were eluted as Cu(II) complexes with 95% ethanol, and the nonprotonated ligands were displaced from the column with ammoniacal ethanol. When an aliquot of 2,5-pentanedione (AcAc) of 194.4 μmol was passed through a Cellex CM–Cu(II) column, eluting with 95% ethanol, the blue effluent was collected and analyzed for copper. The collected fraction contained 89.8 μmol of copper, which deviates from the theoretical yield, assuming a formation of $(AcAc)_2Cu$ complex, by 7.7%.

Discussion

The presence of both protonated and nonprotonated ligands in TSC has been reported: fatty acids, thioacids, polyphenols, and amines are among the known constituents of cigarette smoke (Stedman, 1968). The protonated ligands are those which exchange the available proton(s) for the metal ion, forming zero-charge chelates. The nonprotonated ligands form with the metal ionizable complexes of the type $[L_nM]^{2+}2X^-$. When we tested our TSC fractions obtained from the Cellex CM–Cu(II) column for the copper distribution between an aqueous phase and an immiscible solvent, by using the method reported by Michael et al. (1971), we found that F_2 had the largest activity in extracting the copper ions into the organic phase. These results prove that most of the protonated ligands of TSC are found in F_2.

Furthermore, the capacity to extract copper into the organic phase found with the unfractionated TSC was almost completely duplicated with the collected fractions. The behavior of known copper complexing agents when chromatographed through a Cellex CM–Cu(II) column showed that the protonated ligands occur in F_2 fraction.

This method of fractionation has permitted us to isolate from a mixture of a thousand or more constituents of cigarette smoke those agents which have ability to bind transition metals. These agents may be noxious components of cigarette smoke, they may upset the normal trace metal metabolism, and they may also be cocarcinogenic by inhibiting certain metal-activated enzymes—e.g., benzpyrene hydroxylase (Dixon et al., 1970). Studies on the biological and biochemical activities of these fractions are currently in progress.

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NOTES

Chemiluminescent Reactions of Oxygen Atoms with Reactive Hydrocarbons. I. 7000–9000Å

Barbara Krieger, Mazen Malki, and Ralph Kummler[1]
Department of Chemical Engineering, Wayne State University, Detroit, Mich. 48202

■ The reaction of oxygen atoms with unsaturated hydrocarbons at pressures of approximately 1 torr produces intense emission in the spectral region from 7000–9000Å. Absolute intensity spectra have been obtained using NO + O as an actinometric standard. The signal-to-noise ratio for the spectra obtained in this work appear to be much larger than the chemiluminescence recently reported at similar pressures for $O_3 + C_2H_4$; the combination of the wavelength region and the banded rather than continuum structure of the atom-originated emission offers a potential for chemiluminescent monitoring of reactive hydrocarbons under conditions analogous to their direct role in photochemical smog formation.

The successful commercial implementation of the homogeneous gas phase $NO + O_3$ chemiluminescence (Fontijn et al., 1970; Fontijn and Ronco, 1971; Stuhl and Niki, 1970; Hodgeson et al., 1971) for the monitoring of NO, NO_2, O_3, and/or NO_x and the homogeneous reaction (Nederbragt et al., 1965; Warren and Babcock, 1970) of $O_3 + C_2H_4$ at atmospheric pressure for the detection of O_3 has generated applied interest in other chemiluminescent reactions as potential sensors for air contaminants (Kummer et al., 1971). We wish in this work to shift the focus from ozonolysis reactions to atomic oxygen attack at low pressure which yields

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[1] To whom correspondence should be addressed.

structured emission rather than continuum emission. The existence of a strong line or lines which might result in the possibility of reactive hydrocarbon monitoring is the motivation for this discussion. Since the EPA's air quality standard for hydrocarbons is based on the hypothesized correlation between maximum oxidant and the 6–9 A.M. nonmethane hydrocarbon concentrations, it is clearly important to have a direct measure of the reactive hydrocarbons. The presently approved technique of obtaining the total HC by flame ionization, the methane by gas chromatography, and the nonmethane HC by difference has resulted in numerous cases of negative nonmethane concentration (Heuss et al., 1971). Clearly, a direct method for monitoring reactive hydrocarbons is needed. King (1970) has suggested FID modifications which might achieve the objective. In the present work we suggest $NO + O_3$ detector modification which might permit reactive hydrocarbon measurement. It is conceivable that such a measurement would be a direct measure of the classical reactivity needed for the oxidant-related hydrocarbon standard, because conditions might be found under which the light intensity is proportional to the product of the rate constant for O atom attack times the hydrocarbon concentration. This point is under continued investigation.

Experimental

All studies were performed in the discharge flow system shown schematically in Figure 1. Molecular oxygen (American Cryogenics, purity 99.6%) was discharged in an Evenson Cavity at 2450 MHz using a Raytheon PGM 10X2 diathermy system. The discharge was pulsed at 238 Hz for simultaneous infrared measurements which will be reported elsewhere. The discharged oxygen was passed into the flow tube reactor through a Teflon tube with a radially multiperforated exit stream which permits excellent mixing with a second gas and prevents discharge region radiation from reaching the observation ports. The stainless steel reactor is lined with a Teflon sleeve which largely prevents wall recombination of the atomic species. The inside diameter of the reactor is 1 in., and typical gas velocities are 30–40 m/sec through a Heraeus Engelhard E-225 mechanical pump. Six ports permit radial viewing through KBr windows using an RCA C31025C uncooled photomultiplier on a Jarrell Ash scanning quarter meter monochrometer with a Keithley 602 Electrometer recorded on a Honeywell Electronik 194 recorder. Signal-to-noise ratios were such that no damping or time integration of signals was necessary.

The hydrocarbons employed as reactant gases were methane, ethane, propane, ethylene, propylene, trans-butene, and acetylene. Formaldehyde, which is probably an intermediate for the chemiluminescence as it is for the overall reaction (Niki et al., 1969) was also used as a reactant gas. Linde research grade methane and ethane were employed. Union Carbide chemically pure propane was used. The propylene and trans-butene from Cryogenic Sales had purities of 95 and 99%, respectively. Several runs were made with "house" methane with no perceptibly different results.

Oxygen atom concentrations were determined through NO_2 titration; typically, 1% atoms were present. The spectral response function for the system was determined using the $NO + O$ chemiluminescence as an actinometric standard (Fontijn et al., 1964).

The $C_2H_4 + O$ signal was maximized with respect to a set of flow conditions by scanning all wavelengths between 7000–9000Å and monitoring the signal at the contact times determined by the position of the KBr windows (contact time in the system at a given pressure is from 3–5 msec, depending on the viewing port). For this total pressure of 1.280 torr and a C_2H_4 partial pressure of approximately 20 mtorr, the first window gave the largest signal, about 3×10^{-9} A. The signals from the other hydrocarbon plus atomic oxygen reactions were also monitored at the first window and comparable concentrations. Consequently, the intensities may not be the maximum obtainable for any of the other hydrocarbons although the intensities of the signals from the various species correspond to roughly the same experimental conditions. Under these conditions rapid depletion of O atoms by butene, for example, produces an attenuated signal relative to ethylene despite its larger rate constant for O attack.

Since the capability of monitoring the hydrocarbon (for example, via the ethylene plus atomic oxygen signal) in the presence of NO ($NO + O$ signal) is necessary, these two components were introduced to the O_2 stream at the same time in equal concentrations, and the resultant signal monitored. A current of 1.6×10^{-9} A was input to the electrometer to partially suppress the $NO + O$ continuum signal (about 4–10 times the $O + C_2H_4$ signal) and to allow the full-scale sensitivity to be the same as for monitoring the $O + C_2H_4$ signal.

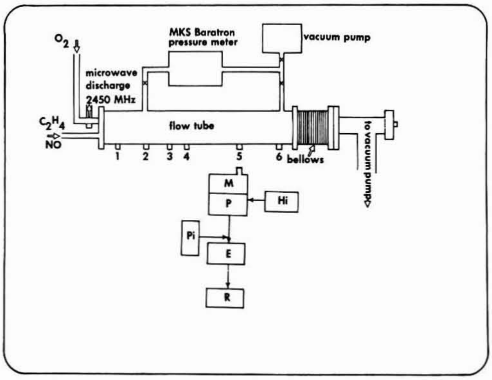

Figure 1. Schematic of discharge flow tube reactor and detection system

M = monochromator, Jarrell Ash, quarter meter, scanning
P = photomultiplier, RCA C310250 (uncooled)
E = electrometer, dc amplifier, Keithley 602
Pi = picoampere source, Keithley 261
R = recorder, Honeywell Electronik 194
Hi = High-voltage dc power supply, Power Designs Pacific Model 2K-10

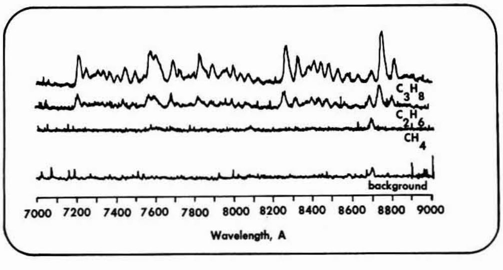

Figure 2. Intensity of chemiluminescence in the 7000–9000Å region from O atom attack on saturated hydrocarbons

Total pressure is 1.28 torr and the hydrocarbon partial pressure is 20 mtorr

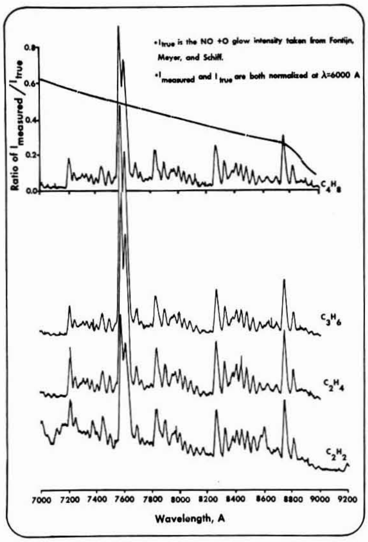

Figure 3. Intensity of chemiluminescence in the 7000–9000Å region from O attack on unsaturated hydrocarbons

Total pressure is 1.28 torr and the hydrocarbon partial pressure is 20 mtorr

Results and Discussion

The chemiluminescent spectra generated by the reaction of oxygen atoms with a series of saturated and unsaturated hydrocarbons are presented in Figures 2 and 3 along with the spectral response of the photomultiplier–spectrometer system, as determined through calibration with NO + O. At the first window, the signal was scanned over the sensitive wavelength range of the photomultiplier. The spectra of olefin plus oxygen atom reactions had several major peaks in the 3000–7000Å range, and the emission in the 7000–9000Å region was characteristic of the OH Meinel bands plus a strong band near 7620Å which could be $O_2(^1\Sigma)$ emission. The intensity of the Meinel bands is a strong function of the contact time whereas the $O_2(^1\Sigma)$ emission is much less sensitive over the contact time range of this experiment (although it is clearly not background discharge emission).

The O plus reactive hydrocarbon emission is structured, and nearly as strong as the NO + O emission in the wavelength region from 7000–9000Å, which suggested the possibility of detecting, for example, unsaturated hydrocarbons in the presence of an equal amount of NO. We tested this hypothesis by introducing equal amounts of NO and ethylene. Figure 4 presents the resulting spectrum from 7000–8000Å. The C_2H_4 + O emission peaks are clearly distinguishable superimposed on the NO + O continuum emission.

While acetylene exhibits the same structure in the 7000–9000Å region as do olefins, the spectrum from 2500–7000Å is quite different with strong emission near 6000Å, which should be readily observable in the presence of NO as well, provided that appropriate spectral resolution is provided. Formaldehyde also yields the same spectrum as the olefins with an enhanced continuum between 3500 and 4500Å.

The signal-to-noise ratios for the spectra shown in the figures are much better than the signal-to-noise ratio for the equivalent spectra generated by the ozonolysis reactions taken by Kummer et al. (1971). Because the NO + O glow is stronger than the NO + O_3 glow, we can estimate that the sensitivity of this O atom and hydrocarbon technique should be at least as good as that of Fontijn et al. (1970) for NO—i.e., in the ppb range. Even better results might be anticipated for electronic emission from OH near 3000Å generated by O atom attack on olefins.

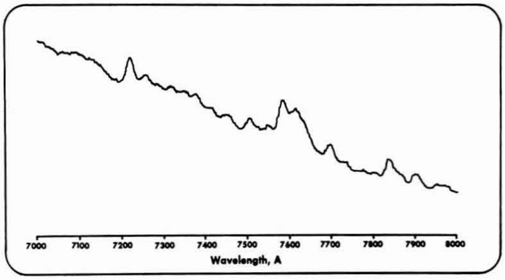

Figure 4. Intensity of chemiluminescence from simultaneous O atom attack on C_2H_4 and NO in equal concentrations of 20 mtorr

In summary, the reaction of oxygen atoms with reactive hydrocarbons yields a characteristic chemiluminescence which we believe will permit the detection of this important class of hydrocarbons in the ambient atmosphere using a low-pressure, rather than a high-pressure, discharge and narrow band optical filters which discriminate against the NO + O glow.

Acknowledgment

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Mercury Uptake by Polyamine–Carbohydrates

M. S. Masri and Mendel Friedman[1]

Western Regional Research Laboratory, Agricultural Research Service, USDA, Berkeley, Calif. 94710

■ Chitosan (deacetylated chitin), other polyamines derived from cellulose, polyamines derived from dialdehyde starch, and poly(aminostyrene) bind mercury in large amounts from water solutions of $HgCl_2$. In contrast, unmodified starch and cellulose adsorb very little mercury, while chitin (with acetylamino groups) binds much less than chitosan. In several instances the adsorbents bound more than one atom of mercury per nitrogen and more than their own weight of mercury. These results show that amino groups in natural and synthetic polymers are effective binding sites for mercuric chloride and point first to the possible utility of such polymers as adsorbents for mercury, and second, to the possible role of naturally occurring polyamine polymers in the distribution of mercury in the environment.

One way to immobilize an enzyme on a water-insoluble matrix is to couple the protein to a poly(diazonium salt) derived from a water-insoluble resin such as poly(*p*-aminostyrene) or *p*-amino-benzylcellulose (Goldstein et al., 1970). Recently, Goldstein et al. (1970) described a new, easily prepared, diazotizable carrier matrix made by condensing dialdehyde starch (DAS) with the diamine *p,p'*-diaminodiphenylmethane (methylene dianiline, MDA) to form a poly (Schiff's base), which they reduced with $NaBH_4$. The extent of cross-linking of the polymeric chains of the DAS by the bifunctional diamine and the extent of its one-point attachment (thus leaving one amino group of the diamine free) depend on the proportion of MDA in the reaction mixture. Thus, resins with as much as 48% MDA were prepared, equivalent to about one molecule of MDA per hexose residue. A structure for the resin was proposed (Goldstein et al., 1970).

The high nitrogen content of this insoluble resin prompted us to test its ability to remove mercury salts from aqueous solutions. Various agricultural products are being evaluated in this laboratory as possible practical means to recover mercury from wastes and contaminated water (Friedman and Waiss, 1972; Friedman et al., 1971; Webb, 1966). In this paper we compare mercury binding by the DAS derivatives with binding by several natural and modified carbohydrates, by poly(amino-styrene), and by wool.

Results in Table I show the high affinity and capacity of DAS–MDA resin for binding mercury from aqueous solutions of $HgCl_2$. Under some conditions it takes up more than its own weight of mercury. A similar DAS resin, prepared by substituting *p,p'*-phenylenediamine (PDA) for MDA, behaved similarly. Both DAS–MDA and DAS–PDA resins are more effective in binding mercury from acid than from neutral solution; this pH dependence is minimized if the Schiff's base resins are reduced by $NaBH_4$; ($RCH{=}NR'$ to RCH_2NHR').

In contrast to these diamine-modified dialdehyde starch resins, unmodified potato starch or DAS, itself, adsorb very little mercury under the test conditions. Results are also included in Table I for underivatized celluloses (essentially nil uptake), ion-exchange celluloses (moderate uptake) and wool fiber for comparison. The high uptake by the chitosan (deacetylated chitin), point to the efficacy of the free amino groups for mercury binding. The binding of Hg to chitosan is about five times higher than to chitin, which is a linear polymer of *N*-acetyl-2-deoxy-2-amino glucose with a 1,4 β-linkage between the monomer units as in cellulose.

Although we do not know the structure of the mercury resin complexes, data in Table I show that the ratio of gram-atom Hg bound/gram-atom nitrogen ranges from 0.18 to 2.26. (The ratios were calculated for the experiments at the higher initial level of 40 mg Hg/ml and the experimental nitrogen values of the resins.) These results suggest that the extent of binding is related to the nature of the substituent on nitrogen; evidently, nitrogen tied by acetylation or as a Schiff's base is a less effective binding site than primary or secondary amino nitrogen. Nitrogen combined as a Schiff's base is less effective in "water" than the reduced (secondary amine) form, although equally effective in strong acid. The greater binding capacity of the reduced DAS resins is presumably the result of the enhanced basicity of the nitrogen atom in the reduced form.

We used mercuric chloride for most of this work. However, a few experiments were done with the more toxic and less water-soluble methyl mercuric chloride. Chitosan, poly(*p*-aminostyrene), and DAS–MDA were equilibrated 24 hr at 25°C with solutions containing 4 mg of methyl mercuric chloride per ml in aqueous methanol (1:1 v/v). The liquid-polymer ratio was 25 ml/gram. Polymer samples were recovered by filtration, then rinsed with methanol and air-dried. Weighed samples were then oxidized with $KMnO_4$ in sulfuric acid, and mercury contents determined by atomic absorption. Observed uptakes were 28, 36, and 26 mg of Hg per gram of chitosan, poly(*p*-aminostyrene), and DAS–MDA, respectively, corresponding to 35, 45, and 32% of the amount of Hg initially present. It appears that these polymers bind about one third as much mercury from methyl mercuric chloride in 1:1 methanol–water as from aqueous mercuric chloride under similar conditions. For wool this ratio is about one fifth (Friedman et al., 1971).

In summary, these results suggest that polyamino derivatives of carbohydrates may be useful to remove and recover mercury compounds from water. They suggest also that free amino groups and possibly other basic groups in proteins and other biological materials are important in the natural accumulation and distribution of mercury in the biosphere. Finally, the natural occurrence of mucopolysaccharides in the *N*-acetylated or *N*-sulfated forms—e.g., chitin, chondroitin, hyaluronic acid, heparin—may provide a mechanism for the exclusion of nitrogen-metal complex formation in certain biological structures and functions.

Experimental

Materials. Dialdehyde starch, a 100% periodate-oxidized preparation was originally obtained from the Northern Regional Research Laboratory, Peoria, Ill. Methylenedianiline was prepared by condensing aniline and formaldehyde in hydrochloric acid according to Scanlon (1935). *p*-Phenylenediamine was from Eastman Kodak; the ion-exchange celluloses (aminoethylcellulose, N = 0.4%; DEAE—cellulose,

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[1] To whom correspondence should be addressed.

Table I. Mercury Uptake by Carbohydrates and Derivatives[a]

Solid polymer tested	Aqueous medium $HgCl_2$ solution		Hg removed		
	ml/g polymer	Initial concn, mg Hg/ml	mg Hg/g polymer	Initial Hg in medium, %	g-atom Hg/g-atom N
Cellulose, starch, or DAS	25	4	5–12	5–12	
DAS–MDA	17	4	64	94	
DAS–MDA	25	40	280	28	0.23
DAS–MDA (0.1*N* HCl)	25	40	970	97	0.80
DAS–MDA (0.1*N* HCl)	50	40	1,050	52	0.86
DAS–MDA, reduced	25	40	617	62	0.55
DAS–MDA, reduced (0.1*N* HCl)	25	40	830	83	0.69
DAS–PDA	25	4	96	96	
DAS–PDA	30	40	705	59	0.46
DAS–PDA (0.1*N* HCl)	30	40	999	83	0.65
DAS–PDA, reduced	33	40	1,033	78	0.68
DAS–PDA, reduced (0.1*N* HCl)	33	40	993	75	0.65
DEAE–cellulose	25	40	290	29	2.26
Aminoethyl cellulose	25	40	55	5	0.98
Aminoethyl cellulose (0.1*N* HCl)	25	40	128	13	2.25
p-Aminobenzyl cellulose	25	40	90	9	1.58
p-Aminobenzyl cellulose (0.1*N* HCl)	25	40	120	12	2.11
Chitin	25	4	33	33	
Chitin	25	40	175	17	0.17
Chitosan	25	4	100	100	
Chitosan	25	40	948	95	0.76
Chitosan	50	40	1,425	71	1.15
Poly(*p*-aminostyrene)	25	4	100	100	
Poly(*p*-aminostyrene)	25	40	912	91	0.54
Poly(*p*-aminostyrene)	50	40	1,450	72	0.86
Wool fiber	50	4	116	58	
Wool fiber	50	40	510	25	[b]

[a] Unmodified celluloses used were absorbent cotton and chromatography grade cellulose powder; starch was purified from potato, DAS was the same used to prepare DAS–MDA and DAS–PDA resins. Mercury concentrations or uptake are on basis of Hg, not $HgCl_2$; thus 4 mg Hg/ml refers to 0.02*M* $HgCl_2$. The medium was prepared by dissolving $HgCl_2$ in H_2O or, when indicated, in 0.1*N* HCl (aqueous). Usually tests were performed in both media (H_2O or 0.1*N* HCl) but results in 0.1*N* HCl are listed only when they appeared different from those in H_2O.

[b] ~3 g-atom Hg/g-atom N of basic amino acid residues (arginine, histidine, lysine); 0.75 g-atom Hg/g-atom N of lysine.

N = 0.9%; *p*-aminobenzylcellulose, N = 0.4%) from Biorad Laboratories, Richmond, Calif.; poly(*p*-aminostyrene) from Polysciences Inc., Rydal, Pa.; chitin (shellfish) from Nutritional Biochemical Co., Cleveland, Ohio; chitosan by alkali deacetylation of chitin (Peniston and Johnson, 1970).

Dialdehyde Starch–Methylenedianiline (DAS–MDA) Resin. This was prepared according to Goldstein et al. (1970) using 10 grams DAS and 30 grams of MDA; after about two days at room temperature with stirring, the precipitated dark yellow orange resin was collected, filtered, and washed with water and methanol (yield about 18 grams; N = 8.46%). This resin was tested for mercury uptake both as prepared and after reduction with sodium borohydride.

Dialdehyde Starch–*p*-phenylenediamine (DAS–PDA) Resin. This was prepared in a similar manner as DAS–MDA but with 5 grams DAS and 10 grams PDA in the carbonate buffer–methanol. After about three days of stirring at room temperature, the purple-black precipitate was collected, washed, and dried (yield 4.5 grams; N = 10.7). This resin was similarly tested for mercury uptake as prepared and after reduction with sodium borohydride.

Measurement of Mercury Uptake. This was done by equilibrating a weighed sample of adsorbent in a measured volume of $HgCl_2$ solution of known initial concentration for one day at room temperature (25°C) with a mechanical shaker. The concentration in the mother liquor was then measured. The difference between this and the initial concentration was used to calculate the amount of mercury taken up by the solid. Mercury concentrations were determined by atomic absorption using a Perkin-Elmer Model 303 spectrometer with an acetylene–air burner. In most tests showing high mercury uptake, the measurements were corroborated by weighing—i.e., compatible weight increases were observed with polymers that were equilibrated with $HgCl_2$ solutions, then rinsed with H_2O followed by methanol, and air-dried.

Acknowledgment

Thanks are given to W. H. Ward for constructive contributions to this manuscript.

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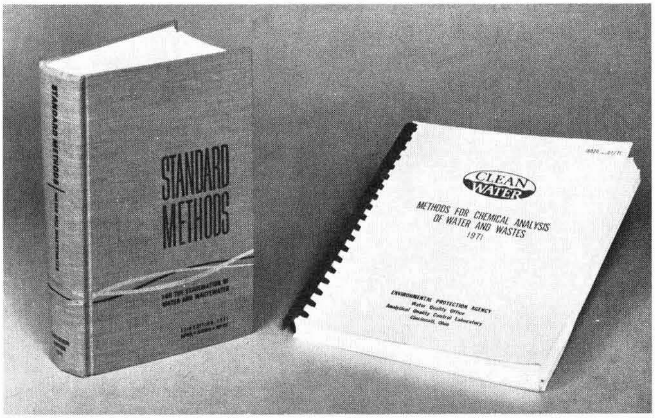
Received for review January 12, 1972. Accepted May 24, 1972. Reference to a company or product name does not imply approval or recommendation of the product by the U.S. Department of Agriculture to the exclusion of others that may be suitable.


Bendix
NO-NO$_2$-NO$_X$ ANALYZER


STANDARD METHODS
CLEAN WATER
METHODS FOR CHEMICAL ANALYSIS OF WATER AND WASTES
1971
ENVIRONMENTAL PROTECTION AGENCY


HACH

industry trends

Neptune Meter Co. has completed a multimillion-dollar water meter manufacturing facility in Talahassee, Ala. The plant will partially replace a similar operation in Long Island City.

Yoder-Trotter-Orlob and Associates, a subsidiary of Systems Associates, Inc., has received a grant for a waste water management study for the Natomas area of Sacramento County, Calif.

Peabody Galion Corp. will acquire American Brattice Cloth Corp. (Warsaw, Ind.) for an undisclosed amount of Peabody stock. American Brattice is a major supplier of cloth fabric and tubing for mine ventilation and safety.

B.F. Goodrich Chemical Co. will convert some coal-fired boilers to units which burn oil at the company's Avon Lake, Ohio, general chemicals production plant. The conversion is required to meet state air pollution requirements.

Burns and Roe Construction Corp. has received a contract from the Office of Saline Water to manage, operate, and maintain the OSW Roswell test facility, Roswell, N.M.

Southwest Factories Inc., has received four orders from various cities for the company's newly developed municipal solid waste disposal system. The system is a shredder disposal plant.

Bethlehem Steel Corp. Supply Division will be the marketing agent for Fram Corp.'s Oily-Water systems, fluid analyzers, and trace-oils analysis kits.

Systems Capital Corp. (Phoenix, Ariz.) will build the first commercial in-ground tank for storage of liquefied natural gas (LNG). Systems will rent the facility to Union Carbide.

Computer Sciences Corp. (Los Angeles, Calif.) has received a contract from the U.S. Coast Guard for conceptual studies of the Coast Guard's role in developing new procedures to reduce marine casualties, improve environmental protection, and implement vessel traffic management.

Systems Control, Inc. (Palo Alto, Calif.) has received a contract from Snohomish County, Wash., for a comprehensive waterway pollution and control planning study for the Snohomish and Stillaguamish river basins. Contract is valued at $260,000.

Grow Tunneling Corp., a subsidiary of Alpha Portland Industries, Inc., and Andrew Catapano Co., Inc., are corecipients of a $17.3 million contract awarded by the City of New York for a new sector of interceptor sewers.

Raytheon Co. has received a $130,000 contract from Massachusetts' Department of Natural Resources for a survey of sand and gravel deposits in the Commonwealth's territorial waters.

Witco Chemical is in the first stage of an expansion of its Kenite Division's Quincy, Wash., calcined diatomite products plant.

Environmental Tectonics Corp. (Southampton, Pa.) has been awarded a contract by the Office of Saline Water to provide a four-stage portable thermal distillation desalinator prototype. Value of the contract is about $200,000.

Waste Resources Corp. (Philadelphia, Pa.) has acquired Material Control, Inc., Ft. Worth, Tex.; Fleet Disposal, Inc., Los Angeles, Calif.; and Area Disposal, Inc., Detroit, Mich. Terms of the transaction were not announced.

CorBan Industries (Tampa, Fla.) has received a contract from Florida Power Corp. of St. Petersburg, Fla., for more than 5000 feet of large-diameter Fiberglas-reinforced plastic (FRP) pipe.

SCA Services, Inc. will acquire eight businesses with aggregate revenues in their most recent fiscal years of about $8 million. Seven businesses are active in solid waste management. The eighth provides building maintenance services.

Laboratory Data Control has been appointed distributor for Hirama Laboratories' new photoelectric filter photometer.

Babcock and Wilcox has received a contract from Texas, Inc. to construct four B&W boilers at three refineries. The boilers will fire carbon monoxide off gas generated by fluid catalytic cracking.

Pittsburgh & Midway Coal Mining Co. and **Rust Engineering** have signed an agreement to build a solvent-refined coal pilot plant at Ft. Lewis, Wash., near Tacoma. Construction of the plant is expected to begin in July, with completion set for late 1973.

Hercules Inc., has acquired AB Purac of Lund, Sweden—a company specializing in waste water engineering. Hercules also bought part of the ion exchange business of Mibis, AB, of Sweden.

PRC Systems Science Co. (McLean, Va.) has been awarded a subcontract on a study of a coastal water quality monitoring network being performed for EPA by Interstate Electronics Corp. One of the tasks PRC will perform is an assessment of existing water quality laboratories in coastal states.

Wellman-Power Gas Inc. will undertake a $45 million smelter pollution control project for Inspiration Consolidated Copper Co. at Inspiration, Ariz. The project involves installation of an electric furnace, five siphon converters, and a Lurgi sulfuric acid plant. All fumes and dust will be recycled, says the company.

Delmarva Power and Light Co. has given $25,000 to the Institute of Energy Conversion at University of Delaware, Newark, Del. The money will be put toward construction of a model house in which the feasibility of using a solar cell to produce electricity will be tested.

Browning-Ferris Industries, Inc. (Houston, Tex.) is continuing its aggressive acquisition program and has completed a stock exchange transaction with CESCO, Inc., a specialty chemical services firm experienced in liquid waste processing.

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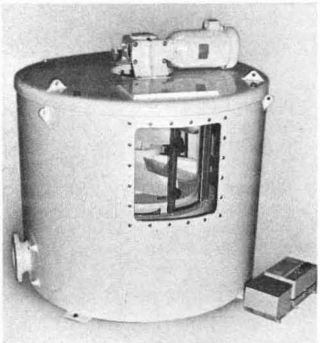

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Centrifugal waste water concentrator handles industrial hydraulic flows from 250 to 1000 gpm. Suited for majority of effluent and waste water streams in paper, textile, tobacco, meat packing, potato, and poultry industries. Sweco, Inc. 61

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Electromagnetic micromill pulverizes and mixes wet and dry powdered pollution samples for laboratory analysis. Breaks down particulate matter for spectrophotometry, X-ray, or spectral analysis. Geoscience Instruments Corp. 66

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Filter's removal efficiencies are 90–95%. Uses about 1–2 lb of media per million gal. of filtered water. Hayward Filter Co. 69

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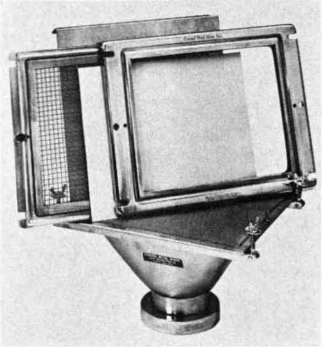
Transistorized portable pH meter is calibrated from 0–14 pH or ±500 mV with an accuracy of 0.05 pH. Brinkmann Instruments, Inc. 70



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Filter paper cartridge complements full line of high-volume air sampling equipment. Permits changing filter paper under controlled laboratory conditions rather than adverse field conditions. General Metal Works, Inc. 71

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Pulsafeeder is available in three basic design configurations. Offers leakproof metering in modern treatment systems—industrial and municipal water and waste water treatment operations. Pulsafeeder Products 72

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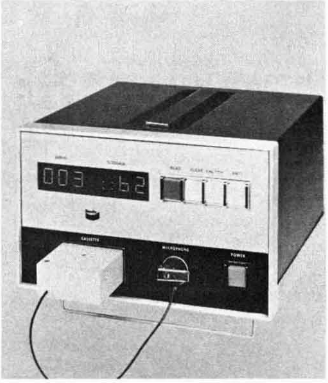
Electronic instrument, BODI, automatically measures BOD of waste water. Direct indication of BOD in mg/l. on the front panel. Reduces labor by two-thirds over that required by the standard BOD test procedure. Ecological Controls, Inc. 73



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Solid-state photoelectric unit provides continuous, accurate monitoring of opacity and overall indication of equipment efficiency. Broad application for general opacity monitoring in chemical, power, and other industries. Robert H. Wager Co., Inc. 74

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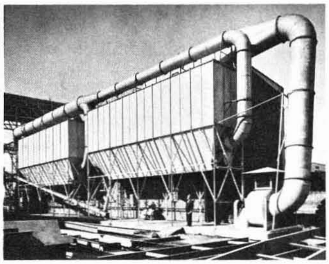

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Installation removes very fine dust and other pollutants from air and other gases at rate up to 5,300,000 cfh. One hundred percent efficiency achieved with particles as small as 0.004 mm. Commercial Division of the Netherlands Consulate Division 78

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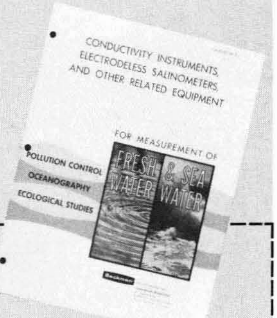
Water-monitoring remote station meets most recent EPA and Corps of Engineers specifications. Transmits up to 16 data channels to the central console. EMR Instruments 79



Gas monitor

Instrument will detect gasoline, propane, methane, smoke, most industrial solvents, and carbon monoxide. Features a remote sensor, a buzzer alarm, a meter indicating gas concentration, and selector to adjust alarm to gas concentration level desired. International Sensor Technology 84

Stack reference standards

Kit contains eight stack emission reference standards—aluminum oxide, red iron oxide (2), carbon black, titanium dioxide, zinc oxide, feldspar, and fly ash. Duke Standards Co. 85

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All-electric water level sensor measures ranges of water level variations from a few feet to 100 ft, at depths of several hundred feet below ground. Signal can be transmitted over long distances without preamplification, and is independent of temperature, pressure, and specific gravity. Metritape, Inc. 86

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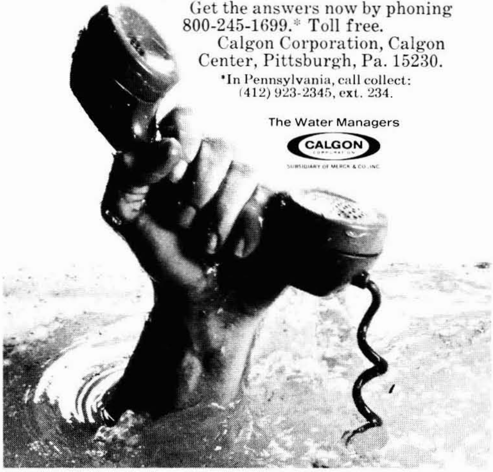
SE-600 fluid sampler is capable of sampling liquids with solids measuring 2 in. in diam. Sampling rate adjustable from 0.2 sec to 60 hr between samples. Brandywine Valley Sales Co. 89

Brushes

Cylinder brushers designed to remove solid contaminants that have been collected on belts or drums through filtration or precipitation processes. Brushes operate continuously while subjected to corrosive liquids, extreme atmospheric conditions, and high temperatures. M. W. Jenkins' Sons, Inc. 90



new literature

Quarternary ammonium. Report tells of uses of company's biodegradable quarternary ammonium compounds for microbiocidal or microbiostatic applications. Lonza, Inc. 91

Capacitance manometry. Six-page bulletin describes applications of capacitance manometry for pressure measurement. MKS Instruments, Inc. 92

Diatomite filter. Step-by-step booklet tells how to operate and maintain a diatomite pressure filtration system. Witco Chemical 93

Apparatus. New 24-page brochure gives specifications and prices of company's offering of water pollution testing apparatus. Wheaton Scientific 94

Carbon. Bulletin describes lignite-based carbons for adsorption of impurities from municipal water supplies. ICI America, Inc. 95

Reverse osmosis. Bulletin tells of water treatment problems that find solutions in spiral wrap system of reverse osmosis equipment. Envirogenics, Inc. 96

Afterburners. Brochure pictures, charts, and describes turbine-type afterburner and element for odorless hydrocarbon cleanup. TEC systems, Inc. 97

Chlorinated solvents. Company offers booklet which describes the effects of the Clean Air Act of 1970 on chlorinated solvents. Dow Chemical Co. 98

Catalog. Four-page bulletin describes line of fabric filter dust collectors. Includes cut-away photos showing features of construction. Dustex Div., American Precision Industries, Inc. 99

Fuel oil treatment. Brochure describes a five-step program for fuel oil servicing with company's additives. Gamlen Chemical Corp. 100

Catalog. 40-page catalog lists supplies for pH meters and electroanalytical instruments. Gives data on selection of electrodes, buffers, and peripheral equipment. Beckman Instruments, Inc. 101

Air purification. Bulletin entitled "Beat the Energy Shortage by Air Recirculation and Activated Carbon Purification" tells how to save on power consumption by recirculating heating or air-conditioning air. Barnebey-Cheney 102

Catalog. Maker of corrosion-resistant pumps, filter systems, and waste water treatment equipment offers handy 8-page reference catalog. Sethco Mfg. Corp. 103

Application data. Sheet describes new analyzer for measuring dissolved oxygen in parts-per-billion range. Beckman Instruments, Inc. 104

Additives. Brochure details advantages of company's additives in reducing fouling, corrosion, and pollution while increasing efficiency of utility power station boilers, turbines, and condensers. Apollo Chemical Corp. 105

Books. Flyer lists current titles of several pollution control books published by society. Instrument Society of America 106

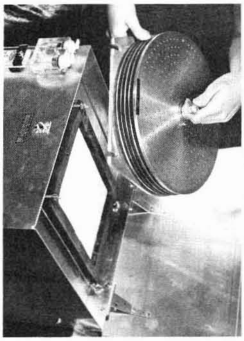
Sewer problems. Brochure details steps taken by a sewer-cleaning contractor to restore a 100-year-old structurally sound sewer to full carrying capacity. National Power Rodding Corp. 107

Carbon adsorption. Booklet distills applications and advantages of using carbon adsorption treatment for a variety of uses. Illinois Water Treatment Co. 108

Data sheet. Analysis data sheet shows use of atomic absorption spectroscopy in quantitative determination of silicon. Barnes Engineering Co. 109

Ferroalloys. Beautifully illustrated booklet "Ferroalloys—how they are made and used" describes topic in language the man on the street can understand. Airco, Inc. 110

Water treatment. Eight-page illustrated booklet explains why water needs treatment, and how it can be treated. Describes chemicals available for treating cooling water, boiler water, closed systems, and potable water. Universal Oil Products Co. 111



Valve actuators. New literature is available on manufacturer's line of pneumatically operated rotary valve actuators. Specifications, applications, and torque curve charts are included. Arcas Co. **112**

Standard solutions. Listing of atomic absorption spectroscopy standard solutions spans a product line of 21 metal ion solutions. MC/B Manufacturing Chemists **113**

Flotation. New bulletin describes company's dispersed air flotation process for economical industrial waste water cleanup. Denver Equipment Div., Joy Mfg. Co. **114**

Services. Brochure tells of company's analytical, research, and process development service to laboratories. Roy F. Weston, Inc. **115**

Boiler deposits. Technical paper describes external and internal treatment for prevention or correction of boiler deposits. Betz **116**

Testing. Six-page brochure describes capabilities of company in air, water, and sound measurement. Company has 12 labs in U.S. and Canada and has fully equipped mobile laboratories. Commercial Testing & Engineering Co. **117**

Fan noise. Bulletin explains the relationships between ratings of fans and noise perceived by those in the vicinity. Aimed particularly at implications of recent Occupational Safety and Health Act regulations. Aerovent Fan Co. **118**

Flocculants. Bulletin describes new concentrated liquid form of polymers for flocculation and coagulation. The liquid form is claimed to dissolve more effectively than dry polymers, and booklet has pictures comparing liquid and solid dissolution. Nalco Chemical Co. **119**

Filters. Bulletin gives features of two types of horizontal tank-type filters: sluicing filters and dry cake discharge filters. Applications include waste disposal, food and beverage processing, and filtration of chemical solutions. The Duriron Co. **120**

Cloth filters. Brochure contains specs, dimensions and complete description of After-Filter line of cloth tube filters. The filters are designed primarily to remove dust from contaminated air and to return clean air into work areas. Filters that are equipped with exhausters are also described. Aget Mfg. Co. **121**

Water treatment. Brochure describes Cairox method of water treatment. Method uses oxidizing properties of potassium permanganate in small doses to destroy unpleasant tastes and odors and to remove iron and manganese. Carus Chemical Co. **122**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.

bookshelf

AMBIO, Vol. 1, No. 1. Eric Dyring, Ed. 42 pages. Royal Swedish Academy of Sciences, Universitetsforlaget, P.O. Box 307, Blindern, Oslo 3, Norway. 1972. $13 per vol. of 6 issues, paper.

A journal published by the Royal Swedish Academy of Sciences and devoted to the human environment. Concentrates on areas of environmental research and management. Divided into two main sections—the first includes overview and debate articles, and the second section consists of shorter reports of original environmental research. ■

Waste Treatment with Polyelectrolytes. Sidney Gutche. viii + 237 pages. Noyes Data Corp., Park Ridge, N.J. 07656. 1972. $36, paper.

Information in the book is based on U.S. patents relating to treatment of pollutant wastes with polyelectrolytes. Covers anionic, cationic, nonionic, and natural source polyelectrolytes; polyelectrolytes in general; synthesis of polyelectrolytes; and sewage treatment systems. ■

Metallic Contaminants and Human Health. Douglas H. K. Lee, Ed. xvii + 241 pages. Academic Press Inc., 111 Fifth Ave., New York, N.Y. 10003. 1972. $7.00, hard cover.

First of four books on the aspects of environmental health. Editor Lee hopes the text "will help those who need to know the state of current knowledge on the health significance of metallic contaminants." Covers arsenic, beryllium, cadmium, chromium, fluoride, lead, manganese, mercury, nickel, and vanadium. ■

Erosion and Sediment Pollution Control. R. P. Beasley, viii + 320 pages. Iowa State University Press, Ames, Iowa 50010. 1972. $11.95, hard cover.

Explains how erosion occurs, and evaluates the various factors that affect the degree and extent of erosion. Emphasizes the need for integrating mechanical, agronomic, and management practices into a plan that will control erosion, improve productivity of the land, increase the efficiency of the farm as a production unit, and reduce sediment pollution problems. ■

Mutagenic Effects of Environmental Contaminants. H. Eldon Sutton, Maureen I. Harris, Eds. xiv + 195 pages. Academic Press Inc., 111 Fifth Ave., New York, N.Y. 10003. 1972. $7.50, hard cover.

Discusses the current burden of mutation as human genetic disease, molecular biology of mutation, practical and feasible tests for screening potentially mutagenic agents, methods of determining the human mutation rate, interrelationships between mutagenesis, carcinogenesis, and teratogenesis, and a catalog of mutagens currently in use. ■

Biological Transmutations. Louis C. Kervran (English version, Michel Abehsera). Swan House Publishing Co., P.O. Box 638, Binghamton, N.Y. 13902. 1972. $5.95, hard cover.

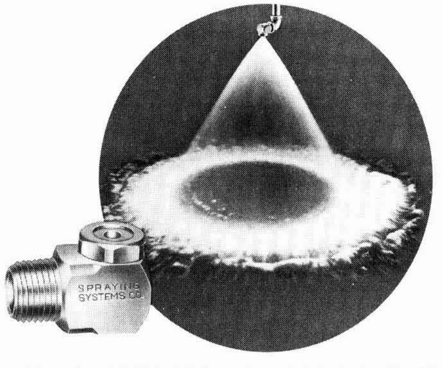
Describes how various elements change into others. Biological transmutation, say the publishers, can transmute radioactive wastes into harmless elements, and waste and garbage can be reutilized. ■

America's Land and Its Uses. Marion Clawson. x + 166 pages. Johns Hopkins Press, Baltimore, Md. 21218. 1972. $8.50, hard cover.

Designed for college students and general readers. A compact, nontechnical account of the nation's land and its uses—past history, present trends, and future possibilities. Separate chapters on the three great traditional uses—farming, grazing, and forestry—and on the two uses that present the greatest number of new problems—urbanization and outdoor recreation. ■

To Live on Earth. Sterling Brubaker. xiv + 202 pages. Johns Hopkins Press, Baltimore, Md. 21218. 1972. $6.95, hard cover.

Provides perspective on environmental threats and man's response to them. Says Stewart L. Udall, "Sterling Brubaker has written a book which has the balance and scope to encourage a problem-solving dialogue between industrialists and environmentalists." ■



August 21-24

Pennsylvania State Univ., EPA, and others

Symposium on Recycling Treated Municipal Wastewater and Sludge Through Forest and Cropland

University Park, Pa.

Purpose is to define the present state of the art of using the landscape for disposal of treated municipal waste water and sludge. Write: Conference Center, Continuing Education, J. Orvis Keller Bldg., Pennsylvania State University, University Park, Pa. 16802

August 20-25

Engineering Foundation

Particulate Matter Systems Conference

Saxtons River, Vt.

Conference fee: $160. Contact: Engineering Foundation Conferences, 345 E. 47th St., New York, N.Y. 10017

August 27-30

American Institute of Chemical Engineers

73rd National Meeting

Minneapolis, Minn.

Includes many sessions on environmental topics. Contact: American Institute of Chemical Engineers, 345 E. 47th St., New York, N.Y. 10017

August 27-September 1

American Chemical Society

164th ACS National Meeting

New York, N.Y.

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

August 30-September 7

U.S. National Committee for the International Biological Program and others

Fifth General Assembly of the International Biological Program

Seattle, Wash.

Two main symposia: productivity of world ecosystems and human populations, urban and migrant. Contact: James S. Bethel, Chairman, Subcommittee on Local Arrangements, University of Washington, Anderson Hall AR-10, Seattle, Wash. 98195

September 6-7

American Flame Research Committee and U.S. EPA

Flame Days Symposium

Chicago, Ill.

Papers on combustion technology. Theme is "Pollutants from Continuous Combustion Sources: the Interface of Research, Development, Control Strategy, and Regulations." Contact: Secretary of the American Committee, A. A Putnam, Battelle, Columbus Laboratories, 505 King Ave., Columbus, Ohio 43201

September 11-12

American Medical Association

32nd Annual AMA Congress on Occupational Health

Chicago, Ill.

Contact: AMA, 535 N. Dearborn St., Chicago, Ill. 60610

September 11-13

American Society of Mechanical Engineers

1972 Aviation & Space Conference

Anaheim, Calif.

Sessions will cover aerospace technology relating to environment, public safety, medicine, public service, transportation, and energetics. Write: J. J. Donohue, Jr., Manager, Conferences and Divisions, 345 E. 47th St., New York, N.Y. 10017

September 11-13

Marine Technology Society

Eighth Marine Technology Society Conference and Exposition

Washington, D.C.

New feature is federal briefing session of what is being done about marine environmental quality. Write: Marine Technology Society, 1730 M St., N.W., Washington, D.C. 20036

September 13-15

IEEE

1972 IEEE International Conference on Engineering in the Ocean Environment

Newport, R.I.

Contact: OCEAN 72, Newport Harbor Treadway Inn, Newport, R.I. 02840

September 17-20

American Mining Congress

1972 AMC Mining Convention

San Francisco, Calif.

Will cover international and national policies, environmental aspects, mineral processing, geology, and other related topics of mining. Contact: American Mining Congress, 1100 Ring Bldg., Washington, D.C. 20036

September 17-20

Canadian Pulp & Paper Association

Seventh Air & Stream Improvement Conference

Vancouver, B.C., Canada

Write: R. A. Joss, CPPA, 2300 Sun Life Bldg., Montreal 110, Que., Canada

September 17-21

American Society of Mechanical Engineers

Joint 1972 Petroleum and Pressure Vessel & Piping Conference

New Orleans, La.

Includes environmental sessions on water and air pollution abatement, pollution control at the well, practical correction of noise, liquid line leak detection, and control of hydrocarbon emissions. Write: Paul Drummond, Manager, Conferences and Divisions, ASME, 345 E. 47th St., New York, N.Y. 10017

September 18-21

Canadian Society for Chemical Engineering and others

Sixth Canadian Chemical and Process Equipment Exhibition

Toronto, Ont., Canada

Major emphasis on pollution control techniques and equipment. Contact: James T. S. Creighton, Show Manager, Canadian Chemical and Process Equipment Exhibition, 1450 Don Mills Rd., Don Mills, Ont., Canada

September 18-22

International Assoc. of Water Pollution Research and AIChE

International Conference on Applications of New Concepts of Physical-Chemical Treatment Process Design

Nashville, Tenn.

Will explore new concepts and engineering applications of physical-chemical treatment to municipal and industrial waste waters. Write: W. W. Eckenfelder, Box 6222, Station B, Vanderbilt Univ., Nashville, Tenn. 37235

September 19-21

American Nuclear Society

20th Remote Systems Technology Conference

Idaho Falls, Idaho

Topics include hot cell operations, radiation source processing, fuel handling, and other related subjects. Write: J. P. Bacca, Technical Program Chairman, RSTD Topical Meeting, P.O. Box 2196, Idaho Falls, Idaho 83401

September 19-22

Technical Association of the Pulp and Paper Industry

1972 Secondary Fiber Pulping Conference

Buffalo, N.Y.

Theme "Technology of Secondary Fibers." Contact: H. O. Teeple, TAPPI, One Dunwoody Park, Atlanta, Ga. 30341

meeting guide

September 24-27
U.S. EPA
National Environmental Information Symposium
Cincinnati, Ohio

Forum for producers and handlers of environmental data to identify and explain resources and methods. To bring together groups and organizations to share objectives and interests related to the production, use, and dissemination of environmental information. Contact: Gilbert M. Gigliotti, Director, Public Affairs Office, National Environmental Research Center, U.S. EPA, Cincinnati, Ohio 45268

September 28-29
Paper Technology Foundation, Inc.
Thirteenth Annual Meeting
Kalamazoo, Mich.

Contact: Paul W. Bartholomew, Executive Secretary, Paper Technology Foundation, Inc., Western Michigan Univ., Kalamazoo, Mich. 49001

September 28-30
American Assoc. of Textile Chemists & Colorists
National Technical Conference
Philadelphia, Pa.

Contact: George P. Paine, AATCC, P.O. Box 12215, Research Triangle Park, N.C. 27709

October 2-3
American Medical Association
1972 Air Pollution Medical Research Conference
Chicago, Ill.

Sessions on familial and inherited response to air pollution, air pollution and human illness, health effects research, and epidemiology. Write: Department of Environmental, Public, and Occupational Health, American Medical Association, 535 N. Dearborn St., Chicago, Ill. 60610

October 8-13
Water Pollution Control Federation
WPCF Conference
Atlanta, Ga.

Write: Robert A. Canham, WPCF, 3900 Wisconsin Ave., Washington, D.C. 20016

October 9-12
Association of Official Analytical Chemists
86th Annual Meeting
Washington, D.C.

Papers on analysis of feeds, fertilizers, food additives, pesticides, and related subjects. Contact: L. G. Ensminger, Executive Secretary, AOAC, Box 540, Benjamin Franklin Station, Washington, D.C. 20044

October 9-12
Instrument Society of America
27th Annual ISA Conference
New York, N.Y.

Includes papers on major sectors of instrumentation and automatic control including pollution control. Write: R. I. Gray, ISA Conference Program Chairman, 400 Stanwix St., Philadelphia, Pa. 15222

October 10-11
Industrial Health Foundation
37th Annual Meeting
Pittsburgh, Pa.

Discussions will cover standards for OSHA, toxicology, industrial hygiene engineering, and other related topics. Contact: IHF, 5231 Centre Ave., Pittsburgh, Pa. 15232

October 11-19
Institute of Sanitation Management
15th Annual ISM National Conference and Exposition
Philadelphia, Pa.

Will cover federal environmental standards, planning, and assistance; economics; and education. Write: ISM, 1710 Drew St., Clearwater, Fla. 33515

October 24-26
Engineers Society of Western Pa.
33rd International Water Conference
Pittsburgh, Pa.

Write: W. M. Porter, Secretary, Engineers Society of Western Pennsylvania, William Penn Hotel, Pittsburgh, Pa. 15219

October 24-28
Federation of Societies for Paint Technology
50th Annual Meeting
Atlantic City, N.J.

Includes topics on air pollution control, water pollution control, and solid waste disposal. Contact: Federation of Societies for Paint Technology, 121 S. Broad St., Philadelphia, Pa. 19107

October 25-26
New York State Action for Clean Air Committee
Eighth Annual Symposium on the Environment and Health
Syracuse, N.Y.

Theme "Environmental Education for the Adult Public." Write: New York State Action for Clean Air Committee, 105 E. 22nd St., New York, N.Y. 10010

Courses

August 21-23 and 24-25
University of Texas at Austin
Air Pollution Short Courses
Austin, Tex.

Fee $150 for Engineering the Control of Air Pollution: Fundamentals and $125 for Engineering Applications for Air Pollution Control. Both courses for $225. Write: Engineering Institutes, College of Engineering, c/o Division of Extension, The University of Texas at Austin, Austin, Tex. 78712

August 22-26
Utah State University and others
Multi-level Analysis of Complex Water Resource Systems Short Course
Logan, Utah

For engineers, planners, and public officials. Fee: $75. Contact: Robert W. Hill, Utah Water Research Laboratory, Utah State Univ., Logan, Utah 84321

August 29-31
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September 6-December 22, January 30-May 25
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September 11-13, 18-20
Coulter Electronics, Inc.
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Covers the measurement, sampling, and recovery of particles from process streams. Write: Shepard Kinsman, Fine Particle Group, Coulter Electronics, Inc., 590 W. 20th St., Hialeah, Fla. 33010

(Continued on p 762)

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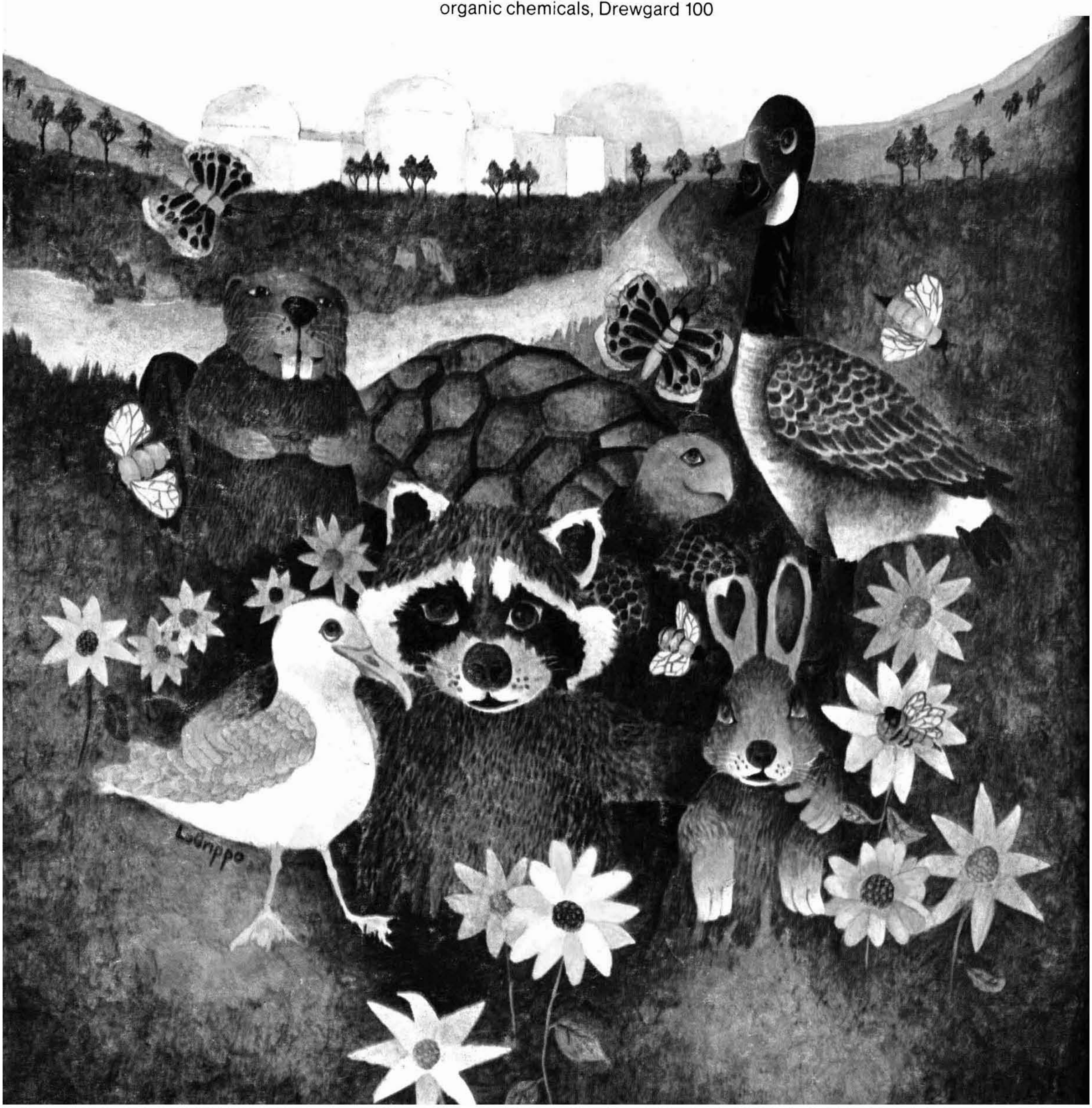
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