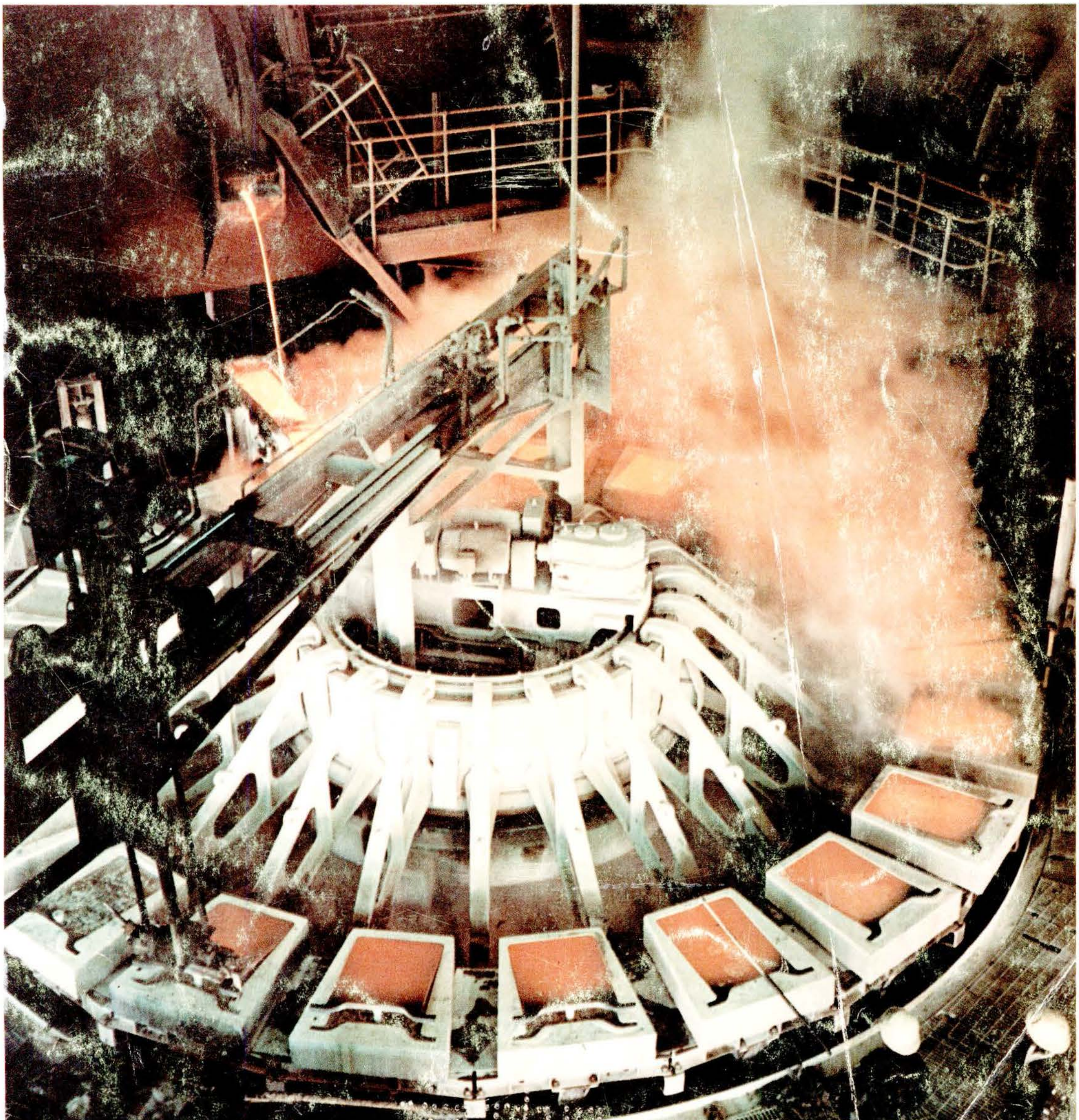
JULY 1970

ENVIRONMENTAL Science & Technology



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ENVIRONMENTAL
Science & Technology

Volume 4, Number 7
July 1970

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Published monthly by the American Chemical Society, from 20th and Northampton Sts., Easton, Pa. 18042. Executive Offices, Editorial Headquarters, and Subscription Service Department, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Advertising Office: 142 East Ave., Norwalk, Conn. 06851. Second class postage paid at Easton Pa. 18042.

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letters

Pollution control: economic problem

DEAR SIR:

Mr. Doan (ES&T, Viewpoint, March 1970) says that if the process of change were linear, our pollution problem would be much easier to solve. Then he makes no attempt to find linearity. Progress is made by taking one step at a time. We make decisions by balancing incremental advantages. On this level, change is linear and there is no need to invent new mechanisms or social processes.

The trouble is not that the problem is not linear, but that we are confused by the insistence of many people that the problem is more social or political than economic. We don't know much about solving social problems on this scale, so we resort to blindly spending more and more tax money . . . on more and more research . . . bureaus on bureaus . . . tax credits . . . subsidies . . . handouts, etc.

Why can't we consider the problem as a purely economic one? Aren't waste and destruction economic losses? As individuals we place monetary value on social activities and even aesthetic delectations. It's our way of life, so why change our preferred frame of reference for working out our environmental problems? The logical common denominator for balancing the so-called benefit-risk equation is the good old dollar. And there is no reason why social and political aspects cannot be weighed in, too—even wildlife, the ole swimming hole, and the loss of peace and quiet—in fact, practically everything we value.

Put in purely economic terms, the problem becomes solvable. The solution lies at the point of diminishing returns where the incremental cost of pollution abatement equals the incremental value of improvement—the point where overall costs are minimized. Economics can and should dictate those priorities that Mr. Doan wants established. Is there any other way to set priorities for the investment and expenditure of money?

Of course, it won't be easy to put a value on some items, but it can be done. We have many methods at our disposal. Technical people forget that prices are more frequently set in the marketplace than in the laboratory or at the estimator's desk, and that our courts are able to award damages for the most unusual offenses. Setting monetary values on destruction caused by each pollutant can be done, and it should be done if we are to approach our environmental problem in an economical fashion. Knowing what damages our effluents cause would make it possible for us to determine the best equipment in each case for minimizing overall costs. Optimization, only possible with this knowl-

(continued on page 536)

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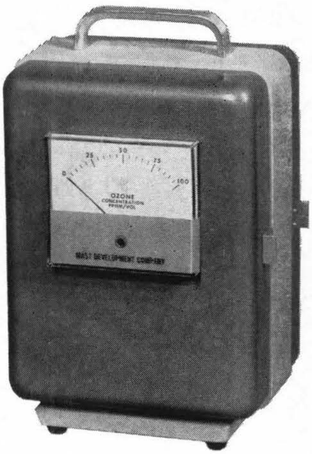

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edge, would be most beneficial for the whole population. Possibly, we can save tens of billions annually by optimizing the use of our abused environment.

How can we force polluters to install the optimum equipment? We can't, but the government can provide the needed incentive by levying a pollution tax equal to *pro-rata* damages caused by each pollutant. License to pollute? Yes, but not the free license to pollute at arbitrarily set permissible levels in accordance with present procedures which have been proven so ineffective. Government handouts are getting some treatment plants built, but there is much attrition as the tax money passes through many hands, and restrictions cause many other inefficiences. Why not let our old reliable profit motive do the work for us? Not consistent with other approaches? I should hope not; we know how ineffective and costly they are. Sure, there are too many taxes already, but it would not increase our overall tax burden (based on what the government spends), while the subsidy approach does increase the burden. Taxing pollution may not be required, but how else can we get the polluters to consider seriously the economic aspects of damages they inflict on the public?

But we are premature in discussing answers before we have decided what we are talking about in the first place. So it's high time we stop talking about abandoning our old methods (the free enterprise system?) and start defining our problem in terms we are capable of understanding.

James O. B. Wright
Consulting chemical engineer
Chattanooga, Tennessee 37402

Plastics study at Battelle

DEAR SIR:

I have noticed in the April 1970 issue of ES&T an error which I should like to bring to your attention. The lead item on page 272 in the section, "Environmental currents," credits a study made three years ago on the role of plastics in solid waste to New York University. I should like to advise you that this research was done at Battelle's Columbus laboratories under sponsorship of the Society of Plastics Industry, Inc. NYU had no role in this original study on plastics problems in solid waste. We note with interest, however, that our former colleague, Elmer Kaiser, has been selected to conduct further investigations in this problem area.

Neil L. Drobny
Environmental Research Group
Battelle Memorial Institute
Columbus, Ohio 43201

Address correction

DEAR SIR:

I would like to correct an error in the address given in my article "Air pollution control through new combustion processes," published in ES&T, May 1970, page 396. My correct address is: Pope, Evans, and Robbins, A Division of Perathon, Inc., Alexandria, Va. ES&T listed Arlington rather than Alexandria.

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Environmental agency idea makes sense

Administration proposal may not banish bureaucracy, but it may well remove some damaging conflicts of interest

The announcement that the Nixon administration is considering a proposal to establish a new environmental "superagency" hardly caught the country—and certainly not official Washington—completely by surprise. For some time it has been apparent that the administration is struck by the inefficiency attending fragmentation of responsibilities for the environment among many government departments. Senator Hugh Scott (R.-Pa.) has counted more than 90 separate federal environmental quality programs, 26 quasigovernmental units, and 14 interagency committees, all sharing in various (and often ill-defined) ways, responsibility for environmental efforts. In February, Senator Scott introduced into the Senate a bill (S. 3388) which would establish an Environmental Quality Administration to consolidate many of these functions into a single agency, and Senator Edmund Muskie (D.-Me.) has also introduced a bill with the same intent (S. 3677).

Mr. Nixon's apparent intention is to effect a reorganization by executive order, something that he has the power to do without the need for legislation if Congress does not veto the plan within 60 days of its introduction. Whether there will be Congressional objections—indeed, whether Congress will actually get to consider the proposal—remains to be seen at the time of writing, but it is certain that powerful interests have already been offended. This administration proposal involves removing several large agencies from government departments whose secretaries must surely have fought doggedly to retain their people and funds and the power that these resources represent. The plan would transfer to the new agency (tentatively called the Environmental Protection Administration) air pollution and solid waste management programs from the Department of Health, Education, and Welfare, water pollution programs from Interior, pesticide research and standard setting from the Food and Drug Administration, pesticide registration responsibilities from Agriculture, and radiation monitoring from the Atomic Energy Commission. Together with a companion proposal to transfer eight other agencies into an Oceanographic and Atmospheric Administration, the reorganization proposal would severely cut into the size of several departments, notably Interior.

What is most remarkable about the administration plans—if indeed they turn out to be plans and not just a case of a new idea being run up the flagpole—is that they do not stop at a consolidation of air pollution, water pollution, and solid waste management programs. Fragmentation of these three functions has been repeatedly criticized and their consolidation into one agency probably is inevitable, anyway; certainly this is provided for in both Scott's and Muskie's bills. But the unexpected strength of the Nixon proposal (one which Senator Muskie's bill also contains) is that it aims at removing the conflicts of interest within government agencies that have too often in the past hindered adoption of truly objective environmental protection measures. Is it, for example, really fair that the AEC should both promote the use of nuclear energy and be charged with the responsibility for setting radiation standards? Obviously, the administration thinks not.

Even if it is perhaps asking too much to expect a newly created governmental superagency to avoid the bureaucracy that has plagued its component parts, it is at least encouraging to think that the proposed reorganization recognizes the need for objectivity in setting and enforcing standards for protection of the environment. On that basis the reorganization makes a great deal of sense and the proposal deserves serious Congressional and popular consideration.

D. H. Michael Bowen

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Ronald Reagan
Governor of California

California sets clean-up pace

Governor Paul Laxalt of our neighboring state, Nevada, likes to tell a story about a friend from Southern California who was invited to spend a vacation at Lake Tahoe—a beautiful alpine lake that lies between our two states. The guest was awed by the cool, blue beauty of the lake and the majesty of the mountains that surround it. But he left for home after four days. "He was terrified," Paul explained, "to breathe air that he could not see."

There is no humor in this story for millions of Americans who have awakened to the fact that a booming economy and the "good life" are good for nothing if our air is too dirty to breathe, our water too polluted to use, our surroundings too noisy, and our land too cluttered to live decently.

In California we are waging a war against pollution on every front. Some of the things we have done and are doing are attracting nationwide and even worldwide attention. Our air is cleaner than it was several years ago, despite the increasing number of motor vehicles on our streets and highways. We have the toughest motor vehicle emission standards in the world, and they are going to get tougher. We are proposing laws that will regulate the makeup of gasoline to eliminate smog-causing gas evaporation and exhaust fumes from truck and auto engines. We will insist that every new vehicle sold in California be equipped with properly adjusted smog controls before it can be registered. Our Air Resources Board is developing an assembly-line method to test every 1972 model vehicle sold in California. We are already equipping some of our state vehicles with dual-fuel systems that will allow them to operate on more smog-free natural gas in metropolitan areas. We are cracking down on industrial and agricultural burning, and we intend to prevent a concentration of fuel-burning power generating plants along our coast by careful siting of these facilities.

Last year the legislature passed, and I signed into law, what the *Los Angeles Times* called "the strongest state water pollution control bill in U.S. history." It provides for fines up to $6000 per day against violators. Last year we adopted a pioneering program to control noise pollution. It calls for the cooperation of aircraft designers and airport operators in the muffling of jet noises. We have insisted that aesthetic and ecological values be given proper consideration in all types of public works—from roads to reservoirs. We have even rerouted highways to protect birds and wildlife.

My purpose in citing some of the steps we have taken to improve the quality of life in California is not to suggest that government can do the job alone. As a matter of fact, some industries are far ahead of government in tackling the problem of pollution. For example, two California private utilities have initiated a program for conversion of their vehicles to a dual-fuel operation to combat smog. One huge refining company has invested more than $10 million to control air and water pollution. A steel plant, through development of a modern recirculation system, has cut its water requirements for processing a ton of steel from 40,000 gallons to 1600 gallons, and a soap manufacturing plant has reduced its water needs from six million gallons per day to about 400,000 gallons.

Other industries are experimenting with methods to recycle waste products and are developing techniques that will lead to practical and beneficial uses for the things we discard. Industry is learning that there is no profit in pollution, and I believe that it must be encouraged to accept the cost of curbing pollution as a part of its normal business expense. I believe, too, that the manufacturer who does this should not be placed at a competitive disadvantage because his competitor does not share in this responsibility.

Free enterprise has given Americans more wealth, more freedom, and a higher standard of living than any other people on earth. It has opened the doors to the universe, and I know that if technology can put a man on the moon, it can bring him back to a world that is not cluttered with the refuse of our own excesses.

Ronald Reagan was elected Governor of California in November 1966

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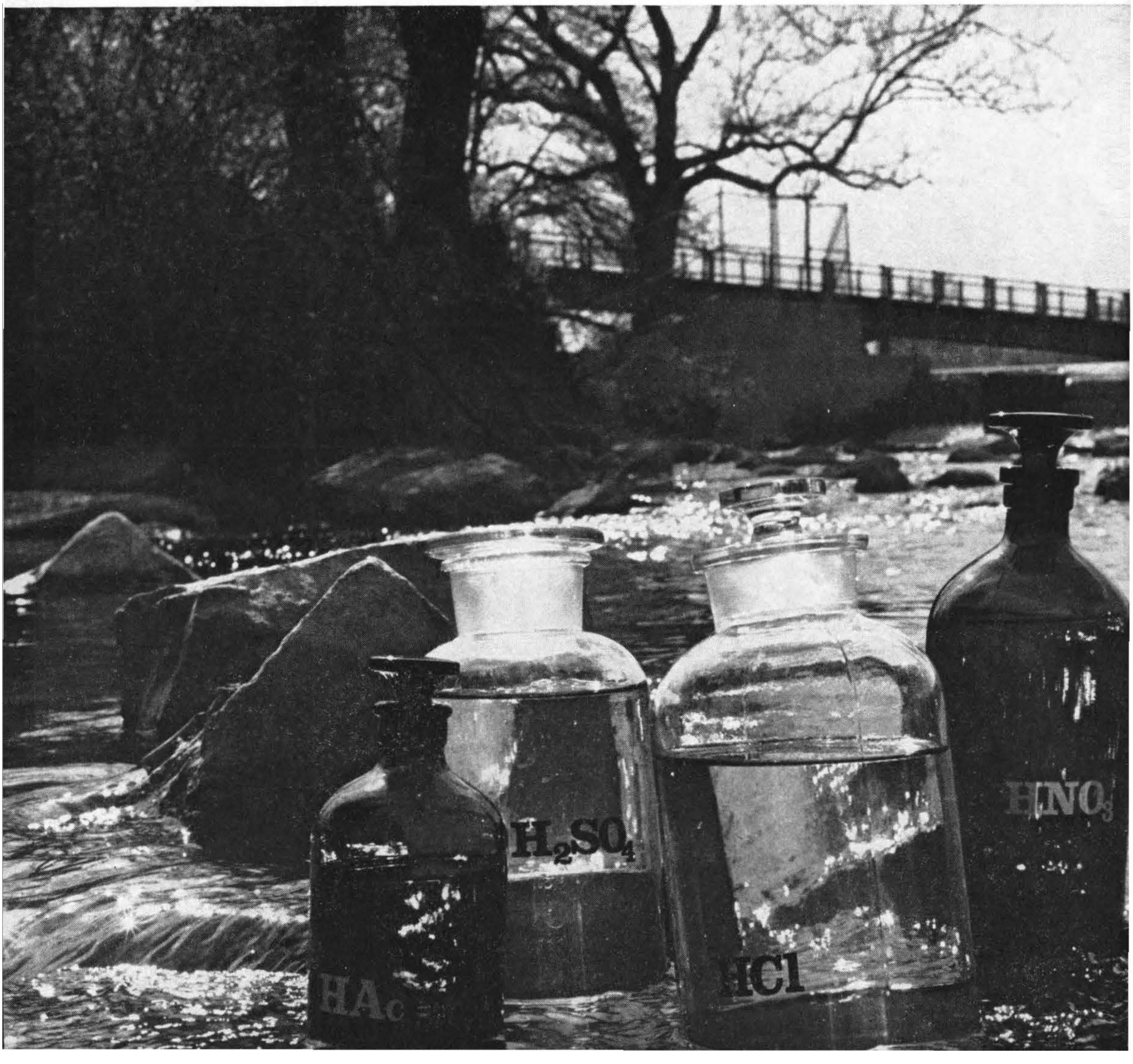

WASHINGTON

Leaded gasoline tax proposal draws Congressional ire

President Nixon's proposed excise tax on lead used in fuel additives drew strong comments from two leading Democractic senators. Sen. Edmund S. Muskie (D.-Me.) notes that the President could outlaw the use of lead in such fuels as gasoline; a provision to do so is contained in the administration's proposal, S. 3466, which would amend the clean air act. The proposal raises another question of public policy: Does the President intend to assign to the tax code, and to the tax code only, the job of protecting the public health from the effects of lead emitted by automobile exhausts? Sen. Warren G. Magnuson (D.-Wash.) notes that some might argue that the President has instituted a general revenue tax measure labeled as an environmental control tax.

FWQA moves simultaneously on several fronts

Two lakes, a river, a state, and five water polluters recently received pollution abatement attention from the Federal Water Quality Administration (FWQA). Last month's Lake Champlain enforcement conference tried to find ways to eliminate the buildup of sludge, while the fifth session of the Lake Erie enforcement conference began a campaign to curb mercury contamination. FWQA advanced recommendations for action in cleaning up the Potomac River by endorsing advanced waste treatment package plants as technological solutions to burgeoning economic and population growth in the Washington, D.C. area. Iowa is on record to provide secondary treatment statewide by the end of 1975. In addition, the Penn Central Railroad (N.Y.), General Aniline and Film Corp. (N.J.), Midwestern Feeding Co. (Neb.), and two municipalities (Kan. and N.D.), have been found in violation of water quality standards.

DOT sets up a noise abatement information center

The Transportation Noise Research Information Service is a new office for which the Department of Transportation (DOT) has funded the National Academy of Sciences. First year's funding amounts to $116,000 and will emphasize highway noise abatement. The new office will have four permanent staff members and an 11-member advisory committee. In addition to the information function, the new unit will • Synthesize information on selected, high-priority topics. • Recommend research and develop leading policies, standards, and procedures for alleviating transportation noise.

Senate airs additional water amendments

Hearings on proposed amendments to water pollution control legislation drew mixed reactions last month. In testimony before the Senate Subcommittee on Air and Water Pollution, Samuel Lenher, the Du Pont executive in charge of the firm's environmental control programs, noted that the administration's proposal (S. 3468) would require a total reexamination of pollution control programs in all 50 states. He went on to warn that changing direction in federal policies would have a disastrous effect on progress now being made. Further, Lenher • Endorsed stronger federal control of waste disposal at sea. • Warned about the probability of unfair application of a bill to establish a national schedule of effluent charges.


Du Pont's Samuel Lenher

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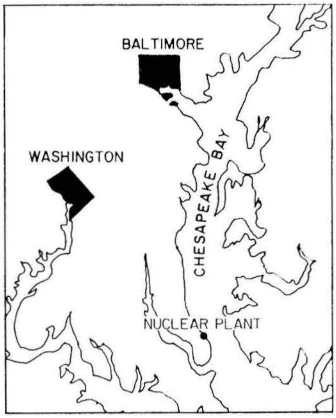
STATES

Georgia has first statewide pollution alert system

Georgia's "air-lert"—an air pollution alert—is an effort to get people to help cut pollution during critical periods by not dumping any more pollutants into the air than is absolutely necessary. Air-lerts will be broadcast on radio and television and publicized in daily newspapers. "It is going to be mostly an individual voluntary pollution control program during the alerts," says Robert H. Collom, Jr., director of the Air Quality Control Branch in the Georgia State Health Department. Jim Mullins, a meteorologist with the department says, "Based on previous years' records, Georgians can expect about six to eight major air pollution alerts in a year, occurring mostly in May and October when large masses of air stagnate over the state."



Maryland issues nuclear plant operational permit

The Maryland Department of Natural Resources (MDNR) recently issued its most restrictive permit ever for the operation of a nuclear electric power generating station on the waters of the Chesapeake Bay. Baltimore Gas & Electric Co.'s two nuclear units, with a combined capacity of 1750 megawatts, will use from 3.5–3.6 billion gallons of cooling water each day. But operation of the plant will be modified or stopped if adverse conditions develop, according to Paul W. McKee, director of MDNR. Limits are set on radioactive and thermal discharges, no chlorine or other biocide is to be used in the condenser system, the velocity of intake water must be low and that of discharge water high, and waters are to be taken from the lower depths of the bay.

Detroit reduces its air pollution burden

Uniroyal's tire manufacturing plant in Detroit, one of the largest tire plants in the world, has converted three boilers from pulverized coal to natural gas firing. The switch will eliminate up to 16 tons of particulate emissions each day as well as most of the noxious sulfur dioxide fumes usually associated with coal burning. Originally the company consumed more than 500 tons of coal and produced 40,000 tires daily. "Gas firing is initially more expensive than coal or oil but greater, long-range economies accrue from reduced equipment maintenance, cleaner operating conditions, and elimination of ash removal," says Morton Sterling, director of the air pollution control division of the Wayne County Department of Health.

Philadelphia continues crack-down on air polluters

Philadelphia proceeded with injunctive action against the Enterprise Rendering plant last month. "The problem was one of consistent strong odor emissions," says Edward F. Wilson, assistant commissioner for the city's Air Management Services (AMS). On four separate occasions, AMS inspectors visited the plant and noted excessive emissions. Enterprise Rendering, one of seven rendering plants in the city, represents the city's eleventh most troublesome pollution problem. The injunction says the company has not taken adequate steps to correct the situation and has failed to submit a schedule for compliance with Philadelphia's new code, according to Wilson. The action also requires the company to pay a mandatory fine of $300 per day for every day the violation continues.

TECHNOLOGY

Detroit sewage plant to use pure oxygen aeration

Detroit's Metro Water Department will become Union Carbide's first major customer for the Unox sewage oxygenation process commercialized by Carbide's Linde division earlier this year (ES&T, May 1970, page 374; February 1969, page 109). Metro's present plans call for an oxygen pipeline from Linde's oxygen plant at Ecorse, Mich., to a new 600-m.g.d. plant now being built on the Detroit River in downtown Detroit. Metro expects to save $6.6 million, or about 25%, in plant capital costs by using the pure oxygen aeration. Earlier testing by Carbide at Batavia, N.Y., indicated that operating costs, too, can be cut by using oxygen instead of air, perhaps by as much as 50% compared with the conventional activated sludge process.

Grace announces phosphate removal processes

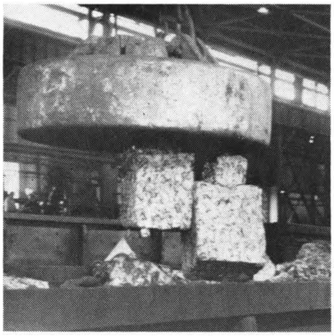
The Dearborn division of W. R. Grace Co. has developed a nonchemical method for removal of phosphate treatment plant effluents. The process is based on the thermal and/or vacuum decomposition of ammonium bicarbonate in the supernatant liquor from the digestor, which contains a high concentration of phosphates. The resulting increase in pH effects the precipitation of magnesium ammonium phosphate and other insoluble phosphates. The recovered compounds are reasonably high-grade fertilizer phosphates and could possibly be marketed as such, but a Grace spokesman says this would probably be feasible only for larger plants.

Used tire conversion plant planned by Firestone

The nation's first pilot plant for destructive distillation of used auto tires is under construction in Akron, Ohio. Firestone Tire & Rubber Co. is building the unit to confirm the encouraging results of preliminary experiments on the process undertaken with the cooperation of the Bureau of Mines in Pittsburgh (ES&T, February 1969, page 119). Joseph R. Laman, manager of environmental engineering for Firestone, says if the pilot plant shows the process is feasible, "and we think it will, we will set up 10 full-scale, 100,000 ton-per-year plants at strategic locations across the country." The Akron plant is expected to be operating by the end of the summer. The earlier Firestone-BuMines work showed that it was possible to produce from one ton of scrap tires as much as 140 gallons of liquid oils and 1500 cu. ft. of gas, equivalent in heating value to natural gas. The solid residue from distillation is a friable material of high carbon content.

Scrap cans make good steel

Tin-free steel cans can be successfully remelted into new steel, according to a three month test program conducted at National Steel's Wierton (W.Va.) works by the Carbonated Beverage Container Manufacturers Association and the Iron and Steel Institute. The tests, which incorporated up to 22 tons of scrap cans into basic oxygen and electric furnace heats, produced steel that could be teemed into ingots, rolled into slabs, and finished into marketable products without difficulty. Steel recovered from each heat was smaller than usual because of the aluminum and organic content of the charge, but chemical analysis of the product was normal. Reclamation and reuse of aluminum cans has already been demonstrated by Reynolds Metals Co. (ES&T, November 1969, page 1157).



Compacted steel cans

INDUSTRY

Trade group receives HEW grant for solid waste recycling

The National Association of Secondary Material Industries, Inc. (NASMI), has been awarded a $364,000 grant by the Department of Health, Education, and Welfare to undertake a study designed to expand opportunities for utilizing solid waste. The actual research study will be conducted by Battelle Memorial Institute (Columbus, O.), under contract with NASMI. According to NASMI technical director Si Wakesberg, the study will take one year to complete and will cover both technical and economic factors. The grant work will focus on scrap copper, aluminum, lead, zinc, nickel alloys and stainless steel, precious metals, paper stock, and textiles. At present, 30% of aluminum raw material supply is accounted for by scrap; comparable figures are 45% for copper and brass, 52% for lead, 20% for zinc, and 25% for paper stock, according to NASMI.

More detergent phosphate substitutions announced

Lever Bros. is the latest detergent-maker to follow the lead of Procter & Gamble, number one in the industry, in planning partial replacement of phosphates with nitrilotriacetic acid (NTA) in as many as nine of its products, the first of which will become available in July. What is likely to pace future inroads of NTA into detergent reformulations is its availability, now only 100 million pounds per year from Monsanto and Hampshire Chemical (W. R. Grace). But Sears, Roebuck & Co. will market a phosphate-free product developed by De Soto, Inc., a major Sears supplier, in which the ingredients were reformulated to achieve cleaning efficiency without a replacement for the phosphate.

Phosphate content of household detergents

Product	*% phosphate**
Biz	73.9
Axion	63.2
Salvo	56.6
Tide	49.8
Drive	47.4
Oxydol	46.6
Bold	45.4
Cold Water All	45.4
Ajax Laundry	44.6
Cold Power	44.6
Punch	44.2
Dreft	41.9
Gain	39.5
Duz	38.3
Bonus	37.5
Breeze	37.2
Cheer	36.3
Fab	34.8
Wisk (liquid)	14.2

* expressed as sodium tripolyphosphate

Source: FWQA

PR firm sets up unit to handle pollution control

Recognizing that public relations efforts in the field of pollution control require special expertise, the Chicago firm of Gardner, Jones & Cowell, Inc. (GJ&C), has established a separate group to help client companies identify and resolve problems of communication regarding their pollution control activities. The new group will be headed by Raymond A. Kulwiec, a former technical journalist, and will be able to call on other GJ&C groups for additional expertise where needed. Kulwiec tells ES&T that the GJ&C move is another example of a growing recognition within the public relations industry that pollution control deserves special communications capabilities. GJ&C is currently providing such services to companies in the pharmaceutical, paper, and metals industries.

Companies invest in air and water pollution controls

Tenneco Chemicals, Inc., has started up an equalization basin at its dyestuffs plant in Reading, Pa. The basin will prevent effluent surges from reaching the city of Reading treatment plant. **Continental Can Co.** has begun construction of a system that will remove colored matter and fibrous waste from effluent at a paper mill in Hodge, La. **Republic Steel Corp.** has broken ground at its south Chicago works for a $5 million electrostatic precipitator system to be used on open hearth furnaces. **American Oil Co.** plans to install $30 million worth of pollution control equipment at the Whiting, Ind., refinery. Included will be a fluidized bed incinerator for sludge disposal and a new sulfur recovery plant. American Oil has also brought on stream at Whiting a tertiary treatment plant using air flotation and chemical flocculation.

CEQ off to an ambitious start

Russell Train's aim is to give federal decision-makers an environmental conscience

The Council on Environmental Quality (CEQ) represents nothing less than a new experiment in government. It will test whether man is wise enough to manage his affairs in ways which recognize his essential interdependence with his environment. After only six months of existence it is, of course, too early to say whether or not CEQ will be successful in its mission. But if it exerts as effective an influence on environmental decision-makers that its sister organization in the Executive Office of the President—the Council of Economic Advisers (CEA)—exerts on financial decision-makers, then the new experiment in government truly will have been well worth the effort.

A basic thrust of CEQ is to ensure that environmental considerations are given careful attention and appropriate weight in all stages of planning and decision-making in every agency of the federal government. "If we can, in fact, cause fundamental changes in the decision-making process within the federal government, I can think of no greater contribution that our Council could make," says CEQ's chairman Russell E. Train.

Already, CEQ has immersed itself in a morass of environmental problems: agricultural pollution, automotive air pollution, junked automobiles, tanker oil spills, pesticides, ocean dumping, solid waste recycling, land use planning, dumping in the Great Lakes, the SST, the Alaskan pipeline, and a host of others. But more important is the fact that this month CEQ presented to the President the first report on environmental quality.

The report

Although unavailable at press time, CEQ's report promises to be a remarkable accumulation of information on the environment. The report is in a form that the general public can read and, hopefully, will find interesting and informative. It covers the air, aquatic, and land segments.

Certainly, finishing the report itself involved the synthesis and integration of myriad pieces of data into a comprehensible whole. However, the translation of environmental data and recommendations into legislative proposals for Congressional action is the challenging problem which still faces CEQ. Understandably, the short time between CEQ's inception earlier this year and its July 1 deadline explains its inability to set forth extensive model legislative proposals in this first report. (The July 1 deadline was set by the same piece of legislation that created CEQ—the National Environmental Quality Policy Act, P.L. 91-190.) Nevertheless, this is exactly CEQ's goal in subsequent reports and actions.

Reportedly, CEQ comments in the report on the international trend in environmental matters. One big, but as yet unanswered question still remains: Will strict U.S. environmental safeguards place the U.S. in an unfair economic disadvantage in world markets? Another question is: How can economic goals be reconciled with goals for the quality of life?

Approaches

To date, Train has announced the formation of several groups which will assist CEQ. They include a group on tax policy and another on the law. Coupled with the National Industrial Pollution Control Council (NIPCO), which was appointed by the President and which will work with CEQ, the approaches seem workable.

The Task Force on the Impact of Tax Policy on the Environment, a first advisory group, is faced with key questions:

"Certainly, if American business does not or will not participate in the task of building a better environment, the job will not be done. I think it will be."

- Do present tax policies encourage undesirable activities vis-à-vis the environment?
- To what extent and how should the tax structure be modified to induce individuals and corporations to meet environmental goals?

The 15-member group will examine the many aspects of the tax system; it will be looking not only at the incentives which can be developed for pollution abatement and solid waste recycling. It also will investigate disincentives which existing tax laws may contain. This group is headed by Prof. Dan Throop Smith, professor emeritus of Harvard Business School.

The second group, a 14-member legal advisory committee, will be studying law and administrative procedures relating to the protection of the environment. This committee will consider case studies and analyses of environmental legal problems. The committee's most important contribution might be

CEQ functions

- To prepare an annual report on the condition of the nation's environment.
- To report environmental trends.
- To coordinate the environmental programs of all federal agencies.
- To review and evaluate all existing and ongoing federal programs from the standpoint of environmental impact.
- To see that environmental factors are properly considered in decision-making.
- To submit policy and program proposals to the President.

". . . the time has come for business to stop looking at environmental quality as a problem and a cost and to start looking at it as a challenge and an opportunity."

its assistance in developing model laws and administrative regulations for use by state and local governments. Chaired by Whitney North Seymour, Jr., U.S. attorney for the southern district of New York, the committee is composed of distinguished lawyers and law school educators.

A third approach that CEQ will be taking involves dialogues with representatives of newly formed NIPCO (ES&T, May 1970, page 371), at a meeting this month. Later, NIPCO will be submitting a number of specific recommendations for future CEQ action, presumably through Commerce Secretary Maurice H. Stans. Ultimately, each of NIPCO's subcouncil chairmen from 29 industries will report on recent pollution control accomplishments within his industry, problems confronting that industry, what can be done in 1970, and timetables for accomplishing certain goals.

Train—the man

Russ Train, the nation's chief adviser on environmental policy, who reports directly to President Nixon, is no Johnny-come-lately on the environmental bandwagon. A highly respected, former tax court judge, Train first became involved with environment after returning from an African safari some years ago. He then became concerned with preservation of certain animal species. Subsequently, he was appointed president of the Conservation Foundation (Washington, D.C.) in 1965, was Nixon's choice for Undersecretary of the Interior, and now is Nixon's man for the environment.

Problem areas

Population growth and land use planning are some of the intertwining top problems of CEQ. The automobile and its air pollution burden, the SST, and mass transit are others. Together these problems cut across many boundaries and have broad impact.

Land use planning, one area where long-range goals have been neglected, is a must. At present, the federal government simply does not have a forum for the adjudication of different interests—those of industry, the private sector, and conservation groups—over the use of land for highways, airports, electric power stations, parks, and the like. No guideline is available to state and local officials on such matters. This lack of a forum has caused much public criticism and concern. Of late, the constant clash of power companies and conservation interests has received regular attention in the press.

The SST is simply an environmental outrage, according to a number of Congressmen. When completed in three or four years, the SST will have cost U.S. taxpayers $3–4 billion. Indeed, $290 million is requested in the Department of Transportation's (DOT) appropriation bill now before a Congressional committee.

Under P.L. 91-190, certain reports are required by the federal agencies commenting on the environmental impact of such programs; CEQ is the catalyst for coordinating these comments. However, the reports from DOT on the SST have not been made available to CEQ. So, the question Congressional leaders are asking is whether Congress should appropriate the $290 million or delay appropriations till DOT's environmental impact reports become available. Nevertheless, the same critical group of Congressmen believes that funds probably will be appropriated before such reports become available.

Several other environmental impact reports and statements from other federal agencies have been filed with CEQ. These submissions include:

- Interior's statement on the environmental impact of its proposed road from the Yukon River to Prudhoe Bay in Alaska.
- Transportation's statement on the construction of a highway in New Hampshire.

Future activities

With the present pressure to create a Congressional committee on environment and technology, it is not too early to predict annual hearings on environment, similar to those by the joint Congressional Committee on Economics, which annually conducts oversight hearings. Indeed, the 1968 colloquium on the environment served as the precursor for such events, and was hailed as a new experiment in Congressional hearings at that time. Plans also are being formed for a White House conference on the environment, scheduled later this year. Other activities might involve a joint CEQ-CEA study on the economic effects of environmental enhancement programs. Another is study of the impact of environmental standards on small business operations.

Environmental problems will probably get worse before the situation gets better, according to Train. Environment is not a fad, as far as he is concerned, although the public's interest, at times, is fickle, he is sure a deeper concern is here to stay.

Canada cracks down on pollution

Federal and provincial moves parallel U.S. efforts, with some important differences

Parliament. *Canadian government legislation usually has easy passage in Ottawa*

There are both similarities and differences between the U.S. and Canadian approaches to air and water pollution programs. Nevertheless, apparent progress is being made by our northern neighbors.

Some of the similarities are in organization. In both countries, control activities span a multiplicity of levels of governments. In the U.S., federal, state, and local governments are concerned with the problem. In Canada, the levels of concern are federal, provincial, and municipal. Like the U.S., Canada has no one agency responsible for environmental management at the federal level. Air pollution responsibility is vested in the Department of National Health and Welfare; water pollution is in the Department of Energy, Mines, and Resources; motor vehicle emissions control is in the Department of Transport, and so on.

Some of the differences result from the forms of government. In the U.S., competition exists between the legislative and executive branches, often over seemingly trivial points. In Canada, there is no separation of powers. Canada has what is called responsible government. The executive—the government—is responsible to the legislature and is an executive committee of the legislature. Unlike the U.S. government, when the Canadian government introduces a piece of legislation into Parliament in Ottawa, it usually passes. If it fails to achieve passage of important items, the cabinet is replaced by another one. In contrast to U.S. law, which usually spells out the specifics, Canadian law is permissive, enabling, and subject to regulations that the government passes later, from time to time. On the other hand, U.S. law is not usually subject to regulations that are spelled out later.

The consensus of key Canadian officials, at both the federal and provincial levels, is that now is the time to make a renewed thrust on environmental programs. Only recently, on the occasion of the 25th anniversary of the Chemical Institute of Canada (CIC), a two-day session on environmental pollution was held at the joint CIC–American Chemical Society meeting (Toronto, Ontario).

Provincial problems

In Canada, municipal and industrial wastes create serious air and water pollution problems. Water pollution alone costs the Canadian economy $1.2 billion each year, according to the Canadian Council of Resource Ministers. Nearly 70% of this cost is shared by two provinces—Ontario and Quebec. Ontario leads with $437.5 million; Quebec is second with $370.8 million.

Of the ten Canadian provinces, Ontario is the most highly industrialized. It is also further along and is setting the pace with its resource management and pollution control programs. Ontario's water program has been underway for more than 15 years. All other provinces now have similar programs, but they have gotten underway only within the last few years.

Of the ten, six provinces have ongoing air pollution control programs; four do not. Ontario's air program has a staff of nearly 200; but the air management staffs in other provinces do not number more than a dozen each.

The Ontario government is in the throes of requesting $92 million for its provincial air and water pollution control programs in the upcoming year. The provincial regulatory agency is the Ontario Department of Energy and Resources Management (ODERM).

"We want industry in Ontario. Make no mistake about that," says Gordon Hampson, executive assistant to George A. Kerr, the Minister of ODERM. "But we want clean industry."

Federal–water

The Canada Water Act (CWA), the controversial water legislation which has been gestating for the past two years, was passed by Parliament last month. The main thrust of the act is

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the joining of federal and provincial powers to move forward on water management on two paths:

- Comprehensive planning and water development.
- Water quality management agencies.

"The Canada Water Act is enabling legislation," says A. T. Davidson, Assistant Deputy Minister for water in the Canadian Department of Energy, Mines, and Resources. "The act is permissive; many options are open as to how it can be applied."

J. J. Greene, Minister of the Department of Energy, Mines, and Resources—the counterpart of the U.S. Department of Interior—personally piloted the CWA through Parliament. Greene is invested with the power to impose and administer the regulations.

"Primarily, it is not a water quality act, although this is the part that is discussed more than any other today," says Davidson. "It puts emphasis on comprehensive planning for water basin management and implementation of water goals by joint federal-provincial commissions or boards."

"In Canada, we have a bias that is a bit different . . . (from the U.S. on water quality)," Davidson explains. "We think that if you can establish management by basins and provide a large number of tools to those basin authorities as to how to achieve their water quality objectives, then over the long pull we get a better result.

"We do not believe it is sensible to try to establish and set national standards and enforce them by federal law all over the country," Davidson says. "We take the view that water quality management should be part of water management in general, and there should be a basin approach to it.

"Specific details are not spelled out in the act," Davidson reiterates. "Many options are open even now that the law has passed. The most likely option in dealing with the provinces is that where provincial water commissions or agencies have been set up and are operating effectively, then the federal government would only need to reach an agreement with these agencies on timetables for achieving water quality goals.

"Water quality management should be seen in the perspective of regional water management and regional development," Davidson says. "A good deal of the responsibility resides with the provinces, and it should reside there. The federal government does not intend to take over the job of water management across the country."

Provincial water spokesman Collins

"The one thing that is unique in Ontario is that every new development—industrial or municipal—has had to meet waste control standards before being allowed to develop."

The major federal concerns for water quality are:

- The Great Lakes, which cause international concern because of treaty obligations.
- The Ottawa River for which the provinces of Ontario and Quebec have failed to reach a water quality management program; the river is interjurisdictional.

Of the 25 amendments to CWA, the one receiving the most attention concerns nutrient additions to receiving waters. The other amendments are largely clarifying in nature. National Energy, Mines, and Resources Minister Greene already has stated publicly that he intends to propose regulations to the cabinet which would have the effect of banning, by August, the manufacture and import of laundry detergent containing more than 20% by weight P_2O_5. He intends to work toward a total ban in 1972.

Provincial-water

The Ontario Water Resources Commission (OWRC), a Crown corporation similar to the Tennessee Valley Authority in approach—was established under the provisions of an act of the Ontario provincial government in 1956. Primarily an engineering corporation, OWRC is in the business of constructing water supply and sewage treatment plants and performing comprehensive planning for development of an area. OWRC serves as the model for other provinces.

D. J. Collins, OWRC's chairman, has 18 years of government services, including three deputy assistant ministerial posts and is the full-time chairman of OWRC. "In Ontario, we have $2 billion worth of facilities in the ground—lines and plants; OWRC gets the money from the communities or the federal government," Collins says. "OWRC is a well balanced organization with concern both for water quality and water quantity. Every municipality in Ontario can qualify for full treatment. For the past ten years, every industry has been required to meet OWRC standards.

"The freezing on area development—perhaps, only possible in the Canadian form of government—is done by the Ontario Municipal Board (OMB). If OWRC is not satisfied with the waste control provisions in an area's development plans, the region is not allowed to develop."

On the other hand, Niagara Falls (N.Y.), is one example of an area which has been allowed to grow and develop at the same time that it continues to dump raw sewage into the river. The situation is similar in Quebec, a province in which growth and development have proceeded without proper waste treatment facilities.

Ontario has some 2000 water-using industries, and more than half are tied in with municipal treatment facilities. Some of the other half of the industries have completed their own treatment facilities, but not others.

The old industries are the big polluters," Collins says. "Pulp and paper and steel are still the major polluters. About half of the mills have treatment underway or planned at this time. Six or seven years ago, muncipalities

Provincial air spokesman Drowley

"We currently require all new stationary sources to obtain a permit of approval prior to construction and, of course, existing sources are required to conform with the specific regulations."

agreed to put in treatment facilities. Now, industries are in that position."

Federal–air

At the federal level, Peter M. Bird heads the Environmental Health Directorate in the Department of National Health and Welfare. "The directorate totals about 270 personnel and is divided into four divisions, one each for air pollution, public health engineering, radiation protection, and occupational health," Bird says.

Until a Clean Air Bill comparable to CWA is passed, Canada will not have a major federal–provincial program in air pollution control. However, John Munro, the Minister of National Health and Welfare, has indicated his intention to introduce a clean air bill to Parliament as soon as possible. It may be introduced in the fall session of Parliament.

"One of our first activities involved a joint meeting of federal and provincial air pollution control officials, which was held late last year," Bird elaborates. The following recommendations came from that meeting:

- To develop under federal leadership a comprehensive national air monitoring network.
- To develop national ambient air quality objectives.
- To formalize federal–provincial working level meetings on air pollution.

"We are nearing the final stage of completing a major air pollution study under the auspices of the International Joint Committee (IJC) in collaboration with other responsible agencies on the Windsor-Detroit air pollution problem." Bird concludes. The report is due later this year.

"The federal air pollution division was added on April 1, operates at a budget level of approximately $600,000 and is expected to grow to a staff of 29 by the end of the year," says S. O. Winthrop, chief of the division. The new division is focusing attention on an inventory of air pollution sources in federal facilities and advice to the Department of Transport on regulations for motor vehicle emissions controls.

Control of motor vehicle emissions in Canada follows the example of the U.S. federal government. Recently, Canada passed its Motor Vehicle Safety Act. Gordon C. Campbell, director of the motor vehicle safety branch in the Department of Transport, notes that regulations are currently being prepared and are expected to be ready for implementation on 1971 model vehicles. So any new vehicles sold in any province will have to meet these standards, which are equivalent to U.S. federal standards. But neither the Canadian nor, for that matter, the U.S. federal government has the responsibility or authority to ensure that the devices are maintained in good control. This is a job for the provinces and states, respectively.

Provincial–air

Provincial control of air pollution in Ontario began in January 1968. Prior to this time, the control power rested with the municipalities. Now Ontario's air management program is billed as the best operated and most comprehensive program in Canada.

W. B. Drowley, director of ODERM's air management branch, explains the provincial philosophy of setting emission limitations. "Ontario has set its emission limitations on the basis of maximum permissible one-half hour concentrations at ground level. This requirement means that we must check each individual source.

"Our procedure is to carry out an emission survey in the plant itself and to give the owner a written report with recommendations as to what he must do to obtain a compliance," Drowley elaborates. "This report is followed by a ministerial order—a legal document requiring compliance within a specific time. The normal appeals procedure is also included so that ODERM's air branch does not become too autocratic."

Commenting on air quality standards, Drowley says. "To me a standard is something that is legally enforceable. I have yet to see how you can enforce an air quality number on a multitude of sources unless you have the capability of being able to assess each individual contribution and require its curtailment.

"Recently, an air pollution index was introduced in metropolitan Toronto," the provincial control official explains. "It allows the curtailment of industry when the index reaches certain values." The index is based on a 24-hour running average of two pollutants—SO_2 and particulates—to produce a number which is based on data from previous air pollution episodes. The index number 32 signifies a desirable air quality. At values of 50–75, emissions may be curtailed. A value of 100 is equated with the beginning of an episode.

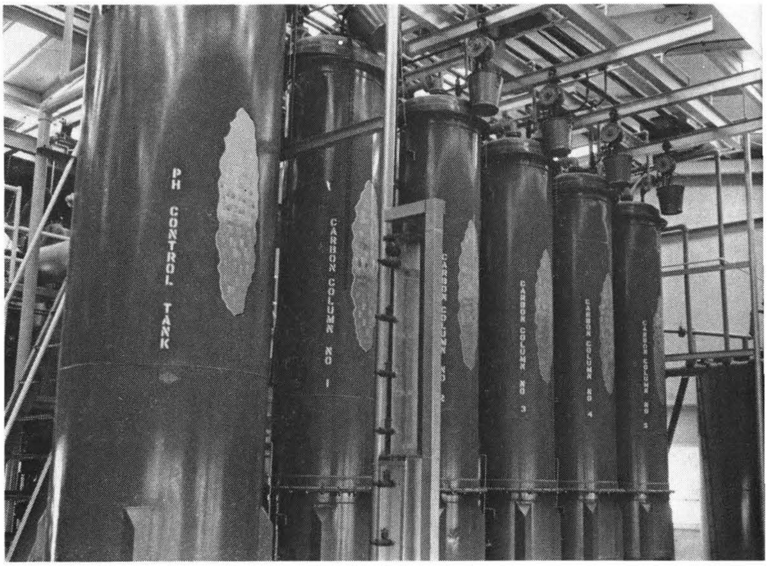
Looking ahead

In 1972, Canada will be sending its delegation to the United Nations meeting on the environment. The Canadian Department of External Affairs—the counterpart of the U.S. State Department—recently established a new division which has the major responsibility of preparing for the forthcoming Stockholm meeting. W. K. Wardroper, chief of the new division of scientific relations and environmental problems, is in the throes of preparing agenda items for the Canadian input to the conference.

The National Research Council of Canada announced a program which promises environmental solutions.

FWQA steps up tertiary treatment study

Pilot plant will evaluate four separate approaches to nutrient removal



Adsorption. *Carbon columns remove last traces of dissolved organic compounds*

Advanced waste treatment is a fairly general term for a broad technological area and in its various usages is often applied to anything from modification of existing treatment practices to such comparatively exotic techniques as gamma irradiation or reverse osmosis. At the Federal Water Quality Administration (FWQA) and the District of Columbia's advanced waste treatment pilot plant in Washington, D.C., however, the common working definition of advanced treatment is an integrated system that can reduce residual pollutants lower than conventional primary and secondary treatment. Within this context, the FWQA-D.C. pilot plant, completed about three years ago, has been studying a wide range of individual treatment steps, including lime precipitation, mineral addition, activated carbon adsorption, oxygenation processes, ion exchange, and sludge handling procedures. Just recently, the pilot plant has undertaken its most ambitious program to date—a side-by-side evaluation of four treatment combinations which show the greatest potential for high level treatment, including better than 90% nutrient removal capability. The study has only recently gotten underway, but Fred Bishop, supervisory research engineer at the pilot plant, confidently says, "We expect to have some fairly definitive results ready for publication in the next ten months."

Four processes

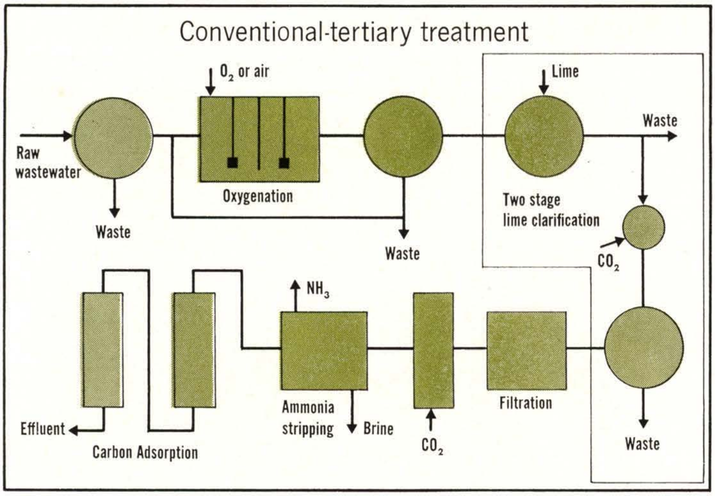
All of the treatment sequences under investigation include processes that have, as yet, found little or no use in municipal waste water treatment. Three of the sequences include conventional primary treatment and secondary biological processes, followed by tertiary nutrient removal steps. Another, an independent physical–chemical system, relies primarily on nonbiological means for both organic and nutrient removal.

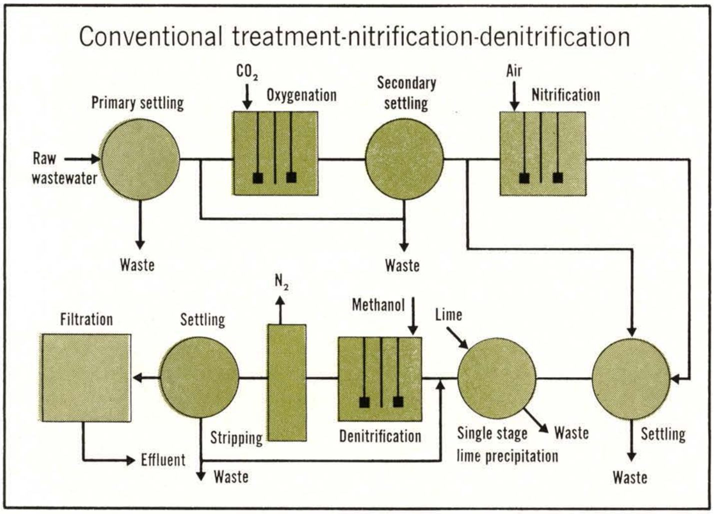
The main features of the treatment sequences—which qualify them as advanced waste treatment—are the capabilities for phosphate and nitrogen nutrient removal. Lime precipitation for phosphate removal, the step for which the pilot plant has accumulated the most data in its two-and-a-half years of operation, is common to all three systems, in either of two basic modes of operation. In the two-stage process, consisting of two clarifiers and a recarbonation tank, the calcium carbonate produced in the recarbonation step is settled in the second sedimentation basin. In single-stage operation, need for the second clarifier is eliminated by precipitation of the excess calcium ions in the first clarifier with sodium carbonate. In one sequence, mineral addition is used for phosphorus removal, wherein aluminum or iron salts are added in the secondary aeration step. Two alternate approaches, biological or physical–chemical, are available for nitrogen removal.

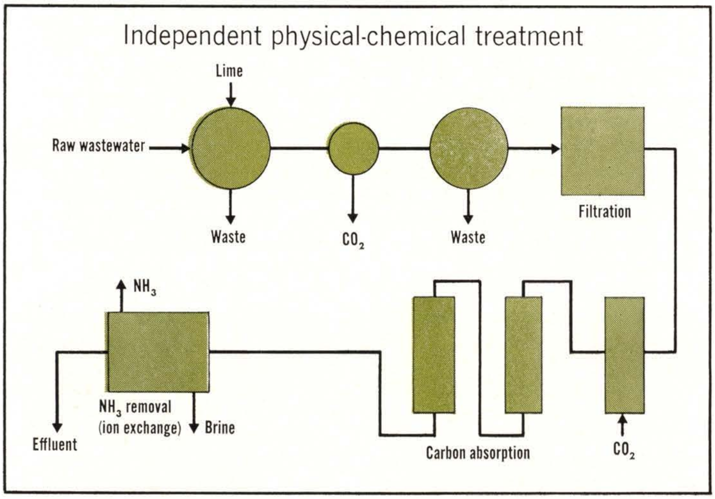
Conventional-tertiary

In the first conventional-tertiary process, after primary sedimentation of the raw waste water, the effluent is biooxidized, either by conventional aeration or with pure oxygen. After settling the secondary solids, the effluent is treated with lime in a two-stage clarification step. Following pH adjustment, the effluent from the second clarifier is treated in a stripping column for nitrogen removal, as ammonia. The final step prior to chlorination and discharge is activated carbon adsorption in a polishing column, to remove the last of the dissolved organic matter. In this process, as well as in the others using lime, recovery of the lime used for phosphate removal is possible. Calcium carbonate from the clarifiers is calcined to regenerate the lime for reuse and produce carbon dioxide for use in the carbonation steps.

The second of the conventional-tertiary processes differs from the first in the nitrogen removal step. Following solids removal from the biooxidation process, the effluent is then reoxygenated to nitrify it, converting the nitrogen from the ammonia form to nitrates. This is followed by single-stage lime precipitation and then by biological denitrification in an anaerobic bacterial process, (as opposed to aerobic bacterial treatment in the secondary aeration). Methanol is used as food for the dentrifying bacteria, and the denitrification may be carried out in a tank or in activated carbon columns. A third system being studied uses biological nitrification–denitrification, but alum is added in the first biooxidation stage to remove phosphorus, eliminating the lime precipitation step from the system.


Conventional-tertiary treatment


Conventional treatment-nitrification-denitrification


Independent physical-chemical treatment

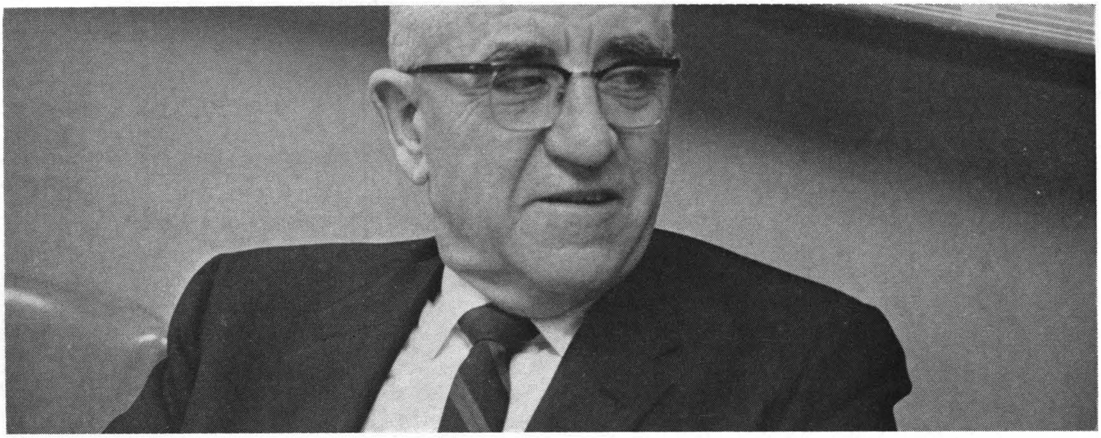
Nonbiological treatment

The other process being evaluated, the independent physical–chemical treatment, bypasses the conventional primary and secondary treatment steps. Instead, the incoming raw waste water is treated with lime in a two-stage clarification process. The effluent from the phosphate removal step is treated in carbon adsorption columns and then undergoes physical–chemical nitrogen removal. The pilot plant staff is studying the possibility of using ion exchange for removing the nitrogen as ammonium ions in conjunction with Battelle Memorial Institute, which has set up an ion exchange unit at the pilot plant, under an FWQA grant. However, ammonia stripping still remains a possible alternative for nitrogen removal in this process but must be employed immediately after lime precipitation.

The independent physical–chemical process, on the surface, appears to be the most attractive, in view of its simplicity, low capital cost, and small land area requirements. Indeed, this process has already been the subject of considerable enthusiasm both within FWQA and elsewhere. But according to pilot plant supervisor Bishop, such speculation is as yet premature. "We can't make any substantive comment on the superiority of any of these systems on the basis of our limited results so far," he says. As to projected costs, he wryly notes that "they'll be more expensive than conventional treatment," and then adds that although the systems are relatively new and untried, they comprise most methods that have reasonable potential for municipal waste water treatment.

Bishop and his staff hope to have some preliminary results on their work ready for presentation this fall and more detailed results in a series of papers to be presented at a meeting of the American Institute of Chemical Engineers in Houston next March. "We hope to have some reliable cost estimates by then," says Bishop.

Purdue conference keeps rolling along



Ringmaster. *Don E. Bloodgood is the driving force behind Purdue Industrial Wastes Conference*

The 25th annual Purdue Industrial Wastes Conference, which has been attacking the subject of industrial pollution since 1944, was held at Purdue University in May. The conference has grown in reputation as well as in size—from 200 attendees in 1944 to over 800 at this year's gathering—yet in format and function it has remained essentially unchanged over the years.

Originally designed as a service to Indiana agriculture and industry (the rationale for its status as a Purdue extension program), the conference nevertheless has broadened sufficiently to be considered at least a Midwest regional affair, if not perhaps a truly national one.

Function defined early

The driving force behind the organization of the conferences, and chairman of all 25, is Don E. Bloodgood, professor of civil engineering at Purdue. Reflecting on the early years of the conference's history, Bloodgood recalls that it was initially rather difficult to get papers from industry: "In those days, people were not so willing to talk about their problems as they are today." Yet representatives of the dairy, brewing, and canning industries in Indiana did indeed discuss their problems at the 1944 conference, and in the presence of many Indiana government officials, thus setting a precedent for the open exchange of ideas and information that has persisted as the main function of all subsequent conferences. Although other industries—petroleum refining, meat packing, and paper manufacturing, for instance—now are on the programs, the agriculture-related industries of Indiana and neighboring states still represent the core of each conference.

It would possibly be unfair to Bloodgood's hard-working associates on the conference organizing staff to describe him as the ringmaster, but nevertheless that seems an apt description. There is no program committee; the final decisions on the suitability of any paper for presentation are made by Bloodgood himself. Working through what he describes as "an informal, worldwide network of 50–60 people," Bloodgood keeps on top of advances in industrial waste treatment and each year invites participants to the conference. In 1970, 150 unsolicited papers were submitted but not accepted for presentation.

At any one time during the conference (which lasts for three days) there are six concurrent sessions, a matter of some aggravation to those who want to hear everything. But Bloodgood is adamant: he wants to cover all of the very broad field of industrial wastes and realizes that to do so he needs a large number of papers (103, at the 1970 conference). An attempt is made to reduce potential conflict between simultaneous papers but, naturally, some tends to occur.

Another matter on which the ubiquitous chairman is adamant is the length of each presentation—30 minutes for the paper and 30 minutes for discussion. Session chairmen who do not abide by the rules are likely to be chided by Bloodgood who has been sitting quiet and unnoticed in the back of the room. Discussion at the conference is lively and stimulating; any discusser who doesn't maintain audibility, however, runs the risk of being sternly reprimanded: "There's a private discussion going on down there, and Bloodgood doesn't like private discussions!"

Recipe for success

The success of the Purdue conferences—and they are by most measures very successful—is probably due to the subject matter, which is almost wholly technical and is treated in an unabashedly pragmatic way. The attendees are, by and large, technical men rather than managers. The practical approach, coupled with the enjoyably human aspects of the conference, makes for a most educational three days. Where else can you hear, on the same program, a federal official ruefully confessing that he has been banned from local fishing contests because of his access to 7-lb. black bass killed by feedlot runoff, a chicken farmer attributing the lack of solid waste disposal problems in his hen houses to "the will of God," and a refinery engineer describing new techniques for waste water treatment?

There are lingering problems, of course. Attendees annually curse the unavailability of papers at the conference and bemoan the fact that conference proceedings are rarely published within 18 months. But these seem small prices to pay for the privilege of attending a conference that really has a function, and actually comes quite near in fulfilling it.

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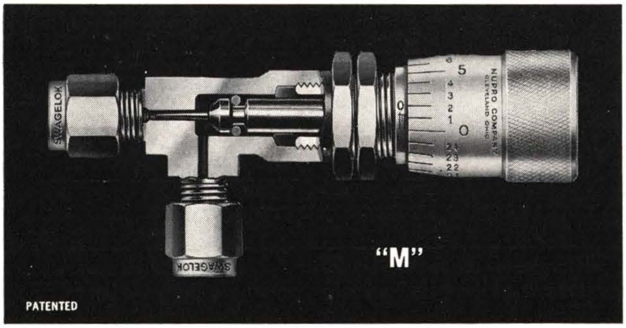

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SO_2 from smelters:

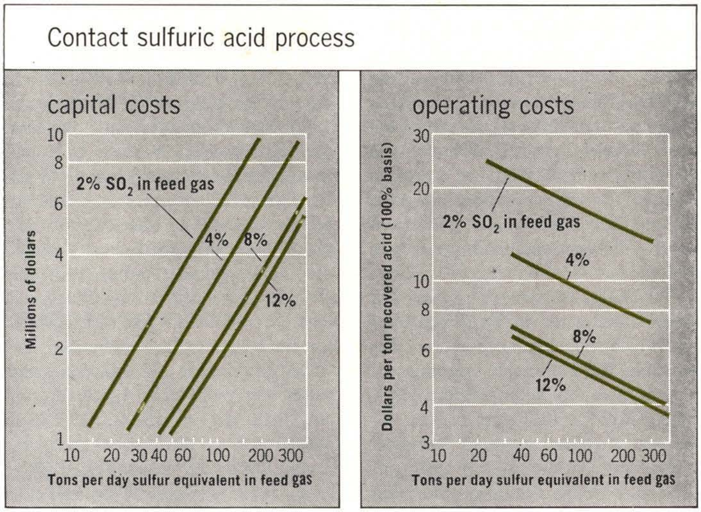
Three processes form an overview of recovery costs

Some 2.2 million long tons per year of sulfur is contained in the sulfur oxide gases generated in the operation of copper, zinc, and lead smelters in the western U.S. Nearly 23% of this is recovered, almost all as sulfuric acid. More acid can be made where markets are available, but many smelter gas flows are too dilute for economic acid manufacture. Costs for concentration of these gases by presently known processes are excessive. To make clear the technological and economic factors bearing on the problem of controlling these sulfur oxide emissions, we undertook a study of primary copper, zinc, and lead smelting operations.

A necessary first step was to learn how much sulfur oxide was being generated, how much was recovered in any form, and how much was getting into the atmosphere. More knowledge was needed about the sources of emissions in the smelters, about the concentrations of the gases, and about the problems involved in controlling emissions, as well as about the methods for sulfur oxide recovery now in use or available for use.

Technical personnel familiar with the industry visited the smelters in 1968 to obtain such information as the amount of sulfur entering each plant in sulfide ore concentrates, and the amount leaving in gases at major

Smelter. *Almost half a million tons of sulfur is recovered every year from western smelters, but three times as much is still discharged into the air*


Contact sulfuric acid process

operating steps. We also looked into the volumes of gases generated or emitted from the various sources, gases fed to recovery units, stack gases, amounts of recovered by-products, and sulfur remaining in the solid residues. No actual measurements or analyses were made during the visits, so the information obtained was limited to what could be made available from operating files at each smelter.

After this information had been gathered, material balances were calculated for each plant. The complexity of operations at copper smelters is such that satisfactory balances for these plants required the development and use of a computer program. The figures obtained should not be viewed as absolute, for in some areas information available was incomplete and may have been inaccurate. In compiling the statistics, allowance was made for changes in smelter operations planned for the last part of 1968 or the first half of 1969. Two new lead smelters in Missouri are not included in the statistics.

A total of approximately 2,165,000 long tons of sulfur is contained in the sulfur oxide gases generated annually at the U.S. copper, zinc, and lead smelters west of the Mississippi River. Of this, 491,000 long tons or 22.7% is recovered; 487,000 tons as sulfuric acid and 4000 tons as liquid sulfur dioxide. The remainder of 1,674,000 tons is emitted to the atmosphere. The quantities of sulfur oxides, in terms of sulfur equivalent, generated and recovered from various sources are presented in an accompanying table.

Weak smelter gases

Recovery of sulfur oxides from smelter gases is difficult because many of the gas streams, at the points where they could be diverted to a recovery process, have been diluted with air and the concentrations of sulfur oxides are low. This has an adverse effect on the recovery operation, since the cost of recovering sulfur oxide is in inverse proportion to its concentration in the gas stream.

An obvious remedy is to develop smelter practices to prevent dilution of the gases with air. This has been done at smelters that have found markets for by-product sulfuric acid made from recovered sulfur dioxide. Not all weak gases can be eliminated in this way, however, and additional recovery of sulfur will be favored by development of processes to extract and concentrate sulfur oxides from weak gas streams at low cost. Many such processes have been proposed, but few have been described in enough detail to give a sound basis for cost estimation.

Sulfur Oxide Generation and Recovery in Western Smelters[a]

	Generated (long tons per year)	Recovered (long tons per year)	Per cent recovered
Copper smelters			
Roasters	307,000	99,000	
Reverberatory furnaces	344,000	0	
Converters	914,000	185,000	
Total	1,565,000	284,000	18.1
Zinc smelters			
Roasters	370,000	165,000	
Sintering machines	15,000	0	
Sinter-roast machines	54,000	0	
Cokers and retorts	1,000	0	
Total	440,000	165,000	37.5
Lead smelters			
Sintering machines	152,000	42,000	
Blast furnaces	3,000	0	
Other	5,000	0	
Total	160,000	42,000	26.3
All smelters	**2,165,000**	**491,000**	**22.7**

[a] Approximate annual rates (as sulfur equivalent) in the first half of 1969.

A satisfactory recovery process should efficiently remove sulfur oxides from gases containing 0.3–4.0%. It should be cyclic and should not consume large amounts of reagents or produce secondary by-products in quantity. Operating costs should be low enough for the recovered sulfur oxide to be used to make sulfuric acid or elemental sulfur at competitive prices.

Unique problems

Recovery problems in copper smelters differ from those in zinc and lead smelters. Indeed, each kind of smelter has its own special recovery problems and any one smelter treating any metal is probably unique. However, in general, existing copper smelters in the western U.S. have particularly difficult recovery problems because of conditions inherent in processing methods: weak reverb offgases and varying flows of converter offgas. Most of these smelters are also poorly located with respect to sulfuric acid markets.

In a copper smelter, the reverberatory furnace emits a steady flow of dilute gas, whereas converter offgas has a higher sulfur oxide concentration but an irregular and cyclical flow. If a roaster is used, the offgas flow from it is steady and the concentration can be about 8% sulfur dioxide, after dust removal, depending on the volume of air drawn into the flue system.

Usually 93–97% of the sulfur in the feed to a zinc smelter is eliminated as sulfur oxides in the offgas from the roasting operation. Offgases from the new fluidized or suspension roasters have from 7–12% sulfur dioxide; older types of roasters emit weaker gases. Sintering of roasted zinc ore in pyroreduction plants produces offgases containing from 0.1–2.4% sulfur dioxide, depending upon the amount of residual sulfur left in the roaster calcine.

The sintering operation in lead smelting eliminates about 85% of the total sulfur from the feed as sulfur oxides. Offgases from a smelter that uses updraft sintering machines may contain from 4–6% sulfur dioxide. Offgases from the first stages of two-stage, downdraft machines can be of this strength, but the second-stage gases contain only 0.8–1.8% sulfur dioxide. One per cent of the feed sulfur is in the very weak blast furnace and dross furnace offgases, and the remaining 14% is retained in the slag and other solid by-products.

Any change in metallurgical practice that results in more concentrated offgases reduces the cost of recovery. Recovery in copper smelters will be favored by development of processes that do away with the cyclic pattern of offgas flows from the converters. Improved metallurgical processes have been adopted by some smelters, and others are being developed or are in use abroad. The improved processes may reduce metal production costs and improve offgas flows and concentrations.

Our study of recovery costs was necessarily limited to three processes for which enough information was available for reasonably accurate estimates of capital and operating costs: contact sulfuric acid manufacture, reduction of sulfur oxides to elemental sulfur, and concentration of weak sulfur oxides by the Cominco absorption process.

Sulfuric acid is made in 12 of the 32 western smelters. One smelter uses a fourth process, dimethylaniline absorption, to concentrate gases having 4–6% sulfur oxides for manufacture of liquid sulfur dioxide. Neither sulfur oxide reduction nor Cominco absorption processes are in use in western smelters, although the Cominco process is in use at the smelter in western Canada where it was developed, and at two chemical plants in Texas.

Recovery as sulfuric acid

The contact sulfuric acid process converts sulfur dioxide to a marketable grade of sulfuric acid (93% or more). It is an efficient, low cost recovery method for a smelter gas having over 4–5% sulfur dioxide, and the process technology is well developed. A problem regarding many smelters is to find markets for the acid near enough so that the freight cost does not exceed the selling price. Another problem is that many of the sulfur oxide gas streams are so dilute that the cost of recovery would exceed any possible revenue from the sale of the acid.

In a contact sulfuric acid unit designed to use smelter gases cleaned in an electrostatic precipitator, the gases go first to a humidifying tower, then to a cooling tower over which a weak acid solution is circulated. The weak acid is cooled in heat exchangers. The gas leaving the tower goes through a gas cooler, condensing some excess moisture, then through an electrostatic mist precipitator. The gas always contains sulfur trioxide, which is largely absorbed in the humidifying and cooling towers. The resulting sulfuric acid may be filtered and added to the product system, but is usually either neutralized and wasted, or used for leaching or other purposes in the smelter.

For maximum efficiency, the feed gas to a contact sulfuric acid unit should have a uniform analysis of sulfur dioxide. Fluctuating concentrations require that the contact sulfuric acid plant be designed for the worst condition, with adequate controls to handle changes in concentration. Changes in feed gas volume are less of a problem and can be handled within limits.

Before reaching the acid plant converter, the gas is dried by direct contact with strong sulfuric acid in a packed tower. Acid strength in the drying acid system is maintained above 93% by the addition of stronger acid from the product absorber. Diluted acid from the drying system is returned to the product system; all water removed from the gas stream in the drying tower dilutes the product acid.

Catalytic

Dried gas flows to the converter, where sulfur dioxide is converted to sulfur trioxide by beds of catalyst in three or four stages. On the way to the converter the gas is heated in a series of exchangers while serving to cool gas coming from the converter stages. This part of the acid unit is similar to the usual sulfuric acid plant operating on gas from a sulfur burner. The converted gas next flows through an absorption tower where sulfur trioxide is absorbed in strong sulfuric acid. Finally, the gas is treated to remove droplets of acid and vented to the atmosphere containing 0.2–0.5% sulfur dioxide.

A typical smelter offgas contains decreasing amounts of oxygen as the sulfur dioxide content increases. For efficient conversion of sulfur dioxide to sulfur trioxide, the feed gas to the acid plant converter needs about 30% more oxygen than sulfur dioxide, on a mole or volume basis. The typical waste gas containing more than 7% sulfur dioxide does not have this excess of oxygen, and dilution air must be added to achieve the desired ratio. The result is that the sulfur dioxide content is reduced to 7.0–7.5% before reaching the converter.

Overall recovery efficiency depends on the amount of sulfur in the waste gas as sulfur trioxide, which is lost as weak acid in the cooling tower, as well as on the percentage conversion of sulfur dioxide to sulfur trioxide. The overall efficiency is expressed as the ratio of sulfur equivalent in the product acid to total sulfur equivalent in the feed gas. Recovery is typically close to 89% for a 2% sulfur dioxide gas, and 93% for an 8% gas. This is lower than the efficiency of conversion of sulfur dioxide to trioxide because the trioxide in the feed gas is extracted as weak acid, often a waste material.

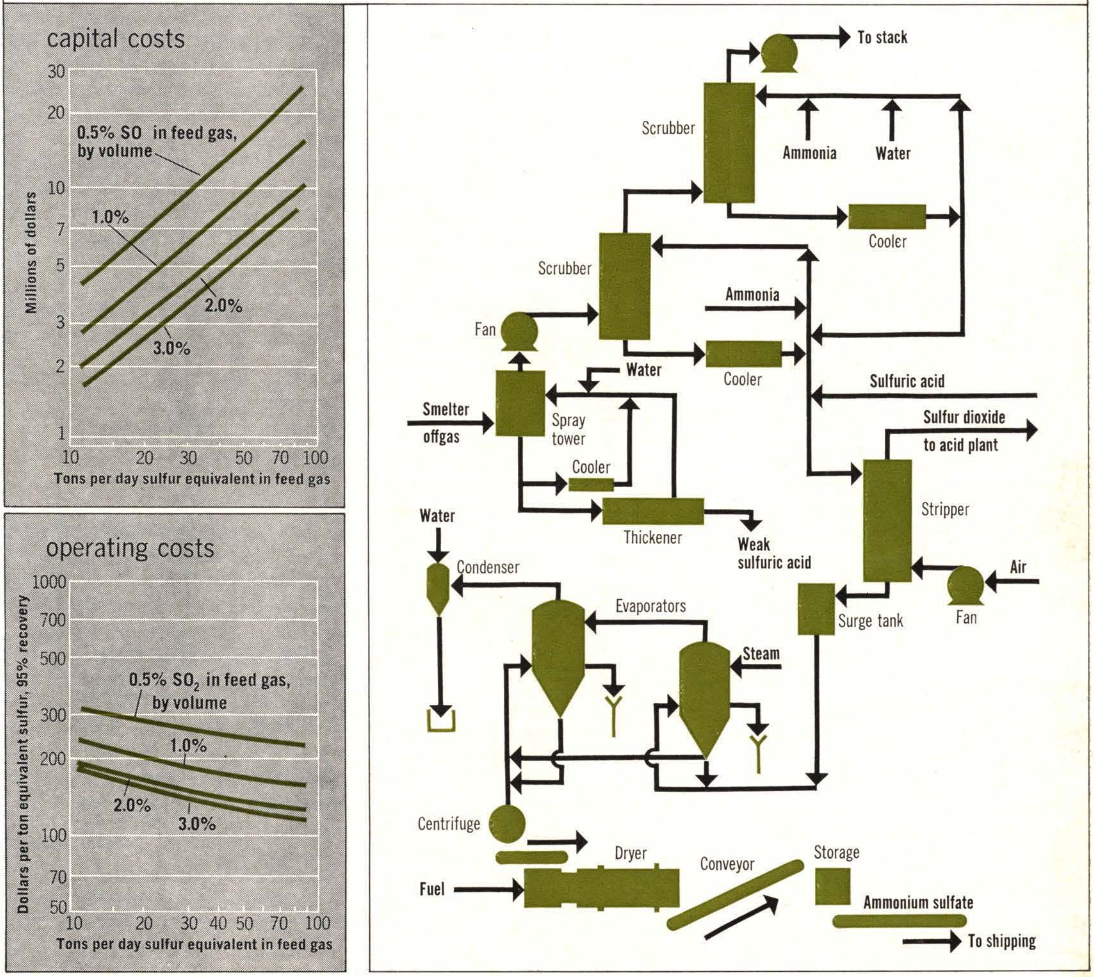
Cominco absorption process

The Cominco process was developed by the Consolidated Mining and Smelting Co. of Canada, Ltd., and plant units have been built at Trail, B. C., and in Texas. The unit at Trail is part of the smelter operations; the Texas units treat tail gases from sulfuric acid plants. Gases with sulfur dioxide concentrations down to 0.5% or even lower can be treated with very good recovery. The sulfur dioxide is concentrated to about 24% by volume. Each of the three units that has been built delivers its sulfur dioxide product to a contact sulfuric acid plant. Ammonium sulfate is a by-product, and some weak sulfuric acid is made when the smelter offgas is given its final cleaning and cooling before it enters the scrubbers.

Possible products

The product gas from a Cominco unit could be a satisfactory feed gas for any of several kinds of conversion units, such as units to convert sulfur dioxide to elemental sulfur, liquid sulfur dioxide, or sulfuric acid, However, the process consumes some sulfuric acid and therefore serves most economically in a plant complex that includes a sulfuric acid unit. The cost of running the Cominco unit appears to limit its application to serving as cleanup and equipment to prevent air pollution. For profitable operation, an acid plant working with a Cominco unit should get a large fraction of its sulfur dioxide feed directly from the smelter

Cominco SO_2 absorption process



operations and only a small fraction from the Cominco unit.

Scrubbers

The gas containing sulfur oxides is scrubbed by a solution of ammonium sulfite and ammonium bisulfite. Sulfur dioxide in the gas reacts with ammonium sulfite to form the bisulfite. Ammonia is added to the recycled scrubbing liquor to reconvert bisulfite to sulfite. The gas passes through two scrubber towers in series and vents to atmosphere. The vented gas contains no more than 0.03% sulfur dioxide by volume if the scrubber solutions are properly adjusted for maximum process efficiency.

Hot smelter offgas is first cooled in a spray tower in the same way as the feed gas to a sulfuric acid unit, and there is a similar weak acid byproduct. The cooled gas enters a scrubber tower where it is contacted with an ammonium sulfite–bisulfite solution. The solution in this first scrubber is maintained at low pH and high salt concentration. Sulfur dioxide is absorbed to form additional ammonium bisulfite. The solution from the bottom of this tower is cooled and recycled to the top of the scrubber together with some solution from the second scrubber. A portion of the solution from the tower bottom is diverted to the stripper.

Scrubbed offgas enters a second scrubber where additional sulfur dioxide is removed by contact with a solution that is at high pH and has a low salt concentration. The solution recycle is cooled and water and ammonia are added. Part of the scrubber solution recycle is diverted to the first scrubber. Offgas from this scrubber is released to the atmosphere. Careful control of pH in the scrubbing steps is necessary for highest recovery.

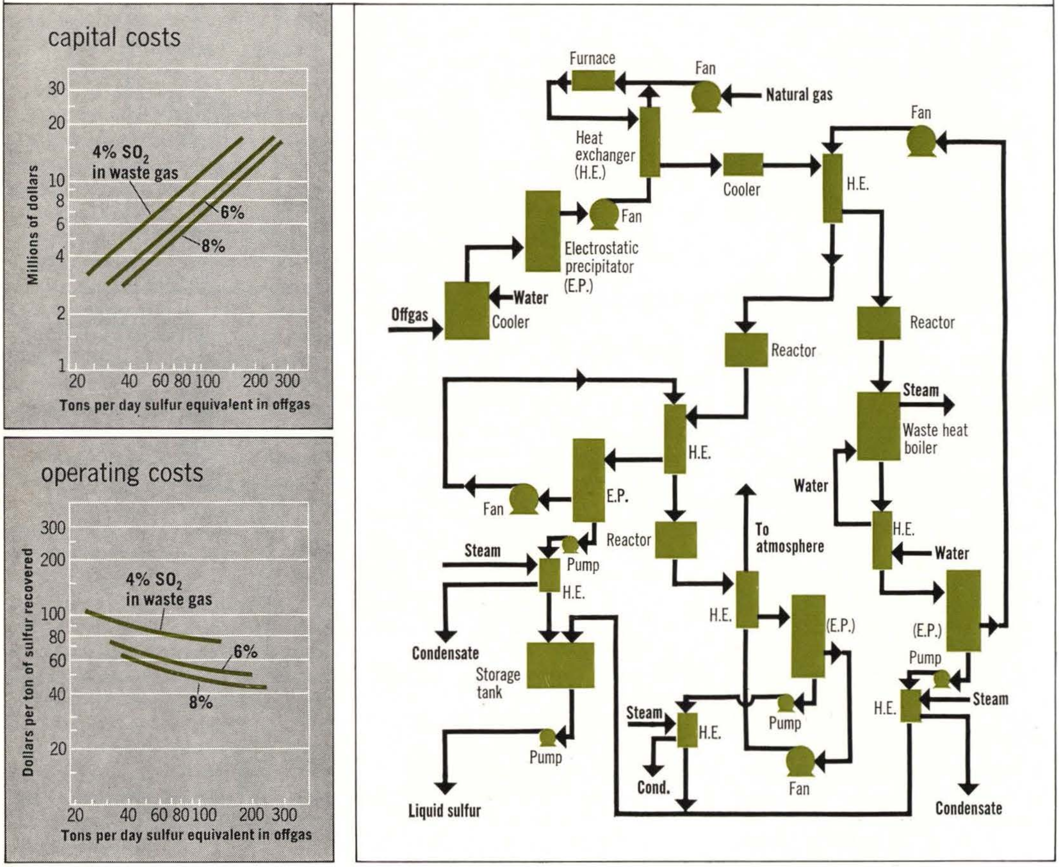
The bisulfite solution diverted to the stripper is acidified with sulfuric acid and stripped with air to produce a sulfur dioxide gas stream suitable for feeding to a contact sulfuric acid unit. As a result of the sulfuric acid reaction and removal of sulfur dioxide, the solution leaving the stripper contains ammonium sulfate, which is recovered.

Production of elemental sulfur from smelter plant offgas is attractive because sulfur is easy to store and shipping costs are much lower than for equivalent amounts of sulfuric acid. Several processes have been proposed and reduction plants have operated at Trail, B.C., and elsewhere.

ASARCO reduction process

The American Smelting and Refining Co. (ASARCO) operated a semicommercial plant from 1940–1944 in

ASARCO SO$_2$ reduction process



which high quality sulfur was produced by reduction from smelter offgas containing 5–7% sulfur dioxide. Natural gas was the reducing agent, and at the same time was burned to supply heat to bring the gases to the reaction temperature of 2200° F. This original ASARCO process is obsolete and costly to build and operate, but can be considered a prototype of recently developed processes now scheduled for commercial operation. It is also the only process for which enough process details have been published for calculation of reasonably accurate costs.

The ASARCO process requires sufficient natural gas to react with all the oxygen present in the waste gas, and enough more to reduce sulfur oxides to elemental sulfur. Some carbonyl sulfide and hydrogen sulfide are formed and subsequently converted to sulfur by catalytic reactions. In the process, the required amount of methane is mixed with hot offgas as it enters a brick-lined combustion chamber packed with a checkerwork of refractory brick. The hot combustion gas is cooled in a heat exchanger that preheats the incoming offgas and controls the temperature in the combustion chamber. Close temperature control is required throughout the process. The primary reaction between sulfur dioxide and methane in the combustion chamber reduces sulfur dioxide to sulfur with formation of carbon dioxide and water vapor. Several side reactions produce hydrogen and carbonyl sulfide.

After further heat exchange the cooled gases are at proper temperature to enter a reactor where contact with a bed of bauxite catalyst converts the carbonyl sulfide to sulfur. The exit gas from this reactor is then cooled sufficiently to allow separation of liquid sulfur in the electrostatic precipitator. Here, about 70% of the sulfur in the smelter offgas is recovered and pumped to storage in liquid form. The gas is then heated to the proper temperature for further reaction to convert hydrogen sulfide to sulfur. The remainder of the process consists of two catalytic reactors in series, and heat exchangers and electrostatic precipitators to recover liquid sulfur.

Pressure losses

Blowers are required in the system because of high pressure losses. Gas temperatures range from 2200° F. leaving the combustion chamber to 260° F. in each of the electrostatic precipitators. Gas volume through the system remains approximately constant except for changes due to varying temperature and pressure. Tail gas containing a small amount of sulfur dioxide is discharged to the atmosphere. Sulfur recovery is 95% of the total sulfur in the offgas.

Economics

A plant using this process could be designed to operate on offgas with a fraction of a per cent sulfur dioxide, but costs would be excessive. Costs are lower with offgases that contain more sulfur dioxide because the consumption of natural gas relative to the sulfur produced is lower. The economics are most favorable with offgases ranging from 5% sulfur dioxide and 12% oxygen to 7% sulfur dioxide and 9% oxygen. In this range production of 99.9% sulfur is feasible.

The exothermic reaction between methane and oxygen produces the high temperature needed for the reaction. A certain minimum oxygen content is required in the feed gas because the reactions between methane and sulfur dioxide are only slightly exothermic.

It should be noted that the pilot work on the original ASARCO process was done before the construction of large numbers of Claus process plant units to produce elemental sulfur from waste hydrogen sulfide. Once the sulfur dioxide in a stream of waste gas has been even partly reduced by natural gas, there is considerable similarity between the process streams in the reduction plant and the Claus process plants. However, where the original ASARCO design called for a number of large and expensive electrostatic precipitators, the Claus process plants are able to make an efficient recovery of sulfur at relatively low cost.

Several other processes for reducing sulfur dioxide to sulfur may offer cost advantages over the process just described, particularly for application to more concentrated smelter offgases. Patents have been issued to Texas Gulf Sulphur (TGS) for a process to recover sulfur from waste gas by direct, low temperature (1500° F.) reduction of sulfur dioxide with methane in the presence of an alumina catalyst. The TGS process will produce high grade sulfur when applied to a waste gas stream containing a high concentration of sulfur dioxide and a low concentration of oxygen. However, preheating may be necessary if the waste gas temperature is low.

The advantages of the TGS process should be most marked in applications where the sulfur dioxide content of the waste gases is above 8%. A pilot plant has been operated but no commercial plants have been built.

Allied Chemical of Canada, Ltd., is now building a plant near Sudbury, Ont., to recover more than 100,000 tons per year of sulfur from offgas from a pyrrhotite roasting operation. No details have been made public, but it seems likely that the process is similar to the other direct reduction processes described. The feed gas to the plant is estimated to contain more than 10% sulfur dioxide with low oxygen concentration.

The catalytic reduction process developed by Princeton Chemical Research (PCR), is a variation of the methane reduction and the Claus process. Elemental sulfur is reacted catalytically with natural gas to form hydrogen sulfide, which is then mixed with flue gas and reacts with the sulfur dioxide it contains to form more elemental sulfur. The sulfur is recovered and a portion is diverted for conversion to hydrogen sulfide. At this point, not enough information is available to justify any conclusions as to its economics.

Direct reduction

Sulfur can be recovered from gas containing sulfur oxides by direct reduction with hydrogen in the presence of a suitable catalyst. A second catalyst stage is required in which hydrogen sulfide formed in the first reactor is reacted with additional sulfur dioxide to form sulfur. In spite of various problems, the process may be attractive for recovery of sulfur from waste gas containing a high concentration of sulfur dioxide and a small amount of oxygen.

Several processes have been developed for the recovery of sulfur from waste gas by direct reduction of sulfur dioxide with coke. Sulfur was produced at Trail, B.C., from 1935 to 1943 by this method. The Imperial Chemical Industries' process was operated at about the same time as was the Boliden process in Sweden. All of these processes pass the hot waste gas through a bed of coke, followed by heat recovery and reaction stages to control side reactions and produce elemental sulfur. Water vapor in the waste gas reacts with coke and sulfur dioxide to form hydrogen sulfide, requiring converters similar to other direct reduction processes.

Costs for the sulfuric acid process

For the purpose of estimating the costs of the contact sulfuric acid process, the following criteria for the feed gas were assumed:

Temperature: 600° F.
Pressure: Atmospheric
Dew Point: Approximately 110° F.
Wet bulb temperature: Approximately 150° F.
SO_2 content: 2–12% Dry Volume basis
SO_3 content: 0.2–0.5% Dry volume basis
O_2 content: 2–16% Dry volume basis
Dust content: 0.1 Grain per standard cubic foot
Waste gas flow: 24 Hours per day

Costs were estimated on the basis of a uniform flow and analysis of the smelter offgas. Such conditions are characteristic of zinc and lead smelters, but not, unfortunately, of a typical copper smelter. Optimum design capacity of an acid plant for a copper smelter requires careful consideration of variations in both flow rate and analysis of the offgas.

If the sulfuric acid plant in a copper smelter is sized for average flow conditions, it will be necessary to bypass part of the offgas during maximum flow. If sized for maximum conditions, the acid plant will be operating below its capacity for considerable periods of time, and the production cost of the acid will be higher. Production costs shown (*see chart*) are minimum for application of this recovery system to copper smelters.

The capital cost curves are based on estimated costs for the construction of a complete plant for sulfur oxides control, designed to operate on smelter gas containing 5% sulfur dioxide, a typical application for this kind of plant. The gas was assumed to contain a uniform quantity of sulfur dioxide and enough oxygen to convert it to sulfur trioxide. Costs include equipment purchase, shipment, unloading, and installation, plus site preparation, foundations, piping, ductwork, electrical, instrumentation, support structures, and necessary buildings as needed for a battery limits plant unit, ready to operate. The costs do not include working capital, cost of land, inventory, interest, offsite utilities, steam generators, plant access, or equipment for preliminary cleaning of the gas.

From the information for this plant, costs were estimated for other plants of similar physical size to handle waste gases containing 2, 4, 8, and 12% sulfur dioxide. A family of curves was then established on a log–log chart (slope of 0.80) to give estimates of capital costs over a range of plant sizes for each sulfur dioxide concentration. The slope of 0.8 was selected as a suitable average for plants costing $1.5 million to $8 million.

The estimates show how the capital cost per ton of sulfuric acid increases when the waste gases are low in sulfur dioxide concentration. The following data compare costs on this basis for the range of 200 to 400 tons per day of sulfuric acid:

% SO_2 in waste gas	**Estimated cost ($/ton/day)**
2	23,000
4	13,000
8	10,000
12	9,000
brimstone plant	5,000

Capital cost for a contact sulfuric acid plant fed with waste gas is considerably more than for an equivalent plant fed with brimstone. Additional equipment is required for cleaning the waste gas and for removal of excess water. When sulfur dioxide content is low, the larger volumes of gas add greatly to capital and operating costs.

A 1600-ton-per-day sulfuric acid plant fed by brimstone has about the same physical size and cost as an 800-ton-per-day plant fed by smelter offgas containing 6 to 8% sulfur dioxide. This is the maximum plant size to which these cost curves apply. Larger installations would be multiple plants not single converter systems.

Estimated operating costs are shown in the table for contact sulfuric acid plants to handle smelter plant offgases containing 2, 4, 8, and 12% sulfur dioxide. The operating costs given are typical for this type of plant. With 100 short tons daily of sulfur equivalent in the feed gas, the acid made from a 2% gas costs $17 per ton, but from 8% gas costs only about $5.50 per ton. Direct and indirect costs are included, but not charges for sales expense or interest on investment. A year of 330 operating days is assumed.

Cominco process costs

The feed gases to the Cominco units are assumed to have the same characteristics as the feed gases to the sulfuric acid units, except that the sulfur dioxide content is 0.5–3.0% by volume, dry basis, and the sulfur trioxide content is 0.05–0.23%. The Cominco units produce 24% sulfur dioxide gas, ammonium sulfate crystals, and a dilute acid waste.

Our estimates of capital costs for Cominco process plants show that a plant to handle 50 short tons of sulfur equivalent (100 tons sulfur dioxide) daily in 3.0% gas costs $5.5 million; with 0.5% gas, the plant cost is $15 million. These are the estimated battery limit capital costs for units constructed in 1968. A cooling tower is included, but costs do not include other offsite utilities, contingencies, working capital, inventory, interest, land, plant access, or gas cleaning equipment that precedes the spray tower. The cost estimates are based on a flowsheet and equipment list developed for a plant to handle smelter offgas containing 40 tons per day of sulfur dioxide (20 tons of sulfur equivalent) at a concentration of 1% sulfur dioxide by volume. The complete plant unit was estimated at $4,800,000.

Changes in tonnage of sulfur dioxide or in gas concentration affect the costs of the four sections of the plant in different ways. For example, a plant for 40 tons of sulfur dioxide daily at 0.5% concentration must handle twice the volume of offgas as the base plant at 1.0%. This requires a scrubber section of twice the gas capacity, but makes no change at all in the costs of the other sections of the plant. By considering each section separately to obtain installed equipment costs, total plant costs were obtained for plants handling 20, 40, 80, and 160 tons per day of sulfur dioxide at 0.5, 1.0, 2.0, and 3.0% levels.

Operating cost estimates

Our calculations of operating costs (costs per short ton of sulfur recovered) are based on uniform feed gas flow rates and concentrates. The following criteria were used in calculating by-product yields and required amounts of raw materials:

- The Cominco unit receives the average feed gas flows and compositions for 330 days per year.
- The unit removes 95% of the sulfur dioxide from the feed gas and

delivers it in the product gas from the stripper at a concentration of about 24% by volume.

- The unit removes 95% of the sulfur trioxide from the feed gas and delivers it as weak acid in the thickener overflow.
- Sulfuric acid used by the unit equals two-thirds mole per mole of sulfur dioxide recovered.
- Ammonia consumed equals 2 moles per mole of concentrated sulfuric acid used.
- Ammonium sulfate produced for shipping equals 0.95 mole per mole of concentrated sulfuric acid used.

The cost of the sulfuric acid used is taken as $7 per ton of 100% acid equivalent. Since the Cominco units would ordinarily operate in conjunction with a sulfuric acid plant, this would usually be an intraplant cost and the actual charge against the Cominco unit for acid would depend on accounting procedures of the operating company. Ammonia, however, would be bought from the most economical outside source. The cost here is taken as $50 per ton. Actual cost would be affected by smelter location relative to ammonia source, as well as by other factors. The main product or by-product is sulfur dioxide from the stripper, but the minor by-product, weak sulfuric acid, is also included as recovered sulfur. Ammonium sulfate is not included in the recovered sulfur equivalent since it is derived from the ammonia and sulfuric acid that are added.

Costs of the Cominco process are lower with larger amounts of stronger gas, but even for 160 tons a day of sulfur dioxide (80 short tons of sulfur equivalent) in 3.0% gas, the operating cost is $116 per short ton of sulfur equivalent recovered. The amount of credit that can be allowed for three by-products will be different at each plant. Weak sulfuric acid may be a liability that has to be neutralized and conveyed to a disposal area. In general, the process does have value as part of a smelter plant where sulfuric acid is made from large flows of more concentrated sulfur dioxide gases and only relatively small emissions of weak gases remain to be cleaned up.

ASARCO process costs

Cost calculations for the ASARCO process were based on 95% conversion of all sulfur oxides in the feed gas to recovered elemental sulfur with the plant operating 24 hours per day and 330 days per year. Characteristics of the feed gas are similar to those previously assumed for the feed gas to the sulfuric acid plant except for SO_2 content (4–8% dry volume basis), SO_3 content (0.26–0.38% dry volume basis), and O_2 content (13.2–7.6% dry volume basis.) The feed gas is of uniform concentration and flow volume. Sulfur oxides are recovered in the form of a 99.9% pure, salable grade of elemental sulfur.

The capital costs for reduction plants using this process are based on a cost estimate of $7.4 million for a plant to recover 91 short tons per day of sulfur from a smelter offgas containing 6% sulfur dioxide. The costs for plants of similar physical size to handle similar volumes of feed gas containing 4, 8, or 10% sulfur dioxide will be the same, since gas volume controls the size of the equipment. A family of curves with slopes of 0.80 was established on log–log graphs to show costs over a range of plant sizes for each sulfur dioxide concentration.

Equipment costs for this process are increased considerably by the need to conserve heat and control temperatures as the gas stream passes through the several stages. This requires extensive use of gas-to-gas heat exchangers. The volume of gas handled does not decrease as sulfur is formed, and large electrostatic precipitators are used to collect small amounts of liquid sulfur from large volumes of hot gas. Multiple stages are required to reach reasonable recovery efficiency. The curves shown are considered reasonable order-of-magnitude estimates. As none of these plants have been built, it is not possible to compare the curves with actual cost figures.

We also studied the effect of sulfur dioxide concentration and quantity on the estimated operating costs for this process. The estimates were calculated for reduction plants of three different capital costs: approximately $3,500,000, $7,430,000, and $12,000,000. Operating costs were estimated for three plants at each capital cost level: one plant to treat a smelter offgas with 4% sulfur dioxide, one for a gas with 6%, and one for a gas with 8%. Direct and indirect costs are included, but no charge for sales expense or interest on investment. The indirect costs consist of depreciation and controllable and noncontrollable costs. Controllable indirect costs include overhead, supervision, and maintenance labor. Noncontrollable indirect costs include insurance and charges for local taxes. The costs include storage of liquid sulfur and loadout to tank cars.

A substantial resource of sulfur is available from the nonferrous smelting industry in the western U.S. Its recovery and utilization present a challenge of considerable proportions to the innovative faculties of the industrial chemist.

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SO_2 from smelters:

By-product markets a powerful lure

A major concern of pollution control authorities is the large quantity of sulfur oxides entering the atmosphere. The public utility industries are major contributors, but the nonferrous smelter industry is also a significant source. At the present time, less than one-quarter of the sulfur in the ores treated at the 26 nonferrous smelters west of the Mississippi River is being removed. The rest, the equivalent of over 1.6 million long tons of sulfur a year, is being emitted as sulfur oxides, and the smelter operators are under pressure from air pollution control authorities to reduce these emissions. Most of these operators recognize their responsibility to reduce air pollution and are seeking economical ways to comply with the control regulations.

Since recovery of sulfur, most frequently as sulfuric acid, is usually the most economical method available to smelter operators for reducing emissions, pollution control could be advanced significantly if markets could be found for the recovered sulfur by-products. Smelters could make one or more of these salable by-products using proven technology: elemental sulfur, sulfuric acid, liquid sulfur dioxide, and ammonium sulfate (or bisulfite).

The western smelters currently produce 1.6 million tons of sulfuric acid—the equivalent of 490,000 long tons of elemental sulfur—from their sulfur emissions. How much more of the sulfur can be recovered and sold (or used by the smelter operators) depends on a variety of factors, the most important of which are selling price and quality of the product, and the size and location of the available markets in relation to the smelter.

The selling price for these by-products is, in turn, related to the production cost, the cost of transporting the by-products to the market, and the cost of selling it in that market. Smelter operators would obviously prefer to sell their by-products at a profit, but the need to control emissions of sulfur oxides may result in the operators building by-product recovery plants that must be operated at a loss. However, we will assume here that the by-products would be produced and sold if its f.o.b. selling price is equal to or greater than the production cost, defined as depreciation and operating cost. A comparison of the cost per ton of producing elemental sulfur, sulfuric acid, and ammonium sulfate at smelters and at conventional plants is as follows:

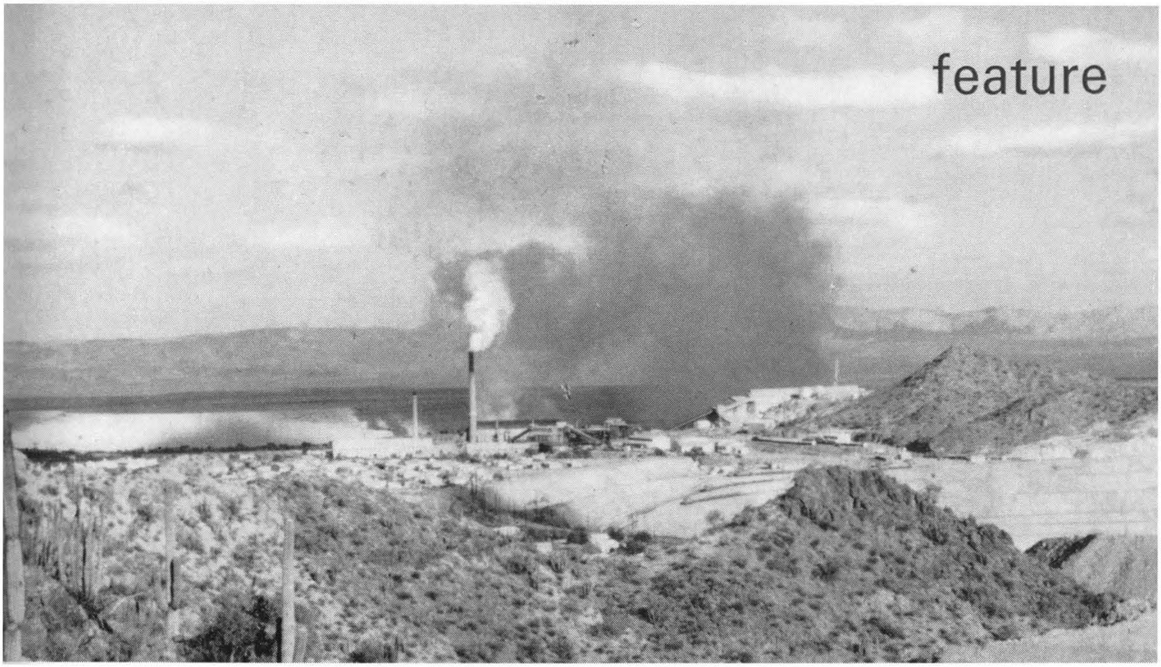
	Conventional ($)	Smelter ($)
Sulfur	10–30	45–100
Sulfuric acid	10–20	4–25
Ammonium sulfate	20–30	

We have not assigned a production cost for ammonium sulfate from smelters because it would be made as a coproduct or by-product along with concentrated sulfur dioxide when the Cominco process is used to recover sulfur oxides from stack gases. The value assigned to the sulfur dioxide and the ammonium sulfate depends entirely on the accounting procedure used by the individual smelter. Therefore, any costs we assigned would be entirely arbitrary.

The total market for liquid sulfur dioxide is so small in the western part of the United States (less than 20,000 tons a year in 1965) that even if all this market could be supplied by the smelters, the resulting reduction in smelter emissions would be insignificant. Therefore, no production or market information was developed.

Elemental sulfur

Elemental sulfur would be expensive to produce at the western smelters—$45–100 per ton, compared with $10–30 per ton for producing sulfur from Frasch mines or recovering it from sour natural or refinery gas. Since the western smelters are surrounded by the largest sulfur producers with the lowest production costs—Texas Frasch mines, recovered sulfur from Canadian natural gas, and recov-


Remoteness. *Barrier to overall economics of SO_2 recovery processes often is distance between smelter and markets for acid*

ered sulfur from refinery streams in California—little opportunity now exists for smelters to produce elemental sulfur and transport it to markets where it can be sold for anything close to its production cost. Obviously, this situation can change if processes can be developed that will permit the smelters to recover elemental sulfur at a lower cost. The Division of Process Control Engineering of the National Air Pollution Control Administration is actively seeking such new and improved processes. However, the development of such a low cost process does not appear imminent and will not be considered further here.

The comparison of costs for production of sulfuric acid at smelters—$4–25 per ton *vs.* the cost of acid production from elemental sulfur of $10–20 per ton—shows that smelters are a competitive source. The quality of smelter acid can be assumed acceptable since it is used in such large quantities today, and the only remaining question is whether or not markets exist or could be developed for the increased quantities of acid that might be produced by the western smelters.

Sulfuric acid

The location of the smelters that could produce sulfuric acid and the location of the acid markets are particularly critical to any determination of the quantities of acid that might be sold. As is well-known, proximity of production site to market is necessary because the acid is a low value commodity that can be made almost anywhere from elemental sulfur, and large shipping charges for the acid cannot be tolerated.

The 26 smelters west of the Mississippi are so located that, for purposes of our study, the smelters have been combined into six groups, each serving separate marketing regions. If all of the sulfur available from these smelters were converted to sulfuric acid, a total of about 7.3 million tons of acid could be produced, including the current production of 1.6 million tons. The smelters in Group I—located in Arizona, New Mexico, and Texas—are capable of producing over 50% of this quantity. Altogether, the 17 smelters in Groups I, II, and III could produce 87% of the total.

The actual 1965 consumption of sulfuric acid in the 22 states west of the Mississippi was a little more ($7.4 million tons) than could be produced by the six groups of smelters at the present time. Almost half the actual consumption occurred in the southwest central states of Texas, Louisiana, Arkansas, and Oklahoma.

Even though the market for acid in the western part of the country exceeds the quantity of acid potentially available from smelters, current production and transportation costs indicate that these markets cannot all be supplied with smelter acid. Our estimate of how much acid from western smelters might have been sold in each of the four major regions of the West in 1965 is based on the smelter operators being willing to sell the acid for $4 per ton, the minimum production cost. Thus, 2.8 million tons that might have been consumed is less than 40% of the total potential production.

Regional markets

The strongly regional character of the potential market for smelter acid is well illustrated by our data. Smelter acid, since it would be produced nearby, could capture the entire market for acid in the Mountain States if priced at $4 per ton f.o.b. At the other extreme, less than 10% of the market in the southwest central region could be captured at the same selling price. The latter market—located along the Gulf Coast—is a long way from most of the western smelters and acid can be produced there at relatively low cost from Texas and Louisiana Frasch sulfur.

The disposition by end use of the 2.8 million tons of smelter acid that could have been consumed in 1965 is given the following tabulation:

End use	Possible 1965 consumption (1000 tons)
Fertilizers	1600–1800
Copper ore leaching	280
U_3O_8 processing	250
All other	470–670
Total	**2800**

The production of fertilizer could have used 60–65% of the total. Leaching of low grade copper ore and processing of uranium ores both could be important uses for sulfuric acid in the West, and would have required 10% and 9% of the acid, respectively, in 1965.

As already mentioned, the western smelters are capable of producing 7.3 million tons of acid, or about 4.5 million tons more than the 1965 markets of 2.8 million tons could have absorbed. Broken down by regions, over 3.2 million tons of acid for which no nearby market exists would be produced by the Group I smelters in Arizona, New Mexico, and west Texas. The smelters in Group III (Idaho and Montana) would have nearly 1.2 million tons available. By comparison, the amounts of extra acid that could be made available from the Group IV (Texas) and VI (Washington and California) smelters would be relatively insignificant (0.1 million ton). The smelters in the other two groups would have no extra acid available.

Future markets

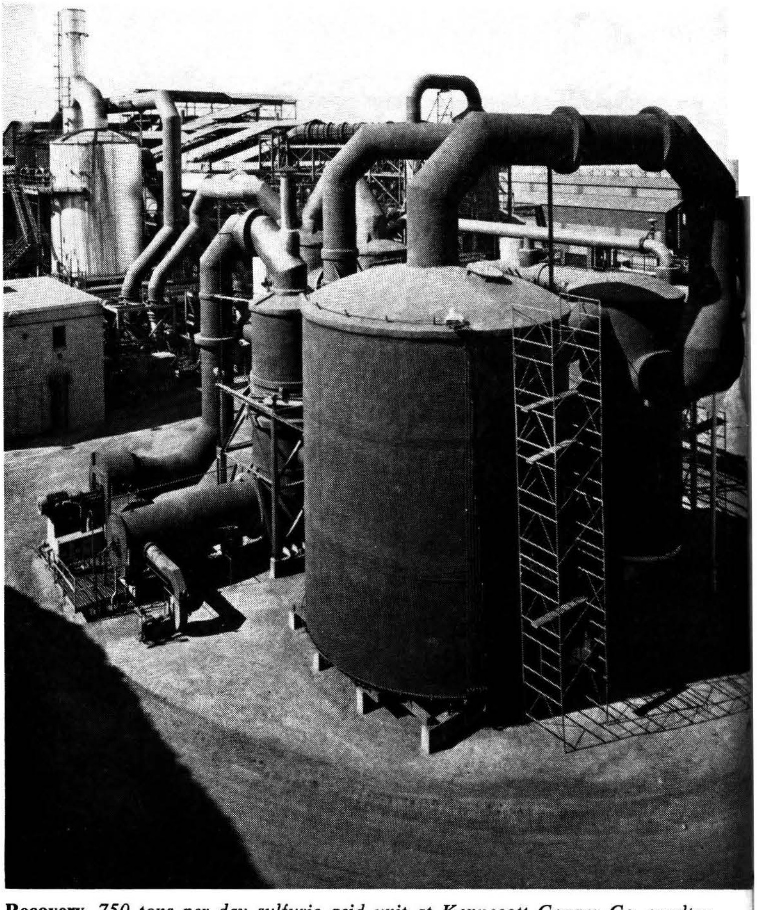
Just because the 1965 markets were inadequate to absorb the potential supply of smelter acid does not mean that adequate markets would not be developed in the future. Therefore, a detailed estimate was made of the 1975 markets that might be served from the Group I and III smelters, from whence most of the unused supply would come. Also, the possible 1975 markets for ammonium sulfate, which might be made from the smelter emissions, were assessed.

The Group I smelters in Arizona, New Mexico, and Texas are not well situated to supply sulfuric acid for fertilizer manufacture. The nearest source of phosphate rock is northern Utah or Wyoming and nearby fertilizer markets are not large. The agricultural markets that could be supplied from fertilizer plants using Group I smelter acid lie primarily in Califor-

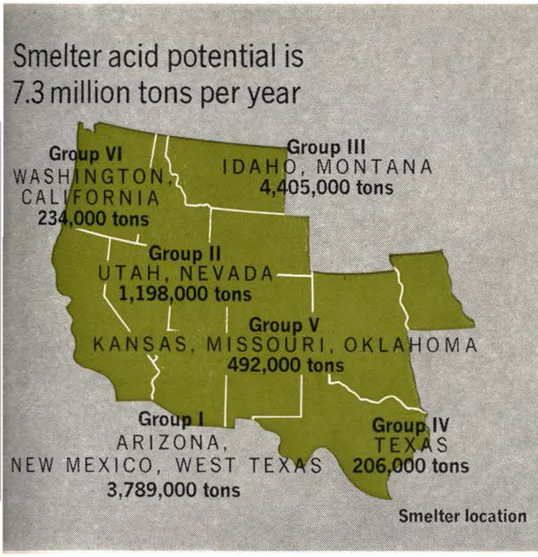
Potential smelter acid markets[a]

	Smelter Group						
Market Region	**I**	**II**	**III**	**IV**	**V**	**VI**	**Total**
Northwest Central				7	456		463
Southwest Central	20			198	36		254
Mountain	271	866	182				1,319
Pacific	280	332	45			109	766
Total	571	1,198	227	205	492	109	2,802

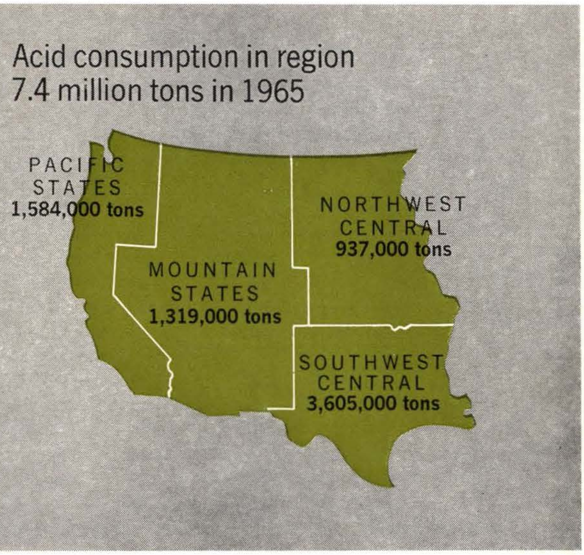
[a] At $4 per ton, based on 1965 consumption



Recovery. *750 tons per day sulfuric acid unit at Kennecott Copper Co. smelter in Hayden, Arizona. Acid is used for leaching of low grade ore at nearby mine*



Smelter acid potential is 7.3 million tons per year



Acid consumption in region 7.4 million tons in 1965

nia, Arizona, and New Mexico, with a smaller market in far west Texas. Approximately 285,000 tons of smelter acid could have been used in 1965 by fertilizer producers in these regions. Our estimates indicate that by 1975 the fertilizer producers in these states will require 440,000 tons more acid than was used in 1965. However, 225,000 tons of this sulfuric acid will be made from sulfur recovered from sour refinery gases in California. Therefore, it is estimated that an additional 215,000 tons of smelter acid might be used annually to make fertilizers for the markets available in these four states in 1975, which would raise the consumption of smelter acid for fertilizer in this area to 500,000 tons in 1975.

Other areas

The only other market for phosphate fertilizer that might conceivably be served from a plant or plants using acid from Group I smelters would be the one in Kansas and Nebraska. Therefore, calculations were made to determine if phosphate fertilizer made in Hutchinson, Kansas, from Idaho phosphate rock and Group I smelter acid could be produced and sold to this market at a competitive price. These calculations show that fertilizer produced in Florida, from sulfuric acid made from Gulf Coast elemental sulfur and Florida phosphate rock, and shipped to the Kansas and Nebraska market would generally cost less than the fertilizer made from Idaho phosphate rock and Group I smelter acid. The latter would cost less only when Gulf Coast sulfur reached \$45 to \$50 a long ton, which is not likely between now and 1975.

Therefore, it appears that only a limited amount of the large quantities of acid available from the Group I smelters can be used economically in the future to produce fertilizers.

Leaching of low grade copper ores, which in 1956 required about 200,000 tons of sulfuric acid in the region near the Group I smelters, is rapidly becoming an important use for acid in the West. Many of the copper companies operating smelters in this region percolate weak sulfuric acid solutions through their mine dumps and wastes whose copper contents are too low to justify concentrating in a conventional mill. The solutions dissolve some of this copper which is recovered by cementation when the solutions are passed through launders full of shredded cans. A few companies are leaching higher grade ores from smaller deposits. One company is recovering anode grade copper by using solvent extraction to prepare a low iron–copper sulfate solution suitable for direct electrolysis to deposit the copper. From 800,000 to 1,100,000 tons a year of Group I smelter acid could be used for leaching copper ores by 1975.

The Group I smelters could also supply the acid requirements of some uranium mills in the southwest. Based on estimates of future U_3O_8 (yellowcake) production made by the U.S. Atomic Energy Commission, these mills could have used 70,000 tons of smelter acid in 1965 and could require 220,000 annually by 1975. An additional 40,000 tons could conceivably be sold for miscellaneous uses.

So, if the markets for smelter acid develop as expected, the Group I smelters will be able to use or sell 1.6 to 1.9 million tons of acid in 1975:

End use	1000 Tons
Copper ore leaching	800–1100
Fertilizers	500
U_3O_8 processing	220
Other	40
Total	**1560–1860**

Based on these estimates, the Group I smelters with sulfur oxides emissions sufficient to produce 3.8 million tons of sulfuric acid a year, could produce 1.9 million to 2.2 million tons more acid than current and foreseeable markets could use.

Fertilizer production

The Group III smelters in Idaho and Montana would appear to be much better located to supply sulfuric acid for the production of phosphate fertilizers. About 16% of the phosphate rock mined in the U.S. comes from nearby—Idaho, Montana, northern Utah, and northwestern Wyoming—and the smelters are near large and growing markets for fertilizers. According to our preliminary estimate of the expected increase in consumption of phosphate fertilizers within shipping radius of 400 miles or so from Butte, Montana, approximately 795,000 tons per year more P_2O_5 will be required in these regions in 1975 than was used in 1967. These 975,000 tons of P_2O_5 could require over 2 million tons of sulfuric acid.

Despite this apparently ideal location, the smelters in Group III supplied to the fertilizer manufacturers only about 130,000 tons, or less than a tenth of the 1.4 million tons of acid they could have produced.

Furthermore, these 130,000 tons of acid represented only about one-quarter of the acid requirements of the fertilizer manufacturers in the area.

Many factors

A complete analysis into the reasons for the currently small usage of Group III smelter acid by the fertilizer manufacturers was not undertaken in this study, but, a combination of factors probably contribute to this situation:

- No strong incentive existed in the past for the smelter operators to find markets for any acid they might produce.
- The acid is controlled by the smelter while fertilizer production and sales are handled by others; frequently the interests and needs of the groups are incompatible.
- The best phosphate rock deposits are found in Idaho and Wyoming —some 300 miles from the nearest Group III smelters.
- The larger markets for fertilizer are in North and South Dakota and in the Canadian provinces of Alberta and Saskatchewan, both considerable distances from the Group III smelters.
- Large quantities of recovered sulfur in Alberta are readily available for production of sulfuric acid on the Canadian prairies.

However, none of these factors is unalterable. Pressure from air pollution control authorities is likely to provide the strong incentive. Joint ventures—such as that undertaken between Stauffer Chemical (a fertilizer and phosphate rock producer) and Bunker Hill (a smelter operator) to manufacture phosphoric acid at Kellogg, Idaho, from sulfuric acid made at Bunker Hill's Kellogg smelter—are effective solutions to the second problem. The third and fourth problems, related to the cost of transporting phosphate rock and fertilizer, could also be overcome by a low price for smelter acid. Canadian sulfur for sulfuric acid production could be displaced by U.S. smelter acid if other markets develop for the sulfur.

Cost comparison

We also made a comparison of the cost of raw materials to produce phosphoric acid at three plant sites: Butte (near the smelters), Kellogg (near the phosphate rock), and Medicine Hat, Alberta (near the large fertilizer markets). Phosphoric acid is currently produced at Pocatello (Idaho) and Medicine Hat but not at Butte. To permit a direct comparison, the cost of shipping the finished acid from Butte to Kellogg and to Medicine Hat is added to the raw material cost component. A comparison of the delivered costs indicates the differential cost of producing phosphoric acid from plants of similar capacity (*see table*).

The raw material costs for phosphoric acid made at Butte ($65 per ton) from Idaho phosphate rock and $9 per ton smelter acid would be lower than the cost of using the same phosphate rock and acid produced locally to make phosphoric acid at the Pocatello ($69 per ton) and Medicine Hat ($73 per ton). However, the raw material cost of the Butte phosphoric acid plus the transportation cost to deliver it to Pocatello would be about $3 per ton higher than the raw material cost of phosphoric acid made at Pocatello and $2 per ton higher than at Medicine Hat. However, this cost disadvantage would be more than offset if the price of the smelter acid were $4 per ton instead of $9 per ton. In this case, the raw material cost component of the phosphoric acid delivered from Butte to Pocatello or to Medicine Hat would be $11 per ton of P_2O_5 less than the locally produced phosphoric acid.

Based on the above data, there is a definite potential for the production of phosphate fertilizers using Group III smelter acid, particularly if the acid can be purchased for less than $9 per ton. Just how much of the acid might be consumed is hard to predict. It does appear, however, that enough of the large and growing fertilizer market delineated earlier is close enough to the Group III smelters that nearly all of the low cost smelter acid made available would be used.

Uranium processing also represents an increasing potential market for sulfuric acid made by Group III smelters. According to AEC estimates, large increases in the use of sulfuric acid for this purpose will occur in eastern Washington and in Wyoming by 1975. The increased use of acid in these areas plus increases in use by the AEC at Hansford, Washington, could provide markets for 225,000 tons of Group III smelter acid by 1975. Leaching of copper ores and other uses from Group III smelter acid are not expected to increase markedly between now and 1975. The potential consumption pattern of sulfuric acid from the Group III smelters by 1975 is as follows:

End use	1000 Tons
Fertilizers	900–1150
U_3O_8 processing	225
Copper ore leaching and other uses	30
Total	**1155–1405**

All, or nearly all of the 1.2 million tons of sulfuric acid that may be produced by the Group III smelters in 1975 could find markets if the selling price were $4 a ton f.o.b. the smelter.

Ammonium sulfate

Ammonium sulfate (or bisulfite) is the only other sulfur by-product the western smelters could produce and sell at anywhere near production costs

Potential consumption and possible excess of H_2SO_4 (1975)

(Thousands of Tons)

Smelter Group	Consumption	Excess Acid[a]
I	1600–1900	1900–2200
II	1200	0
III	1400	0
IV	200	0
V	500	0
VI	110	125[b]
Total	5010–5310	2025–2325

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[a] For which no known market exists

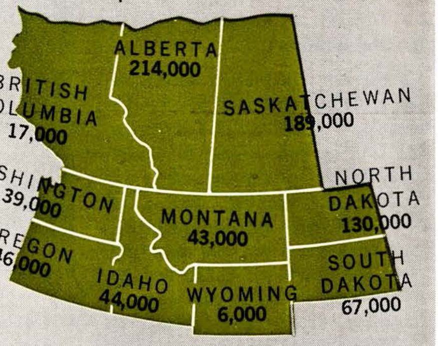
[b] Tentative estimate only

Estimated raw material costs for P_2O_5 production

Location	With Smelter Acid at $9/ton	$4/ton	With Local Acid
Butte, Montana	$65	$52	. . .
Pocatello, Idaho	$71	$58	$69
Medicine Hat, Alberta	$75	$62	$73

Note: Figures show total raw-material costs only per ton P_2O_5, based on phosphate rock from Idaho and acid from the indicated source. P_2O_5 is currently produced at Pocatello and Medicine Hat from Idaho rock and locally produced acid.

Future P_2O_5 consumption[a] near Group III smelters



Total—795,000 tons per year

[a] Estimates for 1975, in tons per year

Close supply. *Kennecott copper ore leaching plant near Superior, Arizona, uses sulfuric acid recovered from smelting operation at Hayden, 22 miles away*

in sufficient quantities to reduce significantly hte amount of sulfur oxides they emit. However, estimating the amount the western smelter operators might sell is difficult. The price the smelter operator would have to receive to break even cannot be determined because, as indicated earlier, sulfur dioxide is a necessary coproduct, and apportioning production costs between the two products varies with different smelter operators. Without an established ratio between production costs and selling price, the degree to which smelter operators could displace existing suppliers from ammonium sulfate markets cannot be estimated. Also, smelter-produced ammonium sulfate would compete for markets with ammonium sulfate produced by others who use smelter acid. Consequently, any estimate of markets for smelter-produced ammonium sulfate is only approximate.

Some of the markets for ammonium sulfate, however, are so located that it would be extremely difficult for the existing suppliers to compete with ammonium sulfate produced at smelters. The amount of ammonium sulfate from smelters that might be sold to such markets in 1975 is:

	1000 Tons of ammonium sulfate
Group I	325
Group VI	75
Total	**400**

Potential increase

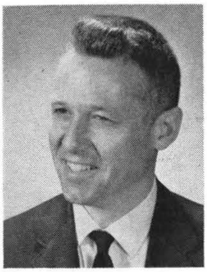
In summary, the western smelter operators might make and sell 5.0–5.3 million tons of sulfuric acid a year by 1975 if they were willing to charge around $4 per ton for the acid at the smelter. This potential increase of about 300% over current production of 1.6 million tons per year would reduce the current emissions by 60–65% from the sulfur equivalent of 1.7 million long tons at present to 600,000–700,000 long tons.

However, to achieve the indicated acid production and corresponding reduction in emissions will require cooperation on the part of the potenial consumers, and some sacrifice on the part of some of the smelter operators. The chemical and mining industries would have to cooperate by increasing their consumption of smelter acid. Fertilizer producers, in particular, would be called upon to increase their use of smelter from approximately 750,000 tons a year as of 1965 to around 3.2 million tons a year by 1975.

Also, the smelter operators would have to sell a large portion of the acid they produce for $4 a ton. Where operators may not be able to produce acid for this price, the difference between the selling price and production cost will have to be charged off as a cost of emission control.

Even if smelter acid production can be increased to 5 million tons a year by 1975, the smelters, primarily those in the southwestern part of the country, would still be omitting enough sulfur dioxide to produce another 2 million to 2.3 million tons of acid a year, for which no markets are foreseen.

Emissions could be reduced below the 600,000–700,000 long tons if the Group I and VI smelters recovered part of the unused sulfur oxides in the form of ammonium sulfate. The additional 400,000 tons of ammonium sulfate that might be produced and sold would be equivalent to 87,000 long tons of sulfur, leaving the smelters with sulfur oxide emissions equivalent to between 510,000 and 610,000 long tons of sulfur annually—a reduction of 65–70% from current emissions instead of the 60–65% reduction if only acid is produced.



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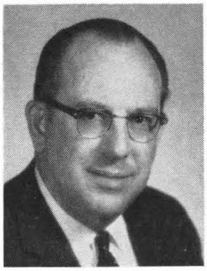

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Measurement and Significance of Adenosine Triphosphate in Activated Sludge

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■ A method for adenosine triphosphate (ATP) measurement in activated sludge has been developed from the firefly reaction of luciferin, luciferase, and ATP, in which light production is proportional to ATP present. Of several technique variables investigated, temperature of ATP extraction from cells was found to be highly critical; extraction solutions a few degrees below boiling yield much less ATP. The finalized procedure is highly sensitive and reliable; relative standard deviations for activated sludge replicates are commonly less than 2%, and recovery of added ATP from activated sludge is nearly 100%. ATP levels in activated sludge are relatively constant under endogenous conditions, indicating the potential of ATP as an estimate of viable biomass, and respond rapidly to induced changes in metabolic activity. The advantages of an activity parameter over historically used biomass parameters for activated sludge operation control are manifold; ATP assay holds promise as a sensitive tool for future research on sludge activity and process control.

Operational control of biological waste treatment has long depended on estimates of *in situ* biomass in the waste stabilization process. A more appropriate and desirable parameter would evaluate the metabolic activity of those organisms responsible for the treatment. The standard parameter of biomass in activated sludge is mixed liquor volatile suspended solids (MLVSS), although it is recognized as an indirect and incomplete measure of the viable sludge floc (Fair and Geyer, 1954; Patterson and Brezonik, 1969). Other biomass parameters have been suggested, including particulate organic nitrogen (Hartmann and Laubenberger, 1968) and protein (Gaudy, 1962), but these are also unsatisfactory because of the variable concentrations of nonviable particulate organic material present in sewage. Furthermore, rapid changes in biological activity are only slowly reflected by changes in any of these parameters.

A parameter must fulfill certain criteria to be a useful and appropriate estimate of biomass. For example, the measured quantity should be proportional to some cellular entity, such as total organic carbon or dry weight. The substance should have a short survival time after cell death; otherwise, it would not be specific for viable biomass. There should also be a sensitive and accurate analytical procedure available to measure the parameter. The authors have investigated the occurrence of adenosine triphosphate (ATP) in activated sludge for the purpose of utilizing this parameter as a measure of metabolic activity and/or biomass.

Theory

ATP is the keystone of all cellular activity; it is a high energy compound in every living cell (Lehninger, 1965). ATP is an essential ingredient in the initial biochemical steps of substrate utilization and in new cell synthesis (Mandelstam and McQuillen, 1968). ATP is synthesized from intermediate and final reactions of substrate oxidation and is also utilized intracellularly for osmotic and mechanical work (Stanier, Doudoroff, *et al.*, 1963).

Sensitive methods for ATP analysis have been developed from McElroy's (1947) finding that luminescence in fireflies has an absolute requirement for ATP. The firefly reaction is unique among bioluminescent phenomena in its requirement for ATP. Luminescence biochemistry has been reviewed in detail (Hastings, 1968).

In vitro light production by firefly lantern extract has been shown to depend upon the presence of luciferin, the enzyme luciferase, oxygen, magnesium ions, and ATP (McElroy, 1947; McElroy and Strehler, 1949). The initial reaction leading to light emission is luciferase catalyzed and involves luciferin and ATP (Equation 1).

$$LH_2 + ATP + E \overset{Mg^{2+}}{\rightleftarrows} E - LH_2 - AMP + PP_i \quad (1)$$

$$E - LH_2 - AMP + O_2 \rightarrow E - L - O^* + \text{Product} \quad (2)$$

$$E - L - O^* \rightarrow E - L - O^- + h\nu \quad (3)$$

The products are an enzyme-luciferin-adenosine monophosphate complex (luciferyl-adenylate) and inorganic pyrophosphate (PP_i). The complex is rapidly oxidized to oxyluciferyl-adenylate (Equation 2), an excited state, followed by release of a quantum of light (Equation 3). When firefly lantern extract is mixed with ATP, there is an initial burst of light which rapidly declines to a low but uniform level of luminescence (McElroy and Strehler, 1949). However, when the reactants are combined in the presence of arsenate buffer, an intermediate level of light emission occurs which decays steadily and exponentially with time (Strehler and Totter, 1952).

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McElroy and Green (1956) have shown that ATP is the only nucleoside triphosphate that will produce light with purified extract of firefly lantern. However, the presence of transphosphorylase enzymes in the crude extract commercially available results in light emission in the presence of molecules other than ATP which contain high-energy phosphate bonds. Holm-Hansen and Booth (1966) investigated 13 such compounds commonly present intracellularly. Of these, only adenosine diphosphate (ADP), cytidine-5-triphosphate (CTP), and inosine-5-triphosphate (ITP) effected light emission. The light intensity from the addition of ADP was less than 1% of an equivalent amount of ATP. However, both CTP and ITP stimulated light production equivalent to ATP response.

The fact that some light might be due to nucleoside triphosphates other than ATP is probably not important since nearly all cells contain other high-energy phosphate compounds similar in structure, function, and free energy of hydrolysis to ATP (Lehninger, 1965). These compounds occur as ribonucleoside-5′-triphosphates (ATP, CTP, etc.), but all obtain their terminal phosphate group from ATP through the action of nucleoside diphosphokinases (Equation 4).

$$\text{ATP} + \text{CDP} \rightleftarrows \text{ADP} + \text{CTP} \qquad (4)$$

The only exception of note is the direct production of one guanosine triphosphate (GTP) molecule in the citric acid cycle; GTP forms an equivalent amount of ATP in a reaction analogous to the reverse of Equation 4. Therefore, each nucleoside triphosphate represents an "equivalent" ATP molecule; they are simply compounds which function to channel ATP energy into different biosynthetic pathways (Lehninger, 1965).

The amount of light produced by firefly lantern extract is directly proportional to the amount of ATP added, and numerous workers have developed ATP assays based upon this concept. These assays require a sensitive means of measuring light emission from the reaction mixture. Some investigators (Forrest, 1965; Holm-Hansen and Booth, 1966; Lyman and DeVincenzo, 1967) developed their own instrumentation, consisting essentially of a photomultiplier tube mounted in a black box and connected to an amplifier and recorder. Others (Addanki, Sotos, *et al.*, 1966; Cole, Wimpenney, *et al.*, 1967) have utilized conventional liquid scintillation spectrometers to measure luminescence. Each procedure, including the one used in this study, was developed for application to the particular biological system under investigation.

Materials and Methods

Luciferin-Luciferase Preparation. Lyophilized aqueous extracts of firefly lanterns were obtained commercially (Sigma Chemical Co., Stock FLE-50) and stored at −20° C. until ready for use. Each vial contains the extract from 50 mg. of firefly lanterns, plus magnesium arsenate buffer. Each vial, which was adequate for 23 ATP determinations, was rehydrated with 37.5 ml. of deionized distilled water. After standing at room temperature for 1 hour, the suspension was filtered (Whatman No. 3) and the filtrate incubated in an ice water bath for 24 hours.

ATP Standards. Crystalline ATP (disodium salt, mol. wt. 551.2) was weighed in 10.92-mg. portions and dissolved in 1 liter of tris buffer (0.025 *M*, pH 7.75). This stock solution was poured into individual test tubes, which were capped and stored at −20° C. until needed. Storage as long as two months showed no loss of strength in the ATP stock solution. When ATP standards were required, a test tube of stock solution was thawed and diluted with tris buffer to the desired concentrations. Usually these were 50, 100, 150, and 200 μg. of ATP per liter, although standards of 1 to 1000 μg. per liter were used occasionally.

ATP Extraction. Samples from laboratory-model activated sludge systems were pipetted into 50.0-ml. volumetric flasks which contained approximately 40 ml. of boiling tris buffer (0.025 *M*, pH 7.75). The flasks were held in a boiling water bath for 10 minutes with occasional shaking. This procedure killed the activated sludge immediately and extracted the cellular ATP quantitatively. The flasks and contents were then rapidly cooled and brought up to volume with additional tris buffer. After thorough mixing, aliquots were centrifuged to bring down cell debris and the supernatant poured into a test tube. For an immediate assay, the test tube was placed in an ice bath. If later analysis was desired, the samples were frozen and held at −20° C. Known concentrations of ATP carried through the extraction procedure showed no loss of activity.

Light Measurement. A liquid scintillation spectrometer (Packard Tri-Carb Model 2002) was used to measure light emission. Gain was set at 53, with a window setting of 50–1000. The spectrometer was set in a repeat count mode, with each 6-second counting interval separated by a 7.5-second data printout sequence.

Background light emission from the luciferin-luciferase preparation was measured prior to each ATP analysis. Exactly 1.5 ml. of the enzyme preparation was pipetted into a scintillation vial through a 0.64-cm. hole bored in the cap. The normal background was 5 to 15 counts in the 6-second counting interval used. Significantly higher counts were considered to indicate glassware contamination, which proved troublesome in the early analyses. To circumvent this problem, a standard cleaning procedure was adopted for all glassware. Following a thorough soak and hot soapy wash, the glassware was boiled for 1 hour in an acid bath and then triple rinsed in deionized, distilled water. No contamination problems occurred after initiation of this cleaning procedure.

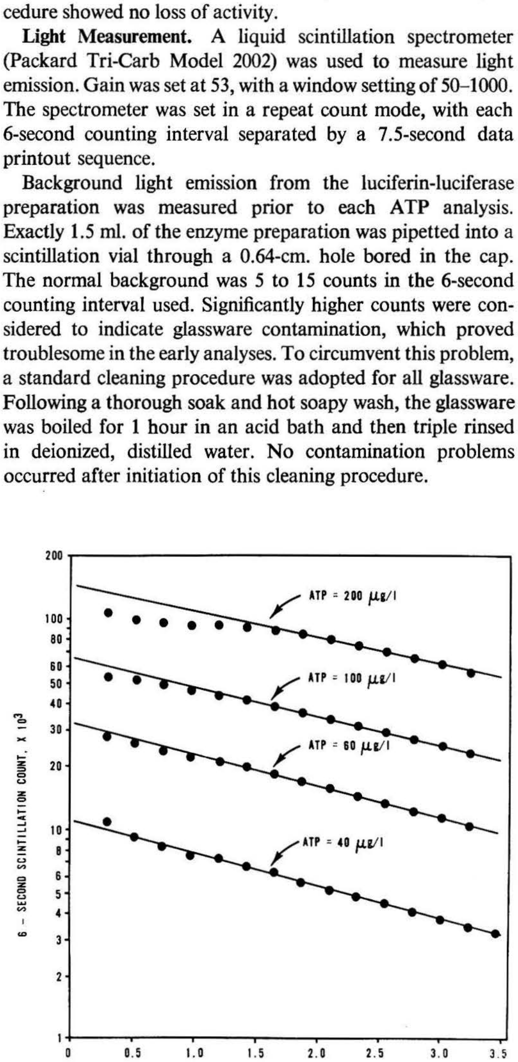

Figure 1. Luminescence decay of ATP–firefly lantern extract reaction with time

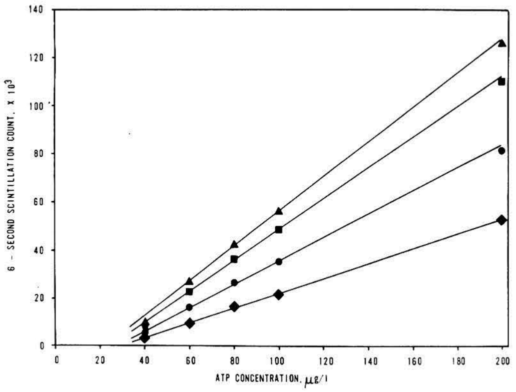

Figure 2. Standard curves for light emission *vs.* ATP concentration at elapsed reaction times of 0.5 minute (▲), 1.0 minute (■), 2.0 minutes (●), and 3.5 minutes (◆)

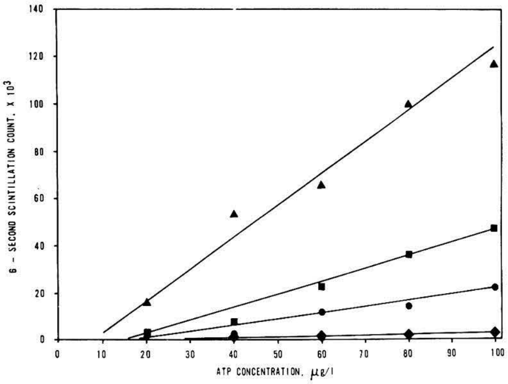

Figure 3. Standard curves of light emission at 1 minute reaction time *vs.* ATP concentration for firefly lantern extract concentrations of 1.27 standard strength (▲), 1.0 standard strength (■), 0.67 standard strength (●), and 0.33 standard strength (◆)

Following the determination of the background emission, 0.5 ml. of ATP standard or sample was added to the enzyme preparation, and the vial swirled to mix the contents. Since luminescence decays exponentially with time, the interval between addition of ATP to the enzyme preparation and initiation of the counting sequence was carefully controlled. Exactly 11.0 seconds after ATP addition, the vial entered the scintillation counting chamber. The first 6-second count began 15.0 seconds after ATP addition. Thus, the median reaction time of the first counting interval was 18.0 seconds, and the median of each subsequent count occurred 13.5 seconds after the previous one. Luminescence rates were normally recorded for 15 sequential counting periods, a total reaction time of approximately 3.5 minutes.

Development of Analytical Procedure. Owing to the inherent random variability of any 6-second count, it was considered more accurate to analyze the data graphically. Figure 1 shows luminescence die-off curves for several ATP concentrations. In most cases, light emission decayed exponentially. However, higher ATP concentrations often resulted in a constant or increasing emission level for the first few counts, exponential decay commonly beginning within 1 minute after the reaction was initiated. The line of best fit to the exponential data points was extrapolated back to 1 minute in those cases where exponential decay began at a later reaction time. This graphical technique yielded linear standard curves for a wide range of ATP concentrations, and the procedure was adopted for both standard and sample ATP analyses.

The 6-second emission counts were plotted on semilog paper *vs.* reaction time (Figure 1) and the count at 1.0 minute read from the exponential line of best fit. Standard curves were prepared in a similar manner. Good correlatiion between standard ATP concentration and counts was obtained for reaction times of 1.0 minute or longer, while graphs of counts *vs.* concentration were more erratic for shorter reaction times. Figure 2 shows standard curves for light emission at various reaction times.

Strehler and Totter (1952) and Cole, Wimpenney, *et al.* (1967) reported reduced luminescent rates or reduction in slope of the standard curve occurring above intermediate ATP concentrations. This slope reduction possibly resulted from plotting short-term emission values directly. Strehler and Totter measured emission for a 12.8-second interval 15 seconds after the reaction began. Figure 1 shows that this procedure would result in an apparent reduction in emission rate for ATP concentrations greater than approximately 100 μg. per liter unless a graphical analysis was employed.

The effects of different concentrations of firefly extract are shown in Figure 3. The highest concentration investigated (1.27 times the normal concentration) resulted in a poor standard curve. The lowest concentration (one-third the normal) showed good correlation for ATP concentration *vs.* a 6-second count, but the flat slope of the standard curve reduced the accuracy of analysis.

The effects of aging on both ATP standard solutions and lantern extract are presented in Table I. Background emission decreased rapidly during the standard 24-hour incubation

Table I. Effect of Incubation on Firefly Extract and ATP Light Emission (6-sec. count)

		6-Second count					
Extract age, hours	Extract background counts	Fresh ATP, μg./l.			Aged ATP,[a] μg./l.		
		20	100	500	20	100	500
2	355	11,200	118,000	430,000			
6	153	7500	121,000	420,000	5050	107,000	418,000
12	63				1070	92,000	383,000
24	15	3350	85,000	400,000	25	56,200	324,000

[a] ATP age was 1 hour less than extract age.

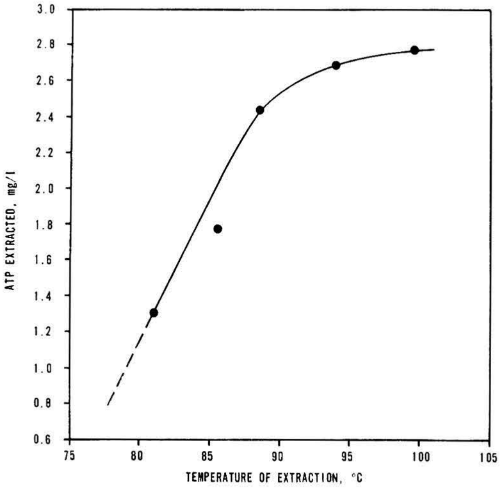

Figure 4. Dependence of cellular ATP extraction on temperature of extraction

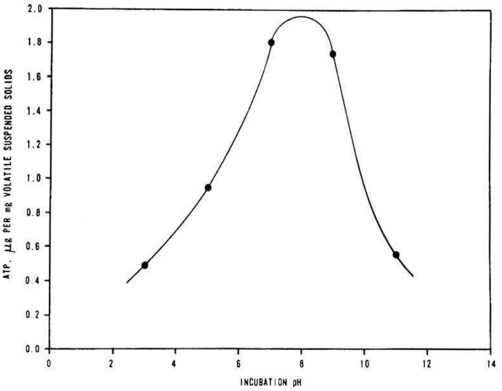

Figure 5. Effect of incubation pH on activated sludge ATP pool

period of the rehydrated firefly extract. Two sets of ATP standards were made up. One set was immediately frozen, then thawed just prior to analysis. The second set was held in an ice water bath with the firefly preparation. Light emission from the freshly thawed standards decreased with the time of extract incubation, indicating a slight loss of enzyme activity over the 24-hour period. The light emission from the aged ATP solution decreased much more rapidly, indicating a loss of ATP from the standard solutions during the incubation period. Because of this rapid loss of ATP, standards were always assayed immediately after preparation.

The effect of temperature on ATP extraction is highly critical. As shown in Figure 4, a reduction in temperature of the tris solution of a few degrees below boiling yielded much lower amounts of extracted ATP. The extraction was therefore carried out in a rapidly boiling water bath to ensure quantitative extraction of ATP. In our procedure, the extraction period was 10 minutes, but other researchers (Holm-Hansen and Booth, 1966; Hamilton and Holm-Hansen, 1967) achieved quantitative extraction from marine samples within 5 minutes.

When known amounts of ATP were added to extracted sample, ATP recovery was close to 100%, indicating that there were no substances present in the extract which suppressed the ATP-induced light emission. For example, 50 μg. per liter of ATP was added to three different activated sludge samples. The mean incremental ATP increase above the original sample levels was 47.5 μg. per liter. The procedure used in this study has proved to be a precise and sensitive measurement of cellular ATP, with replication of activated sludge samples commonly yielding a relative standard deviation of less than 2%.

The sensitivity of the firefly reaction to pH has been investigated by Rhodes and McElroy (1958). They found that light emission increased rapidly from pH 2.0 to 3.8, followed by reduced emission to pH 4.8. From pH 4.8 to 7.0, the highest pH investigated, emission again increased with pH. The emission rate at pH 7 was approximately 25% greater than the maximum at pH 3.8. The complex effects of pH on light emission necessitates a consistently buffered reaction mixture; pH 7.75 was used in our procedure.

The ionic composition of the reaction medium also affects light emission, as shown by the results of Aledort, Weed, *et al.* (1966), in which emission rates were reduced linearly with increasing concentrations of several cations; equimolar concentrations of those cations investigated inhibited light emission in the order of $Ca^{2+} > K^+ > Na^+ > Rb^+ > Li^+ >$ choline$^+$. Aledort, Weed, *et al.* (1966) reported that calcium, in a concentration of 97 m*M* completely suppressed light emission in the ATP range of $1.2–2.2 \times 10^{-7}M$. The problem of variable ionic composition of sample may be alleviated by a high initial dilution, as in the 1 to 25 dilution into boiling tris buffer utilized in our procedure. The ionic strength of normal activated sludge is sufficiently low that inhibitory effects are unimportant with this dilution. Marine samples often require even higher dilution, and filtration may be necessary prior to ATP extraction (Hamilton and Holm-Hansen, 1967).

Application

ATP is a specific indicator of cell viability. Activated sludge samples which had been filtered and dried at 103° C. for 1 hour showed no residual ATP. The same result has been obtained by other researchers when samples were killed by repeated freezing or with cyanide (Holm-Hansen and Booth, 1966).

Several experiments indicate the potential of ATP analysis in studying toxicity effects on activated sludge. Figure 5 shows the ATP pool (μg. ATP/mg. MLVSS) measured in activated sludge incubated for 1 hour at various levels of pH. Maximum ATP pool occurred in the pH range of 7.5 to 8.0, which was the normal operating range of the batch units employed in this particular experiment. The maximum ATP pool measured, approximately 2 μg. per mg. MLVSS, was typical of the indigenous ATP concentrations in these activated sludge batch units. ATP pool was greatly reduced at the lowest pH (3.0) and highest pH (11.0) investigated. The pH data reported are those of the incubation media; the intracellular pH presumably underwent a less drastic change. The reduction in ATP pool might reflect an increased energy demand resulting from the organisms' efforts to maintain homeostasis or alternately indicate a reduction in number of viable cells under lethal environmental conditions.

The effects of some heavy metals on ATP levels in activated sludge have also been investigated. Figure 6 shows the ATP pool in activated sludge samples after 1 hour incubation in the presence of various concentrations of mercuric chloride. The toxicity pattern in Figure 6 shows a rapid drop in ATP pool at low Hg^{2+} levels, a more gradual decrease at intermediate

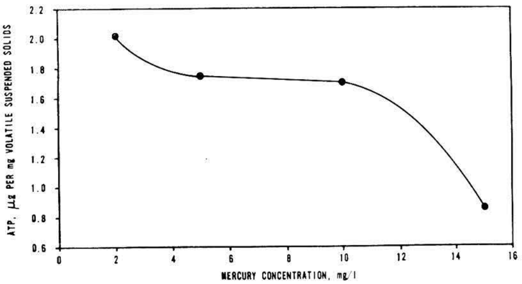

Figure 6. ATP pool toxicity pattern after 1 hour incubation with mercury

concentrations, and an increased rate of pool reduction above 10 mg./l. Hg^{2+} concentration. It should be emphasized that this toxicity pattern might vary substantially for any given toxicant, depending upon the biochemical parameter measured. For example, mercury toxicity as analyzed by ATP pool, dehydrogenase activity, or respiratory activity shows completely different patterns for all three biochemical parameters (Patterson, Brezonik, *et al.*, 1969).

A further precaution with regard to ATP analyses of toxicant effects concerns the effect of the inhibitor upon the firefly extract itself. One of the required reactants of this ATP procedure is the enzyme luciferase present in the lantern extract. Any substance which inhibits luciferase activity will reduce light emission and yield false ATP results. Figure 7 presents the effect of mercury ion on luciferase activity at a known ATP concentration. Incremental increases in mercury concentration rapidly reduce luciferase activity, and consequently, light emission. Sample filtration or high dilution may be utilized for any sample suspected of containing a general enzymatic inhibitor such as heavy metal. While fractional dilutions of samples which do not contain luciferase inhibitors result in a linear relationship between dilution factor and light emission (Figure 8), inhibitor presence is evidenced by a parabolic relationship, the higher concentrations of ATP being accompanied by a higher luciferase inhibitor concentration.

To relate ATP concentration to microbial biomass, it is necessary to know the approximate ATP concentration per cell of the microbial species present. If ATP is also related to metabolic activity, the physiological state of the culture must be determined. Since it is impossible to make a taxonomic analysis of the microbiota present in activated sludge, the accuracy of biomass estimations would depend upon the constancy of ATP pool among species. D'Eustachio and Johnson (1968) investigated the endogenous ATP pool of 13 species of aerobic bacteria (Gram + and Gram −) and found a mean ATP pool of 2.1 μg. per mg. of dry cell material. Their standard deviation across all tested species was 1.1 μg. per mg. A linear correlation existed between endogenous ATP pool and standard plate count for those species investigated. In an earlier study, D'Eustachio and Levin (1967) reported lower levels of ATP in *Escherichia coli*, *Pseudomonas fluorescens*, and *Bacillus subtilis* (0.47 μg. per mg. dry weight cell material) and reported that this ATP pool was constant throughout all phases of growth. ATP was extracted by cell sonication in this study. Chappelle and Levin (1968) reported on the ATP pool in 19 bacterial species during the stationary growth phase. ATP content varied among the species by approximately an order of magnitude, with an overall mean ATP pool of 2.09 μg. per mg. dry weight of cell material. No statistical evaluation was presented for the accuracy and

Figure 7. Inhibition of firefly lantern luciferase by mercury (ATP concentration of 100 μg./l.)

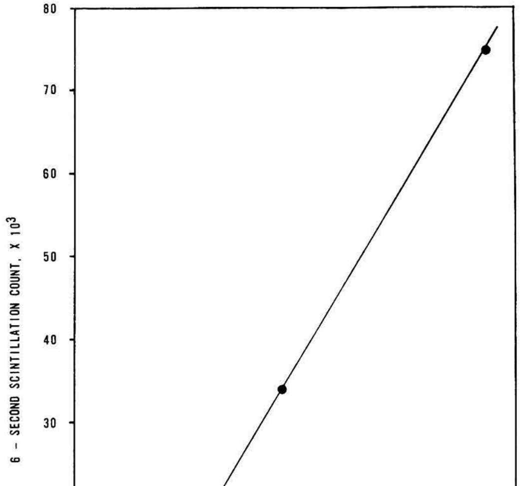

Figure 8. Linear relationship of light emission to solids dilution prior to ATP extraction

precision of the extraction and analytical procedure. However, some of the reported data suggests their extraction of cellular ATP may have been incomplete. For example, the authors report an ATP concentration in *E. coli* of 1.0×10^{-10} μg. per cell with a 1-minute extraction time, and they include this value in their compilation of the ATP content of bacteria. However, they also found 1.5×10^{-10} μg. ATP per cell with 10 minutes of extraction and 1.9×10^{-10} μg. per cell with 30 minutes extraction of the same species. The latter value is nearly twice that reported for *E. coli* in their summary table of ATP in bacteria. Cole, Wimpenney, *et al.* (1967) also measured the ATP pool in *E. coli*. The complex interactions of growth phase and culture media indicated by their results are difficult to evaluate, but three conclusions might be drawn: the ATP pool reported was significantly higher for all growth phases than the values reported by D'Eustachio and Levin, the ATP pool may vary as metabolic activity changes, and the interaction of ATP pool and growth phase is partially dependent upon the culture media. Forrest (1965), in studying the ATP pool in *Streptococcus faecalis* reported an interaction between growth phase and ATP pool, the pattern of ATP change again depending upon the culture medium.

Aside from the values reported by D'Eustachio and his co-workers (1967, 1968), other published values for bacterial ATP pool include for *E. coli* about 3 μg. per mg. (Lehninger, 1965) and 3 to 9 μg. per mg. (Cole, Wimpenney, *et al.*, 1967), for *S. faecalis* 2 to 12 μg. per mg. (Forrest, 1965), and 0.72 to 2.2 μg. per mg. for three marine *Pseudomonas* species (Holm-Hansen and Booth, 1966). The lower limits of these values all approximate the endogenous ATP values mentioned above. Therefore, it would appear that endogenous ATP pool is reasonably constant intergenerically and may yield a good estimate of viable biomass, with an endogenous ATP pool approximating 2 μg. per mg. of cell material. However, some confusion exists as to the response of ATP pool to changes in metabolic activity. If there is no change, or only erratic variation, then ATP could not be used as an activity parameter in studies on activated sludge.

An experiment was therefore designed to determine the pattern of ATP pool response to a change in metabolic activity of an activated sludge culture. Two volumes of mixed liquor were taken from a continuously fed laboratory model activated sludge unit which was maintained on a skim milk substrate. These samples were mixed without feeding for 24 hours, at which time skim milk (BOD_5 = 1000 mg./l.) was added to one. MLVSS and ATP samples were taken periodically on both units before and after feeding; the results are presented in Figure 9. During the 24-hour period prior to feeding there was a slow drop in ATP pool, which leveled out in the unfed sample during the next 24 hours. This correlates with the results of Strange and his co-workers (1963) who reported that neither cell viability nor ATP pool decreased significantly during a 50-hour starvation period of *Aerobacter aerogenes*. The immediate response in the fed sample was a slight drop in ATP, followed by a rapid and significant increase. The maximum increase was 57% above the initial ATP pool and 145% above the endogenous unit level at the same incubation time. These results indicate that ATP pool is affected by the metabolic activity of an activated sludge culture and may be expected to respond rapidly and decisively to an increase in substrate loading, while being only gradually reduced as the organisms enter an endogenous phase.

A similar experiment was carried out on the University of Florida contact stabilization sewage treatment plant which treats a relatively weak sewage, essentially domestic in nature. The contact stabilization process consists of a sedimentation basin, from which settled activated sludge is pumped into a spiral flow sludge aeration basin having a detention time of approximately 12 hours. The sludge then enters the contact chamber, at which point primary settled sewage is added. The contact chamber is also spiral flow, with a detention time of approximately 3 hours. Mixed liquor from the contact chamber is returned to the sedimentation basin. MLVSS and ATP samples were taken along the length of the aeration and contact chambers and ATP pools determined throughout the treatment process. The results presented in Figure 10 show a similar pattern to that in Figure 9, with a relatively constant ATP pool in the aeration tank, followed by an increased pool after substrate addition. MLVSS was approximately 3300 mg. per liter in the aeration chamber and dropped to about 2100 mg. per liter in the contact tank due to the dilution effect of the sewage added. Although the BOD_5 strength of the sewage was not determined in this particular experiment, it is normally in the range 150 to 200 mg./l. Thus, both laboratory and plant-scale studies indicate that ATP is a sensitive parameter of metabolic activity.

ATP analyses on activated sludge samples from both batch fed and continuously fed laboratory units have consistently yielded ATP pools of 1.4 to 2.0 μg. per mg. VSS. The batch unit pool levels were usually determined within a short time after feeding, when metabolic activity would be highest and were in the range of 1.8 to 2.0. The continuously fed units yielded a range of 1.4 to 1.8, indicating a somewhat lower metabolic activity. While neither process should yield a true endogenous metabolic state, ATP pools for both processes correspond to those reported previously for bacterial en-

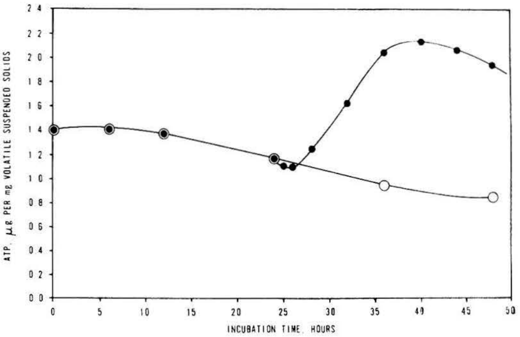

Figure 9. ATP pool response pattern for starved (○) and fed (●) activated sludge

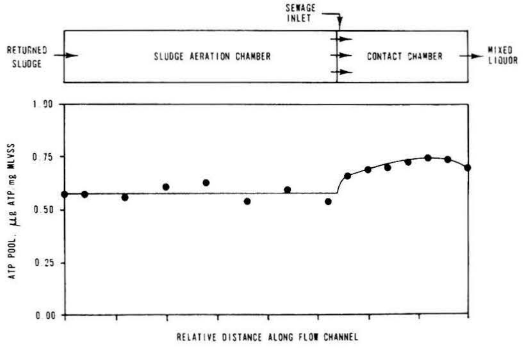

Figure 10. ATP pool response in contact stabilization sewage treatment unit

dogenous activity. This indicates that a significant portion of the MLVSS is nonviable organic material not associated with the oxidative degradation of the substrate. An estimate of the percentage of viable biomass present in activated sludge may be based on an average value of the ATP pool in pure cultures as discussed above and the assumption that neither cell viability nor endogenous ATP pool decreased significantly during the 48-hour incubation period of the unfed unit in the laboratory experiment. After 45 hours of incubation, ATP pool leveled off at approximately 0.8 μg. per mg. VSS (Figure 9). Assuming a mean endogenous ATP pool of 2 μg. per mg., dry cell material would result in an estimate that only 40% of the laboratory unit MLVSS was actually viable cell material. The single experiment carried out in the University of Florida contact stabilization plant indicates that only 15 to 20% of the MLVSS may be active biomass under actual operating conditions.

Summary

A method of analysis for ATP in activated sludge has been developed. The technique has proved sensitive and reliable for quantitative determination of cellular ATP pool. The light emission to which ATP concentration can be related is influenced by several technique variables. These include temperature of ATP extraction, age and concentration of the reconstituted firefly lantern extract, ionic concentration of the reaction mixture, and the presence of enzymatic inhibitors in the extracted samples. An exponential die-off of light emission with reaction time is generally shown, and graphical data analysis has yielded accurate results over a wide range of ATP concentrations.

This study has confirmed published reports of a relatively constant ATP pool under endogenous conditions, although the pool in activated sludge is significantly lower than that reported for pure culture experiments. This lower ATP pool in MLVSS indicates that only a fraction of the total activated sludge solids is viable cell material. As shown by its complete disappearance within 2 hours after cell death, ATP is a specific indicator of cell viability.

ATP pool has been found to reflect the toxicity of pH and a heavy metal to activated sludge cultures and appears appropriate as an estimator of toxic stress on microbial systems. The ATP pool responds rapidly to changes in the metabolic activity of activated sludge, as demonstrated by both laboratory (Figure 9) and field (Figure 10) studies. This may well be the most significant aspect of this investigation since a metabolic activity parameter is more appropriate and desirable than a biomass parameter in control of a biological waste treatment process.

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Received for review August 21, 1969. Accepted February 4, 1970.

Separation of Phenolic Compounds from Carbon Chloroform Extract for Individual Chromatographic Identification and Measurement

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■ A procedure is presented for efficient isolation of many phenols from carbon chloroform extracts (CCE) prior to chromatographic identification. The phenols, as weak acids, are isolated by a Florisil column cleanup of the CCE. Techniques for evaporation and preparation of the extract are given. Application of the method to grab samples as well as qualitative and quantitative determinations are discussed. Recovery data and relative retention times for a gas-liquid chromatographic separation are reported.

Table I. Separation Efficiencies Obtained

Compounds	Dosage, mg.	Evaporation	Per cent[a] recovery from cleanup procedure
Alkyl phenols			
o-cresol	0.16	64	109
m-cresol	0.30	78	88
p-cresol	0.40	93	95
2,3-dimethyl	0.40	75	73
2,4-dimethyl	0.40	75	60
2,5-dimethyl	0.40	75	85
2,6-dimethyl	0.20	85	55
3,4-dimethyl	0.40	79	81
3,5-dimethyl	0.40	95	88
2,3,5-trimethyl	0.80	68	94
2,4,5-trimethyl	0.40	87	90
2,3,5,6-tetramethyl	0.20	60	18
p-tertbutyl	0.30	73	104
2,6-ditertbutyl-*p*-cresol	0.20	75	0
Chlorophenols			
o-chloro	0.40	75	91
m-chloro	0.20	71	92
p-chloro	1.20	90	80
2,3-dichloro	1.20	76	93
2,4-dichloro	1.00	79	103
2,5-dichloro	0.60	78	86
2,6-dichloro	1.00	80	106
3,4-dichloro	0.30	82	95
2,4,5-trichloro	0.15	67	109
2,4,6-trichloro	1.20	87	83
Aminophenols			
o-amino	0.50	13	0
m-amino	0.90	8	0
p-amino	0.80	5	0
m-diethylamino	2.00	36	0
Miscellaneous phenols			
phenol	0.40	75	104
o-nitro	1.20	55	102
4-chloro-2-nitro	1.00	44	91
p-methoxy	1.20	59	107
p-butoxy	0.06	70	109
1-naphthol	1.40	62	77
2-naphthol	0.60	72	111
p-phenyl	0.80	78	103
2-bromo-4-phenyl	0.90	83	94

[a] Corrected for evaporation loss.

Phenols are introduced into surface waters as pollutants from a variety of sources such as industrial effluents, sewage disposal, agricultural runoff, and chemical spills. These compounds are considered pollutants when they are present in sufficient concentration to cause undesirable taste and odor problems. To control this type of pollution, it is important to have the ability to identify and measure individual phenols. Specific identification is often required to determine the source of pollution. Specific identifications also make it possible to carry out more effective monitoring programs.

The carbon adsorption method (Middleton and Rosen, 1956; Middleton, Grant, *et al.*, 1956) used by this laboratory is capable of collecting phenols for analysis. This method used the adsorptive capacity of activated carbon to concentrate organic materials from large volumes of water. The phenols present in the water, along with many other organic materials, are adsorbed on the carbon at the sampling point and desorbed from the carbon in the laboratory by extraction with chloroform (Goren-Strul, Kleijn, *et al.*, 1966). The carbon chloroform extract (CCE) is evaporated to apparent dryness and weighed. Although the method is not quantitative, the concentration of the CCE gives some measure of the degree of organic pollution in a stream.

The identification and measurement of individual phenols in a CCE are extremely difficult because of large amounts of other organic materials which are desorbed from the carbon. Further, the high volatility of many phenols results in large losses when the CCE is evaporated to apparent dryness. Thus, an efficient means of concentrating and isolating phenols from the CCE is needed.

Phenols have been isolated from CCE in this laboratory by use of a modified Shriner-Fuson separation as described by Breidenbach, Lichtenberg, *et al.* (1966) and suggested refinements by Goren-Strul, Kleijn, *et al.* (1966). With both procedures, partitioning of phenols to various solubility fractions and loss of volatile phenols caused by the many manipulations result in poor recoveries. In addition, fractions obtained for gas and thin-layer chromatographic analysis were still not sufficiently free of nonphenolic organic material. The above problems are largely overcome by the method presented here. This method omits the evaporation of the CCE to dryness and employs an extraction of phenols as acids, followed by a Florisil column cleanup of the extract. The proposed procedure yields phenolic compounds sufficiently free of extraneous material for subsequent separation and analysis by chromatographic techniques.

Experimental

Aliquots of CCE samples (140 mg. each) were dissolved in 30 ml. of chloroform to simulate concentrated extracts. These aliquots were dosed in triplicate with selected groups of phenols and an undosed aliquot was used as a blank. The dosing quantities of each compound are listed in Table I.

The 30-ml. samples were quantitatively transferred to 125-ml. separatory funnels with chloroform. Each sample was extracted three times with 15-ml. portions of aqueous NaOH of pH 13. The chloroform layers were discarded and the aqueous layers were combined in 125-ml Erlenmeyer flasks. These extracts were acidified with concentrated HCl to pH 2. The acidified samples were allowed to cool and were returned quantitatively to the separatory funnels. They were then back extracted three times with 15-ml. portions of ethyl ether and the ether layers were combined in 150-ml. beakers.

Glass columns 20-mm. in diameter were packed to 10 cm. with Florisil and topped with 2 cm. of anhydrous sodium sulfate. The columns were washed with 30 ml. of ethyl ether. When the last of the 30 ml. reached the sodium sulfate, the 45-ml. extracts were added and 250-ml. beakers were used to collect the eluates. When the last of the 45 ml. reached the sodium sulfate, a 200-ml. portion of ethyl ether was added to each column and collected in the same beakers. The eluates were evaporated in the beaker on a warm water bath (50° C.) in an exhaust hood. When the volumes reached approximately 10 ml., the eluates were quantitatively transferred to 15-ml. centrifuge tubes and carefully evaporated again to 10 ml. by use of a warm water bath (50° C.) and a gentle stream of air.

The eluates obtained from this procedure were analyzed by gas chromatography to determine recoveries of the phenols and the effectiveness of the cleanup procedure. Eluates containing phenols whose relative retention times are greater than 4.0 were concentrated to 5 ml. for adequate response on the gas chromatograph.

The method was evaluated using 37 phenolic compounds, including alkylphenols, chlorophenols, nitrophenols, and aminophenols. The rentention time of each compound was determined on the gas chromatograph prior to the evaluation of the method. Retention times relative to phenol are listed in Table II.

Six of these phenolic compounds were used to dose four replicate CCE samples to determine the effects of concentration and drying of a CCE for weighing prior to a phenol analysis. The CCE samples (140 mg. each) were dissolved in 3 liters of chloroform, dosed with 0.50 mg. of each of the six compounds, and then concentrated to 150 ml. The concentrated extracts were transferred to 250-ml. Erlenmeyer flasks and evaporated on a warm water bath (70° C.) with a gentle stream of air. Two of the samples were evaporated to apparent dryness according to the normal procedure and two were evaporated to a 10-ml. volume.

Results and Discussion

Figure 1 illustrates the effectiveness of the method for cleanup of a dosed CCE. The removal of the bulk of the extraneous background material permits discrimination of

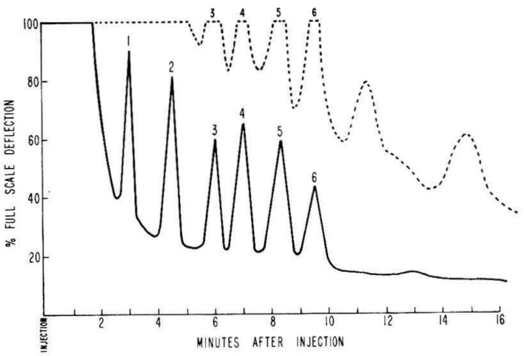

Figure 1. Gas chromatogram of dosed CCE before and after cleanup[a]

(a) ---- Chromatogram of dosed CCE before cleanup. CCE-165 mg./10 ml. $CHCl_3$, injection volume, 3 μl.
(b) —— Chromatogram of extract of same dosed CCE after extraction with aqueous NaOH and Florisil column cleanup; 5 μl. of 10 ml. ethyl ether extract injected.

[a] Phenols dosed: (1) *o*-chlorophenol, (2) phenol, (3) 2,5-dimethylphenol, (4) 2,6-dichlorophenol, (5) 2,4-dichlorophenol, (6) 2,3,5-trimethylphenol

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Table II. List of Relative Retention Times for Compounds Studied[a]

Compound	RR_t[b]	Compound	RR_t
Column temperature 210° C.			
o-chlorophenol	0.63	2,3-dimethylphenol	1.54
o-nitrophenol	0.72	2,4-dichlorophenol	1.70
		3,5-dimethylphenol	1.71
2,6-dimethylphenol	0.78	2,5-dichlorophenol	1.76
2,6-ditertbutyl-*p*-cresol	0.83	2,3-dichlorophenol	1.78
o-cresol	0.98	2,3,5,6-tetramethylphenol	1.83
phenol	1.00	2,4,5-trimethylphenol	1.88
o-aminophenol	1.21	2,3,5-trimethylphenol	1.96
2,5-dimethylphenol	1.24	3,4-dimethylphenol	1.99
2,4-dimethylphenol	1.26	*p*-tert-butylphenol	2.43
p-cresol	1.27	2,4,6-trichlorophenol	2.88
m-cresol	1.30	*p*-methoxyphenol	3.32
4-chloro-2-nitrophenol	1.32	*p*-chlorophenol	3.65
2,6-dichlorophenol	1.46	*m*-diethylaminophenol	7.48
Column temperature 240° C.			
m-chlorophenol	3.12	3,4-dichlorophenol	9.64
2,4,5-trichlorophenol	4.09	1-naphthol	10.90
p-butoxyphenol	5.05	2-naphthol	12.51
m-aminophenol	5.78	2-bromo-4-phenylphenol	18.14
p-aminophenol	5.90	*p*-phenylphenol	22.85

[a] Instrument conditions used to obtain the above data are: Perkin-Elmer Model 800 gas chromatograph with dual F.I.D., sensor and reference columns 10 ft. × 1/8-in. o.d. aluminum packed with HMDS treated Chromosorb W (60/80 mesh) coated with 10% Carbowax 20 *M* terephthalic acid. The carrier gas was nitrogen at a flow rate of 50 ml./min. through each column. Temperatures were: column, as indicated; injector, 260° C.; detector, 210° C.
[b] Retention times are relative to phenol.

components of interest. This accomplishment is particularly noteworthy with regard to the early eluting phenols previously masked by interferences.

Also, by doing a gas chromatographic analysis with a sample cleaned up in this manner, the life of the column is prolonged and the detectors need cleaning less frequently.

The cleanup procedure greatly increases the analytical potential of thin-layer chromatography for phenols. Before cleanup only about 1% of the CCE can be spotted before the adsorptive capacity of the layer is reached. After cleanup, usually the entire extract can be spotted and less background interference is encountered.

In the evaluation of the cleanup procedure it was noted that significant losses of some phenols occurred during the concentration of the Florisil column eluates to 10 ml. Each of the phenols was dosed into three 245-ml. portions of ethyl ether to determine evaporation losses. The amount of the dosage and the recoveries obtained in these studies are reported in Table I. The recoveries from the cleanup procedure, calculated by dividing the recovery from the dosed CCE by the recovery from the ether and multiplying by 100, are also reported in Table I.

Application of the entire procedure and the evaporation of the column eluate control were done in triplicate for each compound, and the average of the three results tabulated. With careful attention to technique, the repeatability of the results can be kept within ±5% of the average.

The method is very satisfactory for 31 of the 37 compounds investigated. With few exceptions, the corrected recoveries are 80% or higher. The average recovery of 85% for alkylphenols and 94% for chlorophenols indicates a selectivity of the method for compounds in these classes. The four aminophenols were not recovered from the CCE but were recovered in small percentages from the evaporation controls. The compounds, as well as 2,6-ditertiarybutyl-*p*-cresol, are not extracted under strong basic conditions. A very small amount of 2,3,5,6-tetramethylphenol was recovered from the CCE. Further studies will be undertaken to develop methods for extraction of such compounds and to reduce evaporation losses. Thus, the method presented here, while not applicable to all phenols, is well suited to the recovery of the majority of common phenols from a CCE.

Because evaporation losses were so significant, special attention was given to selecting the most suitable solvent for the method. Ethyl ether was used because it was found to be most effective in keeping losses to a minimum during evaporation and most efficient in removing phenols from the Florisil column. Evaporation losses of volatile phenols can be excessive using ether if samples are concentrated to volumes below 3 ml.

Analysis of the raw CCE samples concentrated from 3 liters to 10 ml. showed a negligible loss of phenols. Analysis of the two samples dried for three days showed a loss of 10% to 20% for the individual compounds. To minimize the loss of phenols, therefore, it is recommended that the CCE not be taken to dryness before analysis. (If a CCE weight is desired, an aliquot can be analyzed and the remainder dried and weighed.)

That very little loss occurs in the chloroform concentration step when the extract is not dried can probably be attributed to the reflux conditions under which the concentration was carried out. It was noted that removing the solvent vapors with a stream of air tends to sweep out the phenols with the solvent vapor before they can condense on the sides of the vessel. Reflux conditions yield higher recoveries and the use of special concentrating equipment, such as the Kuderna-Danish apparatus, might be advantageous.

The presence of a compound in the extract after a sodium hydroxide extraction and a Florisil-ethyl ether column cleanup is a good indication that it is a phenolic compound. An identification based on a gas chromatographic response, however, should be confirmed by another analytical technique.

The procedure described may also be applied to extracts of water grab samples, bottom deposits, and sewage samples.

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Received for review August 20, 1969. Accepted March 5, 1970.

Volatilization and Nitrification of Nitrogen from Urine under Simulated Cattle Feedlot Conditions

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■ Animals fed for slaughter are being concentrated in large feedlots, and, in some cases, contamination of ground and surface water supplies has resulted. In laboratory model studies, the amounts of ammonia volatilization and nitrate accumulation under simulated feedlot conditions depended on the moisture content of the soil. When urine was added every 2 days to an initially wet soil at the rate of 5 ml. per 21 cm.^{2}, less than 25% of the added N was lost as ammonia and about 65% was converted to nitrate. When urine was added every 4 days to initially dry soil, essentially all the water evaporated between urine additions, and 90% of the added N was lost as ammonia. These findings suggest that the stocking rate and other management factors should be considered in pollution abatement.

The methods of producing animals for slaughter in the United States have changed dramatically during recent years. Animals are being produced in large concentrated feedlots as contrasted to the small individual farm operations of a few years past. The rapid increase in animal production is due not only to increased population but also to increased consumption. The per capita consumption of beef in the United States has doubled since 1940, and half of this increase occurred between 1960 and 1966. Virtually all of the recent growth in cattle feeding has been in feeding units of 10,000 head or more, in which cattle are confined in pens allowing only 6 to 20 m.^{2} per animal.

Animal wastes resulting from these large feeding operations have caused concern in many areas. Disposal of the accumulation of solid wastes is difficult, and, in some cases, runoff from these lots has caused pollution of streams and lakes. Wadleigh (1968) and Loehr (1968) have recently reviewed and discussed many of the problems associated with animal wastes.

Recent studies indicate that feeding operations can cause high nitrate concentrations in the underground water supplies (Smith, 1965). Stewart, *et al.* (1967) showed, however, that there are large differences in the amounts of nitrate found under feedlots: some contain large amounts; others are nearly nitrate-free both at shallow and deep depths. The objective of this study was to simulate some feedlot conditions and study the nitrification and volatilization rates of nitrogen added as cattle urine to soil in an attempt to determine some of the factors governing nitrate accumulation under feedlots. Urine accounts for about half of the nitrogen excreted by cattle.

Materials and Methods

Two sets of soil columns were treated with cattle urine. In one set, which was wetted with water before adding urine, the urine additions exceeded evaporation losses, and there was a net movement of water through the columns. The second set of soil columns was air dry when urine was added initially, and more urine was not added until at least 90% of the water from the previous additions evaporated. These studies will be referred to as the wet column study and dry column study, respectively.

Wet Column Study. Six columns, 5-cm. inside diameter and 35-cm. long, were packed to a depth of 30 cm. with Vona sandy loam obtained near Greeley, Colorado. A total of 840 grams of soil was packed to a bulk density of 1.4 grams per cm.^{3} Each column was fitted at the bottom with a 0.15-cm. diameter porous ceramic tube. The ceramic tube was connected to a suction flask maintained at 0.5 bar suction, which is the equilibrium tension in soil approximately 5 meters above the water table. The suction was maintained by a Thermocap (product or company name is included for the benefit of the reader and does not imply any endorsement or preferential treatment of the product listed by the U.S. Department of Agriculture) relay, which turned on a vacuum pump whenever the mercury in the manometer dropped about 0.5 cm. Solution passing through the ceramic tube was caught and saved for analyses.

The columns were wet with 180 ml. of distilled water, which was sufficient to allow some water to move through the soil. After 16 hours, suction was applied to the ceramic tubes and maintained throughout the experiment. Urine was first added 48 hours after suction was applied, and subsequently in 5-ml. increments every second day. This is equivalent to the average rate that urine is excreted in a feedlot stocked with one steer for every 7 m.^{2} and represents an annual addition of 45 cm. for continuous stocking. The top of the column wall, which extended 5 cm. above the soil surface, was fitted with a rubber stopper, and a constant flow of air pretreated to remove CO_2 and H_2O was passed through the column between the stopper and soil surface at a rate of 55 ml. per minute. This flow evaporated approximately 4 ml. every two days from a column containing a free water surface. Therefore, water additions in the form of urine exceeded evaporation losses by approximately 1 ml. every two days, equivalent to 9 cm. per year.

The air passing over the columns was then bubbled through a KOH solution to remove CO_2 evolved from the column and then through H_2SO_4 to remove NH_3 evolved. Amounts of CO_2 and NH_3 evolved were measured every second day at the time additional urine was added. Temperature of the room was maintained at 30° C.

Leachate passing through the columns was trapped in a flask containing 100 ml. of H_2O. This flask was removed at 2-week intervals and the volume of leachate measured. The solution was analyzed for nitrate, nitrite, ammonium, chemical oxygen demand, and organic nitrogen.

Two columns were removed after 4 weeks, two columns were removed after 8 weeks, one column after 12 weeks, and the last one after 16 weeks. After removal, each column was cut into six sections of 5-cm. lengths and the soil removed. A subsample was used for making a saturated paste, and the pH of the paste was determined with a glass electrode after a

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30-minute equilibration. Water extracts were made on additional subsamples of each section for determining the chemical oxygen demand of the water-soluble compounds (Am. Public Health Assn., Inc., 1965) and nitrite concentration. Nitrite was determined colorimetrically (Bremner, 1965). Additional soil was frozen and later used for ammonium and total nitrogen analyses. Total nitrogen was determined by the Kjeldahl method modified to include nitrate (Bremner, 1965), and ammonium was measured by steam distillation with MgO. A final sample was dried to determine H_2O content, and nitrate analyses were made on the dried samples by the phenoldisulfonic acid procedure (Jackson, 1958) modified to remove chlorides and organic matter.

Dry Column Study. After the first two wet columns were removed, they were replaced by two short columns closed at the bottom and filled to a depth of 5 cm. with soil (140 grams). Urine was added in 5-ml. increments every 4 days. Air was passed over these columns in the same manner as previously described. At least 90% of the H_2O added as urine evaporated before additional urine was added. These conditions represent feedlots that are generally dry. Amounts of CO_2 and NH_3 evolved from these columns were determined as before. Two additional columns were set up 4 weeks later when two more of the wet columns were removed. On May 10, 1968, one of the dry columns that had been receiving urine additions for 8 weeks and one that had been treated for 4 weeks were sampled and analyzed for nitrate, nitrite, ammonium, COD, total N, and pH. The two remaining columns were wetted with 30 ml. H_2O and incubated for 2 weeks.

Results and Discussion

WET COLUMN STUDY

Water Status of Soil in Columns. A balance sheet of the inputs and losses of water from the columns is shown in Table I along with the water contents of the soil. The water content data show that after 4 weeks, the soil was still not in complete equilibrium with the suction being applied through the ceramic tubes. After 8 weeks, however, the water contents remained nearly constant for the remainder of the study. For the period between 8 and 16 weeks, 140 ml. of water was added as urine. Of this amount, 98 ml. was lost by evaporation, leaving a net gain of 42 ml. which compares closely to the 39 ml. that leached through the column during this period. Evaporation losses from the columns closely paralleled losses from a free water surface.

Table I. Water Content of Soils at Various Times, Amounts of Water Evaporated, and Amounts of Water Leached through Wet Soil Columns

	Length of treatment (wk.)			
Depth of soil (cm.)	4	8	12	16
	Water content (%)			
0–5	17.4	16.6	16.1	15.1
5–10	16.7	16.3	15.4	15.8
10–15	17.7	16.4	15.5	15.8
15–20	17.7	15.9	15.3	15.9
20–25	16.8	15.8	14.6	15.2
25–30	15.7	14.5	14.1	14.4
	Water (ml.)			
Added as urine	70	140	210	280
Evaporated	54.0	106.5	156.0	205.0
Leached through column	42.5	71.8	96.8	111.0
Evaporated from passing air over free water surface	52.4	103.2	162.0	223.4

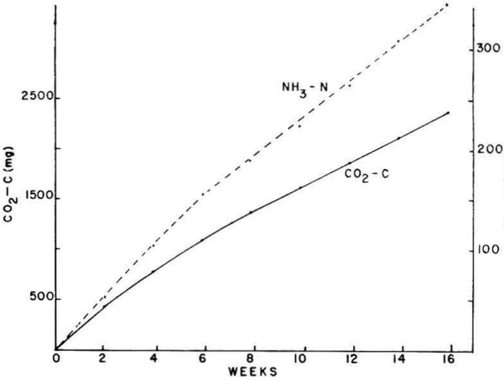

Figure 1. Accumlative NH_3 and CO_2 evolution from soil treated every two days with cattle urine

Carbon Evolved as CO_2. Figure 1 shows the cumulative amounts of CO_2 evolved from the columns. Urine additions were made every 2 days. Three sources of CO_2 contributed to these values: mineralization of soil organic matter, hydrolysis of urea present in the urine, and decomposition of the organic carbon constituents of the urine. No attempt was made to separate CO_2 from these sources. Carbon dioxide evolution was used as an index of microbial activity to determine whether continued additions of urine might noticeably change the rate of microbial action. Data presented in Figure 1 do not indicate any noticeable changes. The gradual decrease in the rate of CO_2 evolution that occurred during the first few weeks was expected, since rate of soil organic matter decomposition normally decreases during this period. During the period between 8 and 16 weeks, CO_2 production was constant with time. Values plotted are the average for the columns available at a particular time, *i.e.*, 6, 4, 2, and 1.

NH_3 Evolved. Ammonia evolved from the columns is also shown in Figure 1. As in the case for the CO_2 data, values shown are the average data from all columns under treatment during the given period. Fairly constant amounts of NH_3 were evolved with time, although there was apparently a slight decrease after the first 6 weeks. Losses of ammonia from these columns accounted for only about 25% of the total N added in the urine.

Chemical Analyses of Soil. Table II shows the soil analyses for the various depths of soil after different durations of treatment with urine. Considerable nitrate was present after 4 weeks and increased both in amount and in depth of location for the later samplings. Nitrification continued throughout the 16 weeks, and there was an apparent increase in the rate of nitrification with increasing time of treatment. Nitrite was present in large quantities only at the end of 4 weeks and only in the surface 5 cm., although there was some nitrite present in all samples.

Ammonium nitrogen did not move rapidly through the soil. Apparently ammonium moved downward only after the cation exchange capacity became saturated with ammonium. Even after 16 weeks of treatment, only negligible amounts of ammonium were present below 15 cm.

Table II. Nitrate, Nitrite, Ammonium, Total N, Chemical Oxygen Demand of the Water Soluble Constituents, and pH for Soil at Various Depths in Columns Treated with Urine for Different Periods of Time

Depth of soil (cm.)	Length of treatment (wk.) 4	8	12	16
	Nitrate (p.p.m. on dry weight basis)			
0–5	864	1642	2360	2270
5–10	402	757	1450	1606
10–15	109	442	899	1338
15–20	61	207	575	963
20–25	48	105	290	540
25–30	43	78	71	270
	Nitrite (p.p.m. on dry weight basis)			
0–5	92.00	9.6	7.8	6.6
5–10	.06	.7	1.2	.7
10–15	.06	.7	1.1	.7
15–20	.04	.3	.7	.6
20–25	.11	.3	.5	.6
25–30	.06	.3	.8	.4
	Ammonium (p.p.m. on dry weight basis)			
0–5	234	757	933	990
5–10	25	170	239	553
10–15	3	3	23	134
15–20	2	1	1	9
20–25	3	2	1	2
25–30	2	1	1	2
	COD of water-soluble constituents (mg./1000 g. dry soil)			
0–5	412	305	527	601
5–10	138	106	150	203
10–15	85	108	106	138
15–20	150	85	81	88
20–25	138	73	89	86
25–30	144	135	129	77
	pH			
0–5	7.5	6.9	6.4	6.2
5–10	6.8	6.3	5.9	5.7
10–15	7.2	6.7	6.5	6.5
15–20	7.4	6.8	6.7	6.7
20–25	7.5	7.1	6.9	6.7
25–30	7.7	7.4	7.1	7.1

Table III. Balance Sheet for the Wet Column Study Showing Initial Soil Nitrogen, N Added as Urine, and Distribution of N after Each 4 Weeks of Urine Additions

	Length of treatment (wk.) 0	4	8	12	16
	N (mg.)				
Organic N[a]	1058	1090	1050	979	991
Nitrate-N	15	205	451	752	958
Nitrite-N	0	12	1.5	1.6	1.4
Ammonium-N	0	35	130	151	226
N leached as NO_3	...	5	16	31	48
N evolved as NH_3	...	104	188	263	345
Total accounted for	1073	1451	1837	2178	2569
N added as urine	0	385	770	1155	1540
Initial soil N + urine N	1073	1458	1843	2228	2613

[a] Total soil N minus nitrate, nitrite, and ammonium.

Values for COD determined on water extracts show that most of the added soluble carbon was being decomposed. Only small amounts of water-soluble carbon accumulated, and then only in the upper 5 to 10 cm. of soil. The pH of the soil decreased, probably because of the acidity released during nitrification.

A nitrogen balance sheet is given in Table III. Organic N remained fairly constant during the study. Nitrate and ammonium both accumulated. Ammonia evolution was also almost a linear function of the length of treatment, although there was some indication that slightly less ammonia was evolved during the later periods of the study. Ammonia evolved from the moist columns represented only about 25% of the total N added in urine. The total amount of N accounted for at the end of each treatment period was only slightly smaller than the sum of the initial soil N plus the N added in urine. The disappearance of this small amount of N indicates that some N may have been evolved from the system in a form other than ammonia.

Amounts and Nitrate Concentration of Leachates. The volumes and nitrate concentrations of leachate obtained from the columns are presented in Table IV. Larger amounts of leachate were obtained during the first few weeks because the soil was coming to equilibrium with the applied suction during this period. Nitrate concentrations of the leachate increased throughout the experiment. The initial increases reflected mineralization of the soil organic nitrogen, but later increases represented nitrate from the nitrification of N in urine. When the soil nitrate data presented in Table II were converted to concentrations in the soil solution, good agreement was obtained between the concentrations in the lower depth of the soil and in the leachates. Amounts of other constituents for which the leachates were analyzed were negligible.

DRY COLUMN STUDY

Ammonia and Carbon Dioxide Evolved. Losses of ammonia were relatively small following the first few urine additions, but these losses increased until they represented 85% to 90% of the total amount of N added in urine (Table V). The wet column study discussed earlier showed losses of only 20% to 25%. Nearly all of the CO_2 evolution occurred in the first 2 days after urine treatment and CO_2 amounts lost following each urine addition were nearly constant. Columns were weighed each 2 days, and weights showed that about 3.5 ml. H_2O was evaporated the first 2 days after urine was added as compared to about 1.5 ml. during the next 2 days.

Analyses of Soil. Table VI shows the analyses of soil taken from the top, middle, and bottom portions of the 5 cm. of soil in the dry columns. Apparently, there was no nitrification during either 4 or 8 weeks of treatment with urine; the values reported are generally about the same as or less than the 18 p.p.m. present in the soil at the start of the study. On the other hand, ammonium concentrations increased markedly, resulting in high pH values. COD values showed accumulations of water-soluble carbon compounds.

After discontinuing two columns, one from each of the treatment periods was wet with H_2O and allowed to incubate for 2 weeks. Analyses of the soil following incubation are shown in the right-hand portion of Table VI. Nitrification did occur during this period, although substantial amounts of

Table IV. Amounts and Nitrate-N Concentrations of Leachate from Soil Columns Treated with Urine for Different Lengths of Time

	Length of treatment (wk.)							
	4		8		12		16	
Period of time (days)	Leachate (ml.)	Nitrate-N (p.p.m.)	Leachate (ml.)	Nitrate-N (p.p.m.)	Leachate (ml.)	Nitrate-N (p.p.m.)	Leachate (ml.)	Nitrate-N (p.p.m.)
2	9.9	22.2	10.2	44.7	11.4	35.2	13.6	57.6
14	16.7	30.9	20.5	39.6	28.7	66.2	25.4	55.0
28	16.0	246	18.1	236	18.8	289	19.8	285
42			13.2	411	12.6	447	12.7	443
56			10.0	529	10.0	596	8.5	589
70					8.4	694	8.3	702
84					6.9	897	6.8	846
98							7.7	958
112							8.2	1317

Table V. Amounts of NH_3–N and CO_2–C Evolved Every 2 Days from Dry Columns Treated with Urine Every 4 Days

Days after initial urine addition	C evolved as CO_2 (mg.)	N evolved as NH_3 (mg.)
2	18.0	5.3
4	0.8	0
6	19.5	9.2
8	0.4	0.3
10	21.8	11.5
12	0.7	0.7
14	23.1	16.5
16	0.8	1.9
18	23.1	17.9
20	1.5	2.0
22	23.2	19.4
24	2.2	4.4
26	25.4	22.4
28	2.0	3.0
30	22.9	18.9
32	1.8	3.3
34	23.5	19.6
36	2.5	2.1
38	22.0	21.1
40	2.2	3.7
42	21.4	20.4
44	2.5	3.0
46	21.9	22.1
48	3.1	4.6
50	21.2	21.9
52	2.2	2.8

Table VI. Chemical Analyses of Soil from Dry Columns after Treatment with Urine for 4 and 8 Weeks with and without Incubation Following Urine Additions

Portion of soil column	No incubation length of treatment (wk.) 4	8	Incubated 2 weeks length of treatment (wk.) 4	8
	Total N (p.p.m.)			
Top	1789	1923	1544	1656
Middle	2008	2149	1585	1663
Bottom	1818	1944	1825	1983
	Nitrate (p.p.m.)			
Top	7	7	88	39
Middle	18	14	87	45
Bottom	25	16	175	56
	Nitrite (p.p.m.)			
Top	2.7	2.2	108	44
Middle	0.3	0.3	57	75
Bottom	0.2	0.2	13	79
	Ammonium (p.p.m.)			
Top	331	218	40	74
Middle	669	669	176	248
Bottom	458	669	349	413
	pH			
Top	9.6	9.9	8.5	9.3
Middle	9.3	9.3	8.7	8.1
Bottom	9.2	9.2	8.1	7.8
	COD of water-soluble material (mg./1000 g.)			
Top	5132	8043	905	2486
Middle	1475	2030	475	781
Bottom	1140	1609	346	607

nitrite also accumulated. The pH of the soil decreased during this period, and there was also a marked drop in the COD values. These data suggest that although no nitrate would be expected to accumulate in feedlots maintained at a fairly dry level, some nitrification could be expected following sufficient rain to maintain moist conditions for several days.

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Received for review August 8, 1969. Accepted February 24, 1970. Research conducted in cooperation with Colorado Agricultural Experiment Station (Scientific Journal Series No. 1437).

Contamination of Roadside Soil and Vegetation with Cadmium, Nickel, Lead, and Zinc

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■ Concentrations of Cd, Ni, Pb, and Zn in roadside soil and grass samples from several locations decrease with distance from traffic. These concentrations also decrease with depth in the soil profile. The contamination has been related to the composition of gasoline, motor oil, and car tires, and to roadside deposition of the residues of these materials.

Easily volatilized at temperatures prevailing in common industrial processes, Cd, Ni, Pb, and Zn are normally present in the atmosphere, especially near urban areas (National Air Sampling Network, 1958, 1962; Schrenk, Heimann *et al.*, 1949). The atmosphere also contains Cd, Pb, and Zn as radioisotopes because of nuclear detonations and, in the case of Pb, radon exhalation by the earth. Cadmium is the most hazardous of the metals with regard to human health; cardiovascular disease has been related to both inhaled (Carroll, 1966) and ingested (Schroeder, 1965, 1966) doses of this metal approximating those suffered in average urban situations. Hazards due to environmental Pb have variously been emphasized (Patterson, 1965) and deemphasized (Kehoe, 1961), and are clearly subject to controversy. The present report deals with Cd, Ni, Pb, and Zn contamination of roadside soil caused by motor vehicles. This is not to detract from the occurrence of other possible sources of these metals in our environment. Of significance regarding food quality is their occurrence as impurities in certain agricultural chemicals, and as regular constituents of others routinely applied to soils and crops (Barrows, 1966; Caro, 1964). Because of their aerial presence, the metals reach soil and plant cover also in precipitation (Terhaar, *et al.*, 1967; McCallum and Woodward, 1965).

Experimental

Sampling sites were selected on level areas adjacent to four heavily traveled roads, *viz.*, U.S. 1 at Beltsville, Md. (Site I), the Washington-Baltimore Parkway at Bladensburg, Md. (Site II), Interstate 29 at Platte City, Mo., north of Kansas City (Site III), and Seymour Road in the northern section of the Cincinnati metropolitan area (Site IV). Information on these sites has been summarized (Table I).

Soil samples were collected as a function of depth in the profile (0-5, 5-10, and 10-15 cm.) and distance from traffic (8, 16, and 32 m.). Ten-g. (d.wt.) aliquots of each sample were agitated for 1 hr. with 20-ml. volumes of *N* HCl and centrifuged. The selection of *N* HCl is based on information indicating that the complex formation of Pb(II), Cd(II), and Zn(II) with HCl reaches a maximum with all 3 metals at the *N* concentration of the acid (Samuelson, 1963). The centrifugates were all analyzed for Cd, Pb, and Zn; in the Maryland samples, Ni was determined also. Grass samples taken at the same sites were digested with hot, concentrated HNO_3 and $HClO_4$ (Toth, Prince, *et al.*, 1949), and analyzed for the same metals as were the corresponding soils. Prior to their digestion, the plant samples had been lightly rinsed until soil dust resulting from splash no longer was visible. [Note: If the metals adhere to the plant, their removal by rinsing prior to analysis is possible but not necessarily probable. Much depends on the physical nature of the plant surface and on the matrices in which the metals occur. Moreover, concurrent removal of metals already inside the tissues may complicate the outcome. Generally, concern for food quality prompts consideration of the fraction of metals adhering to the plant, rather than its elimination.]

The metal contents of soil extracts and plant digests were determined by atomic absorption spectrophotometry, *viz.*, Cd at 2288 Å, Ni at 2320 Å (correcting for backscatter at 2316 Å), Pb at 2833 Å, and Zn at 2139 Å.

Results and Discussion

The results (Table II), which are averages of duplicate samplings and analyses, can be summarized as follows:

The concentrations of Cd, Ni, Pb, and Zn in soil and vegetation all decrease with distance from the road, indicating their relation to traffic. The metal concentration gradients with

Table I. Characteristics of Sampling Sites and Samples

	Site			
	I	II	III	IV
Sampling date	May 1966	June 1966	August 1966	April 1967
Soil type[a]	Sassafras sandy loam	Collington silt loam	Knox silt loam	Cincinnati silt loam
Soil pH[b]	5.9	6.3	6.7	7.1
Dominant grass[c]	Tall fescue	Tall fescue	Blue grass	Orchard grass
Traffic density[d]	20,000	48,000	7500	23,000
Average rainfall[e]	105	105	88	98

[a] As deduced from surrounding land not subject to road building activities.
[b] Of 0–5 cm. layer, as affected by road salts and car exhaust.
[c] Constituting more than 50% of the vegetation.
[d] Cars passing by per 24 hr. in the year of sampling.
[e] In cm. per year.

Table II. Cadmium, Nickel, Lead, and Zinc Contents of Roadside Soil and Grass as a Function of Distance from Traffic and Grass Depth in Profile[a]

			Soil profile layer, cm.			
Site	Metal	Meters from road	Grass	0–5	5–10	10–15
			(milligrams per kilogram dry weight)			
I	West of U.S. 1, near Plant Industry Station, Beltsville, Md.					
	Cd	8	0.95	1.45	0.76	0.54
		16	0.73	0.40	0.38	0.28
		32	0.50	0.22	0.20	0.20
	Ni	8	5.0	4.7	1.0	0.81
		16	3.8	2.4	0.90	0.60
		32	2.8	2.2	0.62	0.59
	Pb	8	68.2	522	460	416
		16	47.5	378	260	104
		32	26.3	164	108	69
	Zn	8	32.0	172	94	72
		16	28.5	66	48	42
		32	27.3	54	46	42
II	West of southbound lanes, Washington-Baltimore Parkway, Bladensburg, Md.					
	Cd	8	0.75	0.94	0.70	0.30
		16	0.63	0.68	0.44	0.18
		32	0.48	0.24	0.18	0.12
	Ni	8	3.8	7.4	5.6	1.4
		16	2.5	4.4	1.6	0.79
		32	1.3	2.4	1.2	0.57
	Pb	8	51.3	540	300	98
		16	30.0	202	105	60
		32	18.5	140	60	38
	Zn	8	40.0	162	86	36
		16	34.5	110	28	20
		32	30.3	44	20	18
III	West of Interstate 29, Platte City, Mo.					
	Cd	8	0.49	0.90	0.66	0.58
		16	0.37	0.77	0.70	0.61
		32	0.25	0.68	0.51	0.52
	Pb	8	21.3	242	112	95
		16	12.5	140	104	66
		32	7.5	61	55	60
	Zn	8	36.3	54	24	16
		16	32.8	60	21	16
		32	29.0	15	11	14
IV	North of Seymour Road, Cincinnati, Ohio					
	Cd	8	0.74	1.82	0.44	0.28
		16	0.49	1.51	0.31	0.26
		32	0.26	1.02	0.24	0.18
	Pb	8	31.3	150	29	11
		16	26.0	101	14	8.2
		32	7.6	55	10	6.1
	Zn	8	85.0	72	24	11
		16	72.4	60	16	10
		32	67.1	34	11	8.3

[a] Averages of duplicate sampling and analysis.

distance follow the order Cd > Pb > Zn > Ni. The concentrations of the metals also decrease with depth in the soil profile. As divalent cations and as metals that are only slightly soluble in an aqueous environment when associated with phosphate and carbonate anions abundant in many soils, their limited downward movement may be expected. The surface-soil concentrations of extractable Pb here measured are by no means extreme. At a site adjacent to Colorado Boulevard at Arcadia, Calif., we found slightly over 2400 p.p.m. Alongside a road following the foothills of the coastal range at Irvine Ranch, also in the Los Angeles metropolitan area, we determined a concentration of 8 p.p.m. Surface-soil accumulation of Pb may create conditions seasonably adverse to the quality of shallow-rooting crops, notably pasture grasses (Mitchell and Reith, 1966).

In spite of the dependence of roadside Cd, Ni, Pb, and Zn on traffic, it appears from Table II that high concentrations of one metal in the soil do not necessarily entail high concentrations of another one of the metals. For instance, the high concentrations of extractable Pb in the soil of Site II are accompanied by Cd concentrations lower than those at Site IV, where the Pb concentrations are lower than those at Site II. A similarly reverse relationship exists between the Cd and Zn concentrations at these sites. This points to the interplay of a number of variables, unaccounted for and perhaps unaccountable. Prime consideration should here be given to the methods of soil engineering applied during the road construction, the length of the period between sampling, and the time the road was completed, the vegetation became established, and traffic started flowing, the presence of cations from deicing road salts competing (perhaps in different degrees) with Cd, Ni, Pb, and Zn for exchange sites on the soil surface, the use of metal-containing pesticides to protect roadside grasses and trees, the presence of local industries discharging one or another of the metals into the air as fume or dust, the proportion between motor vehicles using diesel oil and those that do not, the conversion of the metals once they have lodged in the soil from one matrix to another one, and the contents and availability of Cd, Ni, Pb, and Zn that are native to the soil.

Calculations based on the data in Table II, not further reported, failed to show a consistent relationship between any of the extractable metal concentrations of the 0- to 15-cm. layer of soil and of the vegetation growing in that soil. Comparing the metal concentrations of the 0- to 5-cm. layer of soil with those of the vegetation, an approximately linear relationship over the 32-m. distance exists only for Pb. This suggests that either the deposition of Pb follows a similar pattern on the grass blades as on the soil surface, or Pb contained by the grass and released upon its decay is the main source of Pb in the top layer of soil. With regard to the latter possibility, it should be noted that, generally, Pb is barely, if at all, taken up by the roots of a variety of plants (Hammett, 1929; Hevesy, 1923; Marten and Hammond, 1966).

The concentrations of nitrogen, phosphorus, and halides in topsoil and vegetation also decreased as a function of distance from traffic, suggesting that Pb may have been deposited together with the phosphates and NH_4-halides associated with it in car exhausts (Hirschler, Gilbert, *et al.*, 1957). No simple relationship is evident between concentrations in soil and grass for the other metals. It may here be noted that, in addition to Cd, Ni, Pb, and Zn native to the soil or derived from agricultural amendments, these metals are present in the soil as the result of long-term effects of soil and climatic conditions on aerial deposits. In vegetation, on the other hand, these metals occur as a result of short-term interactions between physiological preferences related to metal uptake through the roots, and aerial deposition of the metals on the surfaces of the plants.

The magnitude of the concentration ratio Pb/Cd of the soil averaged over all profile depths, and distances from traffic at each location exceeded the corresponding value for this ratio describing the vegetation by factors of 9.5 at Site I, 8.1 at Site II, 4.1 at Site III, and 1.6 at Site IV. This indicates that, compared with soil, vegetation accumulated Cd in preference to Pb. Remarkably, this effect was reduced as the soil pH increased, although it was accompanied by a decrease in the Pb/Cd concentration ratio of the soil. In the order of the sites mentioned, these pH values were 5.9, 6.3, 6.7, and 7.1, while the values for the soil-metal ratio Pb/Cd were 596, 384, 150, and 52, respectively. It is reasonable that Cd should be more subject than Pb to competitive effects associated with increasing base saturation of the soil-adsorption complex because, contrary to Pb (Marten and Hammond, 1966), Cd seems to enter plants primarily from the soil (Schroeder and Balassa, 1961). The diminishing magnitude of the concentration ratio Pb/Cd observed when comparing roadside soil and vegetation is part of a broader trend of potential significance: the value decreases from about 260 in urban air (National Air Sampling Network, 1958, 1962) to about 13 in the normal U.S. diet (Schroeder and Balassa, 1961), 3 in the whole human body (Internat. Comm. Radiolog. Protection, 1960) and 0.04 when relating the preferred organs *i.e.*, liver for Pb and kidney for Cd (Tipton, 1960). This trend is apart from considerations on toxicology.

Calculations based on the data in Table II, not further reported, show that the Zn/Cd concentration ratio of the soil averaged over all profile depths and distances from traffic at all four sampling sites only barely exceeded the corresponding value for this ratio describing the vegetation at these sites. That is, local trends notwithstanding, the vegetation generally did not show much preference between Zn and Cd. Contrary to the situation with Pb and Cd, it would suggest that any variation in the plant content of these metals due to aerial contributions is balanced by contributions from the soil, or that the physiological response of plants with regard to Cd and Zn is rather similar. The latter has been observed in animals (Parizek, 1957) and humans (Schroeder, 1965). Again, considerations on toxicology have been omitted.

Origin of Cd, Ni, Pb, and Zn in Roadside Soils

Roadside distribution of Pb is traditionally ascribed to combustion of leaded gasoline by automobiles. In 1964 alone, at least 100,000 tons of Pb, or 10% of the U.S. consumption in that year, were discharged into the nation's atmosphere (Lagerwerff, 1967). The presence of Pb near highways has been related by Warren and Delavault (1962) and others (Cannon and Bowles, 1962; Dunn and Bloxam, 1933; Kloke and Riebartsch, 1964; Leh, 1966; Singer and Hanson, 1969) to density of traffic and to distances as far as 250 m. from the road (Kleinman, 1968). Lead with an isotopic composition typical of gasoline Pb has been detected even at distances of over 100 miles from the nearest metropolitan area (Chow and Johnstone, 1965). The use of nickled gasoline (Sinclair Refining Co., 1964), and atmospheric abrasion of Ni-containing automobile parts, may explain the weak, yet detectable gradient of Ni at sites near dense traffic.

The joint presence of Zn and Cd has been established at this laboratory in oils and motor vehicle tires applying anion-exchange resin techniques (Korkish and Hazan, 1965) followed by atomic absorption spectrophotometry and emission spectrography (Specht, Myers, *et al.*, 1965), respectively. The Cd content of three lubricating oils was found to range from 0.20 to 0.26 p.p.m. and that of three diesel oils from 0.07 to 0.10 p.p.m. This compares with values of 0.54 and 0.42 p.p.m. for two heating oils. One may differentiate between biological (fossil) Cd, Cd as impurity in Zn precipitated for galvanization of tanks and conduits (Amer. Soc. for Testing Materials, 1911, 1949), and Cd as impurity in some of the common Zn-containing additives, *e.g.*, the antioxidant Zn-dithiophosphate in lubricating oil. Regarding car tires, we have found Cd in glass-fiber filters placed behind vehicles driving a dynamometer; since the exhaust fumes were ducted away from the filter, the collected material was mostly tire dust. The Cd content of four tires of different brands we found to range from 20 to 90 p.p.m. This may be associated with the use of technical Zn-oxide and Zn-diethyl or dimethyl carbamate in vulcanization. Generally, all industrial processes involving technical Zn are subject to the presence of Cd because both metals frequently derive from the same source materials and are chemical kin. No Cd could be detected (<0.01 p.p.m.) either in 12 brands of gasoline or in two samples of rocksalt used to deice road surfaces. In the analysis of rocksalt by atomic absorption spectrophotometry, corrections had to be applied for heterochromatic interference due to Na (Koirthyoann and Pickett, 1965; Pulido, Keiichiro, *et al.*, 1966). The effects of wear of Cd-plated engine or chassis parts and traffic lane paints on roadside distribution of Cd have been discounted.

Acknowledgment

The authors gratefully acknowledge the help extended to them by C. S. Brandt and W. W. Heck, Agricultural Activity, and by George Morgan, Laboratory Sciences Activity, Air Quality Emission Data Branch, all of the National Center for Air Pollution, Public Health Service, U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio. They are also indebted to E. J. Pedersen, Soil Conservation Service, Beltsville, Md., the Department of Highways, Columbus, Ohio, the Missouri State Highway Department, Jefferson City, Mo., and the State Roads Commission, Baltimore, Md.

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Received for review July 9, 1969. Accepted March 30, 1970. This report is a contribution from the U.S. Soils Laboratory, Soil and Water Conservation Research Division, Agricultural Research Service, U.S. Department of Agriculture, Beltsville, Md.

Determination of ^{210}Pb Mean Residence Time in the Atmosphere

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■ Rainwater was filtered through a 0.22-μ Millipore filter before radioassay of the resulting dust and filtrate fractions for ^{210}Po. Lead-210 contents of the fractions were obtained by following the growth of ^{210}Po activity in stored samples as a function of time. At the time of rainfall, the ^{210}Po contents of the dust and filtrate fractions were approximately equal, but the dust fractions contained less than 3% of the total ^{210}Pb. Polonium-210 and ^{210}Pb in the dust fractions were already in radioactive equilibrium at the time of the rainfall, suggesting that their presence in the dust was not a result of recent scavenging of ^{210}Pb from the troposphere. Ratios of ^{210}Pb to ^{210}Po used for calculations of mean atmospheric residence time for ^{210}Pb should, therefore, be those of the filtrate. From those ratios, a mean atmospheric residence time for ^{210}Pb of 9.6 days, ±20%, is obtained.

In conjunction with studies of ^{210}Po uptake by plants (Francis and Chesters, 1967), several samples of rainwater were collected for measurement of their ^{210}Po concentrations. From the data obtained, mean atmospheric residence times for some decay products of ^{222}Rn can be estimated. Such residence times depend sensitively on ratios of ^{210}Pb to ^{210}Po, which were found to differ greatly between dust and filtrate fractions of rainwater. Estimates of residence time calculated from these data are compared with those of other investigators whose procedures apparently did not include filtration.

Polinium-210 is an alpha emitter of half-life 138 days and is the fifteenth member of the ^{238}U decay chain. It is the seventh decay product after 3.82-day ^{222}Rn, the species which diffuses from the earth's surface into the atmosphere. Polonium-210 is immediately preceded by 5.01-day ^{210}Bi, which is, in turn, preceded by 22-year ^{210}Pb. The nuclides between ^{222}Rn and ^{210}Pb all have half-lives shorter than 30 min. and can be considered in radioactive secular equilibrium with ^{222}Rn for the purposes of this paper. Previous measurements, as well as those reported here, show that ^{210}Pb, ^{210}Bi, and ^{210}Po are not in radioactive equilibrium with each other or with ^{222}Rn in atmosphere, principally because they are washed out by rain.

When a rain falls, the region of the atmosphere in which it forms is presumably cleansed of ^{210}Pb, ^{210}Bi, and ^{210}Po, but not of the noble gas ^{222}Rn. Thus, in principle, values for the relative amounts of ^{210}Pb and ^{210}Bi, or of ^{210}Pb and ^{210}Po in freshly fallen rainwater, if substituted into the equations that describe successive radioactive decays, allow calculation of the time elapsed since that region of the atmosphere was cleansed of the decay products of ^{222}Rn by the preceding rain. In fact, intermixing among source regions complicates such easy measurement, so that most residence times are based on a model for an average condition of the atmosphere. The concentration of ^{222}Rn and, consequently, the production rate (R) of ^{210}Pb are assumed to remain constant with time. The rate of loss of ^{210}Pb from the atmosphere is presumed to be caused partially by radioactive decay (rate constant λ_{Pb})

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and partially by washout by rain, which is also written as a first-order kinetic process (washout constant k). The net rate of change of concentration of ^{210}Pb in the atmosphere, according to the model, is given by Equation 1, in which the symbol N_{Pb} refers to the number of atoms of ^{210}Pb in the system.

$$(dN_{Pb}/dt) = R - (\lambda_{Pb} + k_{Pb})N_{Pb} \qquad (1)$$

It is next assumed that ^{210}Pb and ^{222}Rn are in steady-state concentration equilibrium in the atmosphere, and Equation 1 is set equal to zero. Similar equations and assumptions are made for ^{210}Bi and ^{210}Po. If the washout constant (k) is presumed to have the same value for ^{210}Pb, ^{210}Bi, and ^{210}Po, then Equation 2 results, in terms of washout and decay constants and the ratio of the number of atoms of ^{210}Pb to ^{210}Po:

$$k^2 + (\lambda_{Bi} + \lambda_{Po})k + \lambda_{Bi}\lambda_{Po} - \lambda_{Bi}\lambda_{Pb}(N_{Pb}/N_{Po}) = 0 \qquad (2)$$

The positive root (k) of Equation 2 is the reciprocal of the mean residence time for ^{210}Pb (and ^{210}Bi and ^{210}Po) in the atmosphere. Such residence times cannot, of course, be more than reasonable estimates of average residence times for the atoms measured. The value of k is not known to be the same for ^{210}Pb, ^{210}Bi, and ^{210}Po, or even to be constant for any one of them. Atmospheric concentrations of ^{222}Rn vary, averaging about 200 d.p.m./kg. of air over land and about 4 d.p.m./kg. over oceans (Israel, 1951).

Lead-210 concentrations in the atmosphere, as determined by direct collection of that nuclide on air filters in the vicinity of Harwell, England, range from about 7×10^{-3} d.p.m./kg. of air at ground level to about 70×10^{-3} d.p.m./kg. of air in the lower stratosphere (around 14 km.) (Burton and Stewart, 1960). The gradient of concentration with respect to altitude was found to be similar to that for fission products. Entry of ^{210}Pb (or its ^{222}Rn ancestor) into the stratosphere along with rising warm air, and then descent at more northerly latitudes, were suggested to explain the gradient. Any ^{210}Pb sampled in tropospheric air or in rain would presumably be partly of recent stratospheric origin and partly of purely tropospheric origin.

The concentration of about 7×10^{-3} d.p.m./kg. of air at ground level is consistent with the measurements of King, Lockhart, *et al.* (1956) at Washington, D.C. Other investigators, *e.g.*, Peirson, *et al.* (1966) made monthly ^{210}Pb measurements over England in 1958 and observed similar concentrations and gradients; however, not as steep as those found by Burton and Stewart (1960).

Burton and Stewart (1960) found the average ^{210}Pb concentration in rainwater at Harwell to be 2.3 picocuries per liter (pCi/l.). King, Lockhart, *et al.* (1956) reported an average of 2.5 pCi/l. for ^{210}Pb in rainwater collected at Washington, D.C., and Glenview, Illinois, and values as much as 10 times less for rainwater at remote island sites. No significant correlation was observed between ^{210}Pb content and character of the rains, the seasons, or the quantities of dust in the water. Fry and Menon (1962) reported values between 1 and 8 pCi/l. for ^{210}Pb in rainwater collected at Fayetteville, Arkansas.

By comparing the quantity of ^{210}Pb in a vertical column of air between the ground and the tropopause with the mean time rate of deposition of ^{210}Pb by rain, Burton and Stewart (1960) obtained a mean tropospheric residence time for ^{210}Pb of 17 days. They commented that the value would be slightly greater if the efficiency of the air filters for trapping ^{210}Pb were less than 100%. The value would be a little lower if the ground-level concentration for ^{210}Pb in air had been used instead of a concentration based on their observed altitude gradient. As a rough check of their value, Burton and Stewart (1960) calculated mean residence times of 29 days for ^{210}Pb of mixed stratospheric origins and 22 days for the purely tropospheric component, based on the $^{210}Pb/^{210}Po$ ratios in their water samples and the model described in detail above.

Fry and Menon (1962) measured $^{210}Pb/^{210}Bi$ ratios in water samples from 12 rains and, using an equation analogous to Equation 2, obtained mean residence times ranging from 2.4 to 25.6 days. The averages of residence times based on data for rains falling in the interval February to April and June to August were 5.9 to 6.6 days, showing no measurable seasonal effects. These values are much shorter than those given by Burton and Stewart (1960) and those of 14 and 33 days based on $^{210}Pb/^{210}Po$ ratios reported by Lehmann and Sittkus (1959).

It would appear from these reports that none of the above investigators filtered the rainwater before concentrating the selected nuclides for radioassay. It could reasonably be assumed that the ^{210}Pb, ^{210}Bi, and ^{210}Po washed out in rainfall would be attached to fine particulate matter present in the atmosphere and that filtration would be unnecessary or unwise. The data presented below seem to suggest otherwise.

Experimental

Samples of rainwater were collected at Madison, Wisconsin, during the summer of 1966. To reduce contamination from dust at ground level, the polyethylene-lined collecting tube was placed on top of a 20-ft.-high building, and only at the onset and for the duration of each rain. Once collected, the rainwater was acidified to 0.03 N with H_2SO_4 and stored in glass containers. Immediately before each ^{210}Po analysis, a 4-liter aliquot was filtered (Millipore, 0.22-μ) to provide a dust fraction (particles of diameter $>0.22\ \mu$) and a filtrate fraction (including any particles of diameter $<0.22\ \mu$). Weights of collected dust were determined after drying the filters in a vacuum oven for 24 hours at 40° C.

Polonium-210 concentrations of the filtrate fraction were determined by evaporating 4-liter portions to about 30 ml., then stirring the concentrated solution for 4 hours at 90° C against a silver disk, onto which the ^{210}Po spontaneously deposited electrochemically with an efficiency of greater than 90%, or quantitatively within experimental error. Dust fractions, before plating, were subjected to H_2SO_4–$HClO_4$–HF digestion, as previously done for soil samples with an efficiency for collection of ^{210}Po of 98 to 100%. The ^{210}Po was determined by alpha-particle counting with a Molechem Model-30 semiconductor detector. Details of these procedures are given by Francis, Chesters, *et al.* (1968).

Results and Discussion

The results are presented in Table I. Growth curves for ^{210}Po from ^{210}Pb were obtained for the May 23, July 14, and July 26 rains by counting several filtered 4-liter portions at different times. Uncertainties given in Table I are standard deviations due to counting statistics.

Dust Fraction. Approximately one-half the ^{210}Po, but only 2 to 3% of the ^{210}Pb, in freshly fallen rain was in the dust fractions. The ^{210}Po in the dust fractions was, within experimental error, in secular equilibrium with the ^{210}Pb in the dust. Any leakage of the ^{210}Po into the filtrate portion from the dust fraction was thus negligible.

The concentrations of dust in the rainfalls vary over a factor of 37 and are inversely related to the amount of each rain, as would be expected if the initial part of the rain cleansed the lower atmosphere of particulate matter. The concentra-

Table I. Polonium-210 Contents of Rainwater During Summer of 1966 at Madison, Wis.

Date of rainfall collection	Size of rainfall (in.)	Counting date	Dust (>0.22 μ) content of rain (mg./l.)	Polonium-210 content of dust (>0.22 μ)		^{210}Po Content of water[a] (pCi/l.)	Total ^{210}Po (pCi/l.)
				pCi/l.	pCi/g.		
May 23	3.64	June 1	...	0.14 ± 0.04	...	0.34 ± 0.04	0.48 ± 0.08
		July 3	...	0.20 ± 0.04	...	1.11 ± 0.07	1.31 ± 0.11
		Aug. 1	...	...	...	2.02 ± 0.10	...
		Sept. 14	...	0.17 ± 0.04	...	3.03 ± 0.09	3.20 ± 0.13
June 2	0.40	June 3	14.85	0.26 ± 0.04	17.5 ± 2.7	0.33 ± 0.04	0.59 ± 0.08
June 5	0.25	June 8	21.87	0.41 ± 0.05	18.7 ± 2.3	0.38 ± 0.05	0.79 ± 0.10
July 12	0.17	July 13	...	0.43 ± 0.05	...	0.17 ± 0.03	0.60 ± 0.08
July 14	1.66	July 17	0.60	0.10 ± 0.03	166 ± 50	0.08 ± 0.03	0.18 ± 0.06
		July 19	0.58	0.07 ± 0.04	121 ± 57	0.13 ± 0.03	0.20 ± 0.07
		Aug. 15	0.55	0.08 ± 0.04	145 ± 72	0.65 ± 0.05	0.73 ± 0.09
		Sept. 14	0.70	0.07 ± 0.03	99 ± 42	1.25 ± 0.05	1.36 ± 0.08
July 26	0.64	July 28	2.72	0.11 ± 0.03	40 ± 11	0.15 ± 0.03	0.26 ± 0.06
		Aug. 28	2.77	0.17 ± 0.03	61 ± 11	0.81 ± 0.05	0.98 ± 0.08
Aug. 15	1.50	Aug. 16	4.96	0.23 ± 0.04	46 ± 8	0.16 ± 0.03	0.39 ± 0.07

[a] Filtrate fraction of rainwater containing particulate matter of <0.22 μ.

tion of ^{210}Po (and ^{210}Pb) in rain due to the dust fraction varies only by a factor of 6, and increases only slightly with the sharp increase in the concentration of dust. The concentration of ^{210}Po (and ^{210}Pb) in the dust itself varies by a factor of 9.5, and shows a strong inverse correlation with the concentration of dust in the rainwater. Thus, it appears that two distinct components of dust may be present in the rainwater, one of higher specific ^{210}Pb activity and present in roughly constant concentration in the water, and one of lower specific activity and of highly variable concentration.

An upper limit of 0.08 pCi/l. ^{210}Pb contribution to the rain and a lower limit of 133 pCi/g. of dust can be set for the first component by presuming it is the only significant component present in the July 14 rain. If the June 2 and 5, July 26, and August 15 rains are "corrected" for such a hypothetical component, the specific ^{210}Pb activities of the second component for those rains are 13, 16, 28, and 34 pCi/g., varying only by a factor of 2.6, a slight improvement over the variation of 3.5 times for the specific activities of the dust taken as a single component for those samples.

The origin of the ^{210}Pb in the dust fraction is puzzling. The radioactive equilibrium between ^{210}Po and ^{210}Pb suggests that the ^{210}Pb was not recently scavenged from the troposphere. The ^{210}Pb apparently cannot be easily leached from the dust fraction. The samples were stored in acid for times as long as months prior to filtration, and there was no decrease in ^{210}Pb for the dust fractions from a particular rain with time of storage (as monitored by the ^{210}Po contents of the dust, Table I). Possibly, the ^{210}Pb and ^{210}Po in the filtrate were originally scavenged from the troposphere by the dust, then readily leached from it by the rainwater or by the acid added to the samples. Clearly, the ^{210}Pb and ^{210}Po remaining with the dust fraction are quite distinct from those components in the filtrate fraction.

The ^{210}Pb in the dust fraction might be of stratospheric origin, suggesting a stratospheric residence time for ^{210}Pb long enough for the ^{210}Pb–^{210}Po equilibrium to be established; that is, a time equal to several half-lives of 138-day ^{210}Po. There seems to be no convincing support for such a hypothesis.

If the dust were ordinary material from the crustal surface of the earth, it would have a ^{238}U content of the order of 2 to 3 p.p.m. The ^{210}Pb in equilibrium with that amount of ^{238}U would be about 1 pCi/g. of dust, which is much lower than that observed or that calculated even for the hypothetical lower-activity component. Several soils were found to have ^{210}Po (and presumably ^{210}Pb) concentrations of 1.4 to 4.4 pCi/g., still well below the observed concentrations in the dust from rainwater.

The ^{222}Rn in a column of air above 1 cm.^{2} of land surface is about 90 pCi, according to the data of Israel (1951), whereas the ^{210}Pb concentration is only about 0.03 pCi/cm.^{2}, so most of the ^{210}Pb is deposited on the earth's surface. Neglecting any contribution to the dust fraction from its rainwater content, assigning to the dust a density of 2 g./gm.^{3}, and taking the observed extreme of 133 pCi/g. and the calculated extreme of 13 pCi/g., the ^{210}Pb deposited from the ^{222}Rn in the atmosphere is distributed over a layer of surface material in the range of 0.4 to 4 cm. thick. It is therefore possible that the dust in rainfall is from the top layers of the earth's surface that receive the ^{210}Pb precipitated by the rain. If so, the mechanism for transfer of the ^{210}Pb from the rainwater to the dust would have to be more complicated than simple adsorption, or else most of the ^{210}Pb in the rain would be found in the dust fraction.

Filtrate Fraction. The filtrate fraction, which includes any particulate matter small enough to pass through the 0.22-μ filter, contains more than 97% of all the ^{210}Pb in the rain. The ^{210}Pb concentrations, computed from the ^{210}Po growth curves to be between 4.6 and 6.8 pCi/l., are somewhat higher than the averages mentioned in the introduction, but compare well with those of Peirson, *et al.* (1966) measured at Ottawa, Canada.

The ^{210}Pb and ^{210}Po in the filtrate fraction may have been attached to particles small enough to pass through the filter. Kawano and Nakatani (1964) found that most dust particles carrying natural radioactivity have diameters smaller than 0.3 μ. While the exact mechanism by which the ^{210}Pb and ^{210}Po arrived in the filtrate fraction is obscure, the lack of radioactive equilibrium between them suggests that they originated in, and were somehow scavenged from, the atmosphere. Only this component, therefore, should be used for estimating the mean residence time for ^{210}Pb in the atmosphere.

The ratio of ^{210}Pb to ^{210}Po at the time of the rainfall is required to solve Equation 2 for the value of k. Concentrations of ^{210}Pb for the rains of May 23, July 14, and July 26 were obtained from the equilibrium values of the ^{210}Po growth curves. These concentrations were then used to correct the measured values of ^{210}Po for the decay of ^{210}Pb and ^{210}Bi between the time of rainfall and the time of measurement. The average ratio of ^{210}Pb to ^{210}Po for the three filtrates is 2.2×10^3 with an uncertainty of about 15%, and its use in Equation 2 yields a mean residence time of 9.6 days, with an uncertainty of about 20%. Because the residence time is so short, about half of the ^{210}Po in the rainwater at the time of the rainfall is in the dust fraction. The average ratio of ^{210}Pb to ^{210}Po *including* the dust fraction is 1.4×10^3, giving rise to an erroneous increase of more than 50% in the mean residence time.

The value of 9.6 days is much shorter than the value of 22 days given by Burton and Stewart (1960) and based on ratios of ^{210}Pb to ^{210}Po in rainwater. A significant dust component in their samples might be partially responsible for the difference. Only three of the samples analyzed by Fry and Menon (1962) yielded residence times longer than 10 days. No significant shortening of their residence times to take into account dust fractions would be needed because the half-life of ^{210}Bi is so much shorter than that of ^{210}Po, and ^{210}Bi is the direct daughter product of ^{210}Pb decay. Quite probably, variations of a factor of 2 or more in mean residence times for different locations are to be expected.

Acknowledgment

We appreciate the partial support of this work by the American Cancer Society through Grant No. IN-35, by Hatch Act funds, and by the National Science Foundation through Grant No. GA-304. This manuscript was approved by the Director of Wisconsin Agricultural Experiment Station.

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Received for review June 13, 1969. Accepted February 3, 1970.

Short-Term Effects of Air Pollution on Mortality in New York City

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■ Mortality, air pollution, and certain meteorological factors during the period November 1962 through May 1965 in New York City are analyzed by multiple regression by use of the least-squares method to obtain quantitative estimates of the relationship between mortality and environmental factors. Mortality from respiratory and heart diseases for ages 64 and under, as well as ages 65 and over, is significantly related to the level of air pollution, with individual categories of respiratory and heart disease mortality being strongly, moderately, or weakly related. Mortality from other causes is not significantly related. The apparent influence of the environmental factors on mortality is limited to the immediate increase in mortality that occurs on the day of increased air pollution and extreme temperature and, to a lesser extent, on the following day. Mortality on any given day cannot be attributed to a delayed or cumulative effect of past environmental conditions.

Although there is considerable evidence to support the belief, now widely held, that air pollution affects human health, very little is known of the qualitative or quantitative nature of the relationship between air pollution and health. As has been pointed out by Sterling, Pollack, *et al.* (1967), "It was only recently that the Surgeon General of the U.S. in his testimony before Congress admitted that substantive evidence of the direct effect of common day-to-day air pollution on health is lacking."

This report discusses the results of a study which investigated two aspects of the relationship between air pollution and health: Is air pollution harmful to human health at levels ordinarily found in urban air as well as at the extraordinarily high levels occurring during air pollution episodes, and what is the quantitative nature of this relationship? What is the role of time, that is, the extent to which health effects are delayed and/or cumulative with respect to exposure to pollution some time in the past?

Method

Data employed in this study consist of measurements of certain air pollutants and meteorologic variables obtained by the Department of Public Health of Cornell Medical College between November 1962 and May 1965 during a study of "Air Pollution and Family Illness in New York City" (McCarroll, Cassell, *et al.*, 1965), and mortality data from the New York City Department of Health. The data are analyzed by multiple regression using the least-squares method to obtain quantitative estimates of the relationship between mortality and certain environmental factors.

The thesis of this paper is that the structure explaining mortality during the period of the available data consists of a systematic part made up of variables that are environmental in nature; further, they are meteorological variables and air pollution. Of course, other factors are important for an individual. For example, one may suffer a heart attack after overexertion or too much excitement. But such factors have only slight effects, if any at all, on variations in daily mortality due to heart disease among the more than 8 million inhabitants of NYC. Even if a large percentage of the daily total of deaths in NYC from heart disease occurred as a result of overexertion or too much excitement, we expect the number of such deaths that cannot be explained by climatic variables such as snowfall (when heart attacks may be expected to increase due to shoveling of snow) to be stable over the period of study. Meteorologic variables and air pollution are the more important explanatory variables, and the net effect of excluded variables will be represented in the disturbance terms of the regression models discussed below.

The period of study is short enough so that certain changes which occur over a longer period of time and would have to be considered were the period of study not limited to 2.5 consecutive years, can be ignored; for example, changing dietary habits and socio-economic status of the population.

Air pollution is included because it is believed it affects human health and is associated with mortality, with deaths due to respiratory and heart diseases regarded as most likely to have been influenced by air pollution. There is considerable evidence to support this. There is probably no one pollutant which invariably effects health given the same atmospheric conditions. This is because health effects are most likely the result of the interaction of pollutant and meteorologic variables. But even if we don't know the specific pollutants or combination of pollutants and meteorologic variables that cause the observed health effects, an appropriate index of air pollution that reflects the presence and action of the harmful environmental conditions would permit meaningful analysis. Sulfur compounds are prime candidates with respect to such an index. They are among the most commonly occurring pollutants in the U.S., are known irritants of the respiratory tract, and have attained high concentrations in all the major air pollution episodes. Since the concentrations of sulfur dioxide, sulfuric acid, and its salts are highly correlated, sulfur dioxide can be used as an index of pollution from these various compounds (U.S. Dept. H.E.W., 1967).

Particulate matter must also be considered as it contains known toxic substances such as lead, the carcinogenic hydrocarbon, benzopyrene, and asbestos. Also, it appears that the combined health effects from sulfur compounds and particulate matter are greater than the sum of effects from corresponding concentrations of the two pollutants taken alone (Lewis, 1965). This synergism occurs because irritants such as sulfur dioxide and sulfuric acid paralyze the hairlike cilia which line the respiratory passages and ordinarily force foreign substances, which enter the respiratory tract out through the mouth, by means of a constant sweeping movement. Sulfur dioxide molecules can thus penetrate deep into the respiratory system, even to the lungs; but they are usually too small to remain in the lungs. However, penetration of dust particles, etc., is easier when the cilia are paralyzed. Also, smaller sulfur dioxide gas molecules are adsorbed on the larger particles which now penetrate to the lungs where they settle and bring concentrated amounts of the irritant sulfur dioxide into contact with the delicate lung tissue.

Sulfur dioxide and the combination of sulfur dioxide and particulate matter even more so are considered severe irritants of the respiratory tract, capable of causing sufficient stress upon the body in times of high air pollution to bring about death, the severe irritation of the respiratory tract may cause the heart to labor so hard to circulate oxygen through the body that the heart fails (Lewis, 1965). Although there are many other pollutants in the atmosphere besides sulfur dioxide and particulate matter, they are the most relevant on the basis of existing evidence and appear well-suited to serve as indexes of air pollution that reflect the presence and action of harmful environmental conditions.

Temperature extremes influence mortality independently of air pollution by causing stress upon the body. Abrupt temperature changes put a strain on the body and nervous system, while prolonged warm or cold spells contribute to exhaustion (Kutschenreuter, 1960). Further, cold decreases mucus transport, which, by means of the cilia, is a primary method of clearing airborne materials from the lung (Kilburn, 1967).

It is not possible to analyze the cumulative or long-run effects of air pollution with the data presently available, that is, the effects resulting from continuous exposure over a prolonged time or the total impact of air pollution occurring during a given period upon future health. The long-run effects of even an extremely severe air pollution episode on a population may be so spread out over time as to be indeterminable, especially when investigation is limited to a period of approximately 2.5 years. But, short-run variations, *e.g.*, day to day, result in a more immediate effect upon health that can be examined. It is this short-run component that will hereafter be considered in this paper.

Previous exposure to air pollution is reflected in the state of health of the population at time t even though it is not known how many persons with, for example, cardio-respiratory disease at time t would have had none, or less severe cases, in the absence of air pollution. The state of health at time t will be taken as given and attention will be directed at how air pollution during period t affects the mortality occurring in some finite number of future periods. The reasons for the prevalence of cardio-respiratory disease at time t, *i.e.*, whether due to air pollution or otherwise, won't be considered. Rather, the question will be: how is air pollution during t influencing short-run future mortality? The analysis will consider only mortality (not morbidity) and only the relation between air pollution and mortality for periods in close proximity.

Statistical analysis

Several types of models will be investigated, the first being linear in all variables with the measure of each variable being the average daily value occurring during each calendar month for the period November 1962 through May 1965. That is, the sample period consists of 31 monthly observations with

R_t = average daily mortality during month t in NYC from causes 2 to 8 of Table I. These are generally respiratory conditions

H_t = average daily mortality during month t in NYC from causes 15 to 18. These are generally heart conditions

O_t = average daily mortality during month t in NYC from all other causes (*i.e.*, O_t = total mortality $-R_t - H_t$). O_t includes, for example, causes 9 to 14, which are accidents, suicides, and homicides

C_t = average daily concentration of particulate matter during month t, measured in coh units (where the concentration of particulate matter for any given day is the average of 12 observations, one observation being taken every 2 hours)

S_t = average daily concentration of sulfur dioxide during month t, measured in parts per million (where the concentration of sulfur dioxide for any given day is the average of 24 hourly observations)

D_t = the average daily number of degree days during month t, where the number of degree days for a given day is the absolute value of 65° F. minus the mean of 24 hourly temperature readings for that day. This definition includes temperature readings that exceed 65° F. as well as those that are below 65° F.

t = 1, 2,. . . ., 31

If the investigator puts no restriction on the coefficients of a model, he must somehow determine the maximum time lag for which the coefficients of the explanatory variables take on nonzero values. One possibility is to let the data determine the maximum time lag. Successive lags of the explanatory variables are added to the model with the best lag being chosen as that for which the multiple coefficient of determination adjusted for sample size ($\bar{R}^2$) is a maximum. A second criterion for choosing the optimal lag might be the closeness of corresponding coefficients of the relations containing lags of optimal and longer lengths (Almon, 1965).

Regressing R_t and H_t separately on C_t, S_t, D_t and then on C_t, C_{t-1}, S_t, S_{t-1}, D_t, and D_{t-1} results in a highly significant association among the variables in each relation. But, when the environment of period $t - 1$ as well as period t is used to explain mortality during period t, the standard errors of the regression coefficients increase and the t statistic values decrease, making the coefficients of some variables go from significant to not significant. Multicollinearity of the explanatory variables prevents very precise estimation of the individual influence of each explanatory variable. The correlation coefficients of 0.77 between C_t and C_{t-1}, 0.80 between C_t and D_t, 0.73 between C_t and D_{t-1}, 0.79 between C_{t-1} and D_{t-1}, and 0.75 between D_t and D_{t-1} indicate how highly intercorrelated are the explanatory variables, except perhaps for S.

In view of the effect of multicollinearity demonstrated above when lagged periods of the explanatory variables are introduced, a moving average of the present and previous periods will be used as the measure of each explanatory variable C, S, and D. For example,

$$C = \frac{\sum_{i=t-j}^{t} C_i}{j+1} \qquad S = \frac{\sum_{i=t-j}^{t} S_i}{j+1} \qquad D = \frac{\sum_{i=t-j}^{t} D_i}{j+1}$$

will be the variables explaining mortality during period t, with the best specification being determined by Theil's criterion of maximum corrected coefficient of determination as the specification corresponding to the value of j for which $\bar{R}^2$ is highest (Theil, 1961). These indexes will reflect the lag effect of the environment on mortality because if mortality during period t does depend on C, S, D during period $t - 1$ then, for given levels of C_t, S_t, D_t, there will be higher mortality during t the higher are C_{t-1}, S_{t-1}, D_{t-1} (then, the higher are $\sum_{i=t-1}^{t} C_i/2$, $\sum_{i=t-1}^{t} S_i/2$, $\sum_{i=t-1}^{t} D_i/2$), and, therefore, the regression employing these moving averages will result in higher $\bar{R}^2$ than the regression employing C_t, S_t, D_t. Although it may appear that the effect of defining the measures of C, S, D in this way is to sacrifice determination of the separate effects of different periods (present and previous) on present mortality, there is, in fact, justification for use of the above indexes for C, S, D. It is that the average of periods gives an index which reflects the cumulative effect of exposure to the environment as well as the lag effect. In other words, the effect of pollution during period t may depend on the pollution during period $t - 1$ making the combined level of pollution a more relevant explanatory variable than the individual levels occurring during periods t and $t - 1$. For example, if a period of high pollution does not immediately result in high mortality but does affect a susceptible group so that a second successive period of high pollution results in high mortality, then the effect of pollution during the second period depends on the pollution occurring during first period and makes it difficult to establish a clear relation between mortality during period t and pollution during periods t and $t - 1$ separately. But using the average pollution over several periods provides a measure of this prolonged exposure to which mortality may be related.

Table I. Categories of Mortality Occurring in New York City[a]

1. Total deaths
2. Tuberculosis of respiratory system
3. Malignant neoplasm of respiratory system
4. Asthma
5. Influenza
6. Pneumonia
7. Bronchitis
8. Pneumonia of newborn
9. Motor vehicle accidents
10. Railway accidents, other road vehicle accidents, water transport accidents, aircraft accidents
11. Other accidents
12. Suicide
13. Homicide
14. Early infancy
15. Vascular lesions affecting central nervous system
16. Arteriosclerotic heart disease, including coronary disease
17. Hypertensive heart disease
18. Rheumatic fever, chronic rheumatic heart disease, other diseases of the heart, other hypertensive disease, diseases of arteries, diseases of veins, and other diseases of circulatory system, certain kinds of nephritis and nephrosis

[a] Tabulated by the NYC Department of Health

Table II gives the results of four different regressions of heart plus respiratory disease mortality ($H_t + R_t$, measured as average daily mortality during month t) on the explanatory variables particulate matter (C), sulfur dioxide (S), degree days (D), where the measure of the explanatory variables is different in each regression, being, respectively, average daily value during month t, during months t and $t - 1$, during t, $t - 1$, and $t - 2$, during t, $t - 1$, $t - 2$, and $t - 3$. The measure of each of the explanatory variables C, S, D is the same in any one regression, with the expression involving V_t at the top of each column indicating the various measures and the corresponding regression results below. Examination of $\bar{R}^2$ reveals that variation in heart and respiratory disease mortality is best explained by variation in the environment during period t and the environment during previous periods does not aid the explanation of mortality during t. In fact, the decrease in $\bar{R}^2$ is quite striking as periods $t - 2$ and $t - 3$ are included. Restricting attention to the results arising from the equation explaining ($H_t + R_t$) by the environment during t, we find the F value of 27.33 to be highly significant indicating a significant association among the variables in this relation, where $F_{0.0005}$ is approximately 8.0 for (3, 26) degrees of freedom (Dixon and Massey, 1957). Looking at the individual explanatory variables we find heart and respiratory disease mortality significantly related to concentration of particulate matter (*C*) at a 0.005 level and degree days (*D*) at a 0.025 level, while sulfur dioxide (*S*) is not a significant explanatory variable. (Critical *t* values can be found in Dixon and Massey, 1957.) The beta coefficients (which are the ordinary regression coefficients after standardizing the variables) give a measure of the relative importance of the different explanatory variables and show air pollution in the form of particulate matter to be a more important regressor than degree days, in the sense that for a typical or equally likely change in both *C* and *D*, the effect on respiratory and heart disease mortality induced by particulate matter is greater than that induced by degree days (Goldberger, 1964).

When time series are employed there is often a lack of serial independence of the disturbance term, with the serial correlation increasing as the period becomes shorter. Serial correlation can be an indication that the model is not correctly specified, often because of omitted variables which are themselves serially correlated and whose influence is represented in the disturbance term (Christ, 1966; Goldberger, 1964; Griliches, 1961; Johnston, 1963; Malinvaud, 1966). The distribution of errors is, in general, not known and cannot be observed, but the least-squares residuals can provide some information about the nature of the errors (Malinvaud, 1966). The Durbin-Watson statistic, for example, can indicate the existence of correlation between the errors of different periods (Christ, 1966; Griliches, 1961; Malinvaud, 1966; Nerlove and Wallis, 1966). From critical values given in Christ (1966) it can be seen the hypothesis of independence of the errors is not rejected at a 0.05 or 0.01 level. This is a very important result since the apparent lack of serial correlation among the successive disturbances eliminates one of the common reasons for questioning the classical regression results when time series are involved, and, further, indicates there is no flagrant misspecification in terms of omitted variables or incorrect functional form.

In summary, the level of respiratory and heart disease mortality over time is quite significantly related to environmental conditions, especially air pollution in the form of particulate matter and temperature in terms of degree days. In fact, 73% of the variation in mortality from heart and respiratory diseases is explained by concurrent variations of air pollution and temperature, with pollution being the more important explanatory variable. That the number of deaths involved is not small is easily demonstrated by means of the regression coefficients. An increase of one unit in the average daily concentration of particulate matter (*C*) during a month results in an increase of 13.35 in the expected average daily mortality from respiratory and heart diseases during the same month. If we consider that the difference in concentration of particulate matter for any two days may be as large as 5 units (or greater on rare occasions), an increase of 2 units in the average daily concentration of particulate matter for one month compared to another month is not unreasonable. The expected increase in average daily respiratory and heart disease mortality corresponding to the increase of 2 units in particulate matter concentration is 26.7 deaths. This is an increase amounting to almost 18% of the average number of deaths per day attributable to heart and respiratory diseases during the sample period (an average of approximately 150 persons a day died of heart or respiratory diseases during the period November 1962 through May 1965 as shown by $\bar{M}$ of Table II).

Analysis of mortality from all causes other than heart and respiratory diseases by the same procedure, however, reveals clearly a lack of association between deaths in this category of mortality and the environment as measured by *C*, *S*, *D*. When the regression results of Table III are compared with the critical values for *F* and *t* statistics, it is easily seen that there

Table II. Regression of Heart and Respiratory Disease Mortality ($H_t + R_t$) for All Ages on Particulate Matter (*C*), Sulfur Dioxide (*S*), Degree Days (*D*)

	V_t	$\sum_{i=t-1}^{t} V_i$ 2	$\sum_{i=t-2}^{t} V_i$ 3	$\sum_{i=t-3}^{t} V_i$ 4
$\bar{R}^2$	0.731	0.720	0.592	0.411
DW	1.659	1.687	1.466	1.299
F	27.33	25.91	14.56	7.28
t value for *C*	3.22	2.90	1.82	0.60
t value for *S*	0.48	−0.48	−0.16	−0.15
t value for *D*	2.36	1.98	1.44	1.44
$\hat{b}$ of *C*	13.35	14.55	12.94	5.59
$\hat{b}$ of *S*	14.18	−19.00	−9.66	−12.85
$\hat{b}$ of *D*	0.49	0.54	0.59	0.82
Beta coeff. of *C*	0.512	0.530	0.442	0.189
Beta coeff. of *S*	0.051	−0.060	−0.025	−0.032
Beta coeff. of *D*	0.385	0.398	0.399	0.539
S.E. est.	8.15	8.31	10.01	11.18
$\bar{M}$	150.55			

$\bar{R}^2$ = corrected multiple coefficient of determination
DW = Durbin-Watson statistic
F = *F* statistic
t = *t* statistic
$\bar{M}$ = average daily mortality during study period
$\hat{b}$ = estimated regression coeff.
Beta coeff. = estimated beta coeff.
S.E. est. = standard error of estimate

Table III. Regression of Mortality from all Causes Other than Heart and Respiratory Diseases for All Ages on Particulate Matter (*C*), Sulfur Dioxide (*S*), Degree Days (*D*)

	V_t	$\sum_{i=t-1}^{t} V_i$ 2	$\sum_{i=t-2}^{t} V_i$ 3	$\sum_{i=t-3}^{t} V_i$ 4
$\bar{R}^2$	0.048	−0.012	−0.071	−0.100
DW	2.227	2.132	2.138	2.091
F	1.49	0.87	0.38	0.19
t value for *C*	0.32	0.61	−0.16	−0.11
t value for *S*	−0.01	0.16	−0.09	−0.04
t value for *D*	0.99	0.22	0.61	0.39
$\hat{b}$ of *C*	0.63	1.48	−0.48	−0.41
$\hat{b}$ of *S*	−0.11	3.03	−2.28	−1.43
$\hat{b}$ of *D*	0.10	0.03	0.11	0.09
Beta coeff. of *C*	0.095	0.211	−0.063	−0.049
Beta coeff. of *S*	−0.002	0.035	−0.023	−0.013
Beta coeff. of *D*	0.304	0.084	0.274	0.199
S.E. est.	3.92	4.05	4.20	4.33
$\bar{M}$	93.01			

$\bar{R}^2$ = corrected multiple coefficient of determination
DW = Durbin-Watson statistic
F = *F* statistic
t = *t* statistic
$\bar{M}$ = average daily mortality during study period
$\hat{b}$ = estimated regression coeff.
Beta coeff. = estimated beta coeff.
S.E. est. = standard error of estimate

Table IV. Regression of Heart and Respiratory Disease Mortality for Ages 65 and Over on *C*, *S*, *D*

	V_t	$\sum_{i=t-1}^{t} V_i$ 2	$\sum_{i=t-2}^{t} V_i$ 3	$\sum_{i=t-3}^{t} V_i$ 4
$\bar{R}^2$	0.676	0.663	0.539	0.364
DW	1.721	1.738	1.544	1.320
F	21.15	20.01	11.91	6.14
t value for *C*	2.42	2.35	1.46	0.36
t value for *S*	0.52	−0.20	−0.01	−0.09
t value for *D*	2.45	1.87	1.43	1.45
$\hat{b}$ of *C*	8.12	9.53	8.15	2.67
$\hat{b}$ of *S*	12.17	−6.56	−0.59	−6.20
$\hat{b}$ of *D*	0.41	0.41	0.46	0.65
Beta coeff. of *C*	0.423	0.471	0.376	0.119
Beta coeff. of *S*	0.060	−0.026	−0.002	−0.20
Beta coeff. of *D*	0.440	0.412	0.421	0.566
S.E. est.	6.59	6.72	7.88	8.83
$\bar{M}$	101.82			

$\bar{R}^2$ = corrected multiple coefficient of determination
DW = Durbin-Watson statistic
F = *F* statistic
t = *t* statistic
$\bar{M}$ = average daily mortality during study period
$\hat{b}$ = estimated regression coeff.
Beta coeff. = estimated beta coeff.
S.E. est. = standard error of estimate

Table V. Regression of Heart and Respiratory Disease Mortality for Ages 64 and Under on *C*, *S*, *D*

	V_t	$\sum_{i=t-1}^{t} V_i$ 2	$\sum_{i=t-2}^{t} V_i$ 3	$\sum_{i=t-3}^{t} V_i$ 4
$\bar{R}^2$	0.759	0.746	0.631	0.472
DW	1.916	2.023	1.698	1.613
F	31.44	29.33	16.98	9.06
t value for *C*	4.63	3.64	2.50	1.25
t value for *S*	0.25	−1.13	−0.56	−0.32
t value for *D*	1.38	1.72	1.16	1.16
$\hat{b}$ for *C*	5.23	5.02	4.78	2.92
$\hat{b}$ for *S*	2.01	−12.44	−9.07	−6.65
$\hat{b}$ of *D*	0.08	0.13	0.13	0.17
Beta coeff. of *C*	0.696	0.635	0.578	0.375
Beta coeff. of *S*	0.025	−0.127	−0.083	−0.063
Beta coeff. of *D*	0.214	0.329	0.307	0.413
S.E. est.	2.22	2.29	2.69	2.79
$\bar{M}$	48.73			

$\bar{R}^2$ = corrected multiple coefficient of determination
DW = Durbin-Watson statistic
F = *F* statistic
t = *t* statistic
$\bar{M}$ = average daily mortality during study period
$\hat{b}$ = estimated regression coeff.
Beta coeff. = estimated beta coeff.
S.E. est. = standard error of estimate

is no significant association between mortality and environment (at least for any level of significance ≤ 0.10).

Total mortality can therefore be separated into two distinct categories: respiratory and heart disease deaths which are definitely related to the environmental factors air pollution and temperature, and the deaths from all other causes which are not related to these environmental factors.

Breaking down heart and respiratory disease mortality discussed above into two age groups, 65 and over and 64 and under and applying the same analysis we obtain the results given in Tables IV and V. The conclusions reached when considering all ages together also apply to those 65 and over and those 64 and under. The influence of the environment on respiratory and heart disease mortality is not limited to those over age 65, *i.e.*, to the age group one might suspect consists of persons whose demise is imminent and just hastened by additional stress upon their already ill bodies. On the contrary, the proportion of variation in the mortality of those 64 and under explained by variation in the environment is over 0.75 (see Table V) as compared to approximately 0.68 (see Table IV) for those 65 and over. Furthermore, from the beta coefficients for *C* and *D* in Tables IV and V it is seen that air pollution, in terms of particulate matter, is a more important explanatory variable and induces a greater effect on respiratory and heart disease mortality than does climate in terms of temperature for those 64 and under, while particulate matter and temperature appear nearly equal in importance as explanatory variables for those 65 and over.

It has occasionally been suggested that the increase in mortality observed, during times of high air pollution, represents bunching together of deaths of persons already ill, whose passing was just hastened by air pollution and presumably would have died shortly anyway. That this is not completely true is demonstrated by the significant relations obtained above. For, if the sole effect of air pollution was to redistribute the deaths within a short time interval, for example, a month or less, then the average daily mortality for a given month would be independent of the concentration of air pollution during the month and no statistically significant relation would be observed between monthly mortality and air pollution.

In an effort to determine which of the diseases included under respiratory and heart diseases respond to environmental factors, these two categories have been broken down as much as the data will allow into ten individual diseases or groups of diseases. Each of the ten categories has been found to have what is arbitrarily designated a strong statistical relation with the environmental factors *C*, *S*, *D*, a moderate statistical relation, or a weak statistical relation. The criteria for strong, moderate, or weak are the levels of significance associated with the *F* and *t* tests commonly used to determine whether or not the environmental factors together and individually explain mortality. The relation is considered strong when *F* is significant at a 0.001 level and the *t* statistics for the regression coefficients are generally significant at a 0.05 level; moderate when *F* is significant at 0.05 and the *t* statistics at 0.10; weak when *F* is not significant at 0.05 and the *t*'s not significant at 0.10. By these criteria the categories of mortality strongly related to *C*, *S*, and *D* are pneumonia, vascular lesions affecting central nervous system, arteriosclerotic heart diseases (including coronary disease, hypertensive heart disease), other diseases of the heart, etc. (category 18 of Table I). Moderately related is bronchitis, and weakly related are tuberculosis of respiratory system, malignant neoplasm of respiratory system, asthma, and pneumonia of newborn.

Although space does not permit detailed presentation of the results obtained for individual categories of mortality, some idea of the magnitude of the response of mortality from various causes to changes in concentration of air pollution is obtained from the estimated regression coefficients. If we consider only the pollution occurring during the present month (*i.e.*, $C = C_t$), Table VI gives, for all categories found to be

Table VI. Expected Increase in Mortality Resulting from a Unit Increase in Particulate Matter (C)

Category of mortality	Age	$\bar{M}$	$\hat{b}$ of C	($\hat{b}$ of C)/ $\bar{M}\times 100$
Pneumonia	all ages	9.40	1.86	20
	65 & over	5.49	NS^a	. . .
	64 & under	3.90	1.13	29
Bronchitis	all ages	0.81	0.17	21
	65 & over	0.50	NS^a	. . .
	64 & under	0.31	0.11	35
Vascular lesions affecting CNS	all ages	17.10	0.94	5
	65 & over	12.91	NS^a	. . .
	64 & under	4.19	0.36	9
Arteriosclerotic heart disease	all ages	85.80	6.78	8
	65 & over	60.91	4.99	8
	64 & under	24.88	1.79	7
Hypertensive heart disease	all ages	8.33	1.55	19
	65 & over	5.49	0.95	17
	64 & under	2.83	0.59	21
Other diseases of the heart, etc.	all ages	18.03	1.71	9
	65 & over	11.63	0.98	8
	64 & under	6.38	0.72	11
Respiratory and heart diseases	all ages	150.55	13.35	9
	65 & over	101.82	8.12	8
	64 & under	48.73	5.23	11

NS^a = not significant at 0.10 level
$\hat{b}$ of C = regression coefficient of C
$\bar{M}$ = average daily mortality for study period
($\hat{b}$ of C)/$\bar{M}$ = % increase

strongly or moderately related to the environmental factors, the expected increases in mortality during a given month arising from a 1-unit increase in the average daily concentration of particulate matter during the same month, expressed as percentages of the average daily mortality in that category throughout the study period. There is wide variation in the percentages of different categories, but for each category except "arteriosclerotic heart disease, including coronary disease" the percentage change is greater for the younger age group.

A very important aspect of the air pollution problem is the threshold levels of noxious pollutants, *i.e.*, the levels at which deleterious effects begin to occur. The existence of threshold levels implies a nonlinear relation between air pollution and mortality. For example, the following transformation of the linear relations considered above has the property that the rate of change of mortality with respect to any one of the explanatory variables is directly related to the value taken by each of the explanatory variables (provided that the coefficient of the explanatory variable with respect to which the derivative is taken is greater than unity).

Considering mortality from respiratory diseases (R_t) for all ages and estimating by ordinary least squares the coefficients of

$$R_t = AC_t^aS_t^bD_t^c$$

or

$$\log R_t = \log A + a \log C_t + b \log S_t + c \log D_t$$

we obtain

$$\log R_t = \underset{}{2.983} + \underset{(0.081)}{0.227 \log C_t} + \underset{(0.043)}{0.053 \log S_t} + \underset{(0.021)}{0.026 \log D_t}$$

$\bar{R}^2 = 0.528$ and $F = 11.81$.

(The figures in parentheses are the standard errors of the regression coefficients.) And for the corresponding linear model, $R_t = A + aC_t + bS_t + cD_t$, we find

$$R_t = 14.75 + \underset{(1.08)}{2.30C_t} + \underset{(7.59)}{6.88S_t} + \underset{(0.054)}{0.10D_t}$$

$\bar{R}^2 = 0.586$ and $F = 14.69$.

It is seen that $\bar{R}^2 = 0.528$ is less than $\bar{R}^2 = 0.586$ obtained for the linear model. But, as Goldberger (1964) points out, the coefficient of determination gives the proportion of the variation in log R_t that is being explained. To compare the nonlinear form with the linear form, the corrected coefficient of determination between the antilogs of calculated values of log R_t and observed values of R_t is compared with the corrected coefficient of determination between calculated R_t and observed R_t. If we make the necessary computations it is observed that $\bar{R}_1^2 = 0.504 = \bar{R}^2$ between the antilogs of calculated values of log R_t and observed values of R_t, where R_t refers to mortality from respiratory conditions during month t, and $\bar{R}^2$ refers to corrected multiple coefficient of determination. If $\bar{R}_0^2 = \bar{R}^2$ for the linear model $= 0.586$, then comparing $\bar{R}_1^2$ and $\bar{R}_0^2$ reveals that the linear model provides a better explanation of mortality from respiratory conditions than $R_t = AC_t^aS_t^bD_t^c$, the nonlinear form. A similar result is found for mortality from heart diseases (H_t), and the linear model is also superior to other nonlinear forms such as quadratic and semilog functions.

The implication of a linear relation between mortality and the environmental factors is that a unit change in the level of air pollution induces as great an increase in mortality at low levels of pollution as at higher levels. Thus, not only are the high levels of pollution to be feared as harmful to health, but also the lower levels often occurring in our urban air.

In addition to the relation between monthly levels of mortality and air pollution, there is an association within months that must be considered. One possible explanation for the positive correlation observed above between monthly mortality and environmental factors is that it just reflects the correlation between mortality and environment for each day within the month. In other words, the real underlying relation between mortality and air pollution is simply that increased pollution on day t induces increased mortality on day t without more delayed effects. Alternatively, the mortality on a particular day may be influenced by the air pollution occurring on many previous days.

As in the monthly models above, including lagged values of explanatory variables in the relations between daily mortality and daily indexes of the environmental factors so increases the standard errors of the regression coefficients that estimates of the contribution of individual regressors cannot be obtained. Therefore, moving averages are again employed as the indexes of the explanatory variables. The best explanation of mortality on day t is given by considering the pollution and temperature on days t and $t - 1$. Including the environment on day $t - 1$ improves the explanation of mortality obtained by day t alone, while adding the environment on days prior to day $t - 1$ does not result in any improvement. Rather, as periods $t - 2, t - 3$, etc., are added to the indexes for C, S, and D, $\bar{R}^2$ steadily decreases. For the functions with maximum $\bar{R}^2$, in which the independent variables reflect only the environment during periods t and $t - 1$, the F and t statistics reveal that air

Table VII. Regression of Daily Respiratory and Heart Disease Mortality on Particulate Matter (C), Sulfur Dioxide (S), Degree Days (D), with the Index for Each Independent Variable V Being $V = (V_t + V_{t-1})/2$ (t refers to day t)

	All ages	65 & over	45 to 64	44 & under
$\bar{R}^2$	0.369	0.317	0.138	0.058
DW	1.352	1.425	1.961	1.936
F	137.28	109.09	38.24	15.18
t value for C	7.95	6.71	4.67	3.18
t value for S	2.76	3.09	0.30	0.71
t value for D	11.77	10.46	6.41	3.44
$\hat{b}$ of C	7.69	5.29	1.86	0.53
$\hat{b}$ of S	20.68	18.85	0.92	0.92
$\hat{b}$ of D	0.67	0.49	0.15	0.03
S.E. est.	16.39	13.36	6.75	2.84
$\bar{M}$	150.55	101.82	40.76	7.97

$\bar{R}^2$ = corrected multiple coefficient of determination
DW = Durbin-Watson statistic
F = F statistic
t = t statistic
$\bar{M}$ = average daily mortality during study period
$\hat{b}$ = estimated regression coeff.
S.E. est. = standard error of estimate

pollution and temperature, together and individually, are highly significant in explaining respiratory and heart disease mortality. Sulfur dioxide, as well as particulate matter and temperature, are found to be important explanatory variables in contrast to their significance in the monthly models. This may result from the larger number of observations in the daily models which permits more precise determination of the individual effects of the correlated variables C, S, and D. It is thus clear that the state of the environment on any given day, and the combined state on that day and the previous day even more, induce a significant and immediate effect on respiratory and heart disease mortality.

The influence of C, S, and D on mortality within different age groups can be observed from Table VII, which gives the relations between daily mortality from respiratory and heart diseases and C, S, D for all ages, ages 65 and over, ages 45 to 64, and ages 44 and under. The environment is found to influence the level of mortality within each age group considered; those ages 44 and under are affected as well as those 45 and over, although to a lesser extent.

When one compares the daily models in Table VII with the monthly models in Tables II, IV, and V a striking difference is noted between the $\bar{R}^2$'s for corresponding categories of mortality and age groups. Although the daily models reveal highly significant associations between mortality and the state of the environment (on the basis of the F and t statistics), the $\bar{R}^2$'s are much lower than the corresponding $\bar{R}^2$'s in the monthly models and attain half the $\bar{R}^2$ in the monthly model only for the category respiratory and heart disease mortality for all ages.

The initial inclination is to argue that this indicates the existence of a more complex process relating mortality to the environment than simply an association between concurrent daily mortality and daily indexes of C, S, and D. The total impact of even a day of extremely high concentration of air pollution on the mortality of a population may be so spread out over time as to be indeterminable, making it impossible to isolate the influence of any one day's air pollution in, for example, January on the mortality of a particular day during the following February. Indeed, such future effects may be negligible. However, the deaths of individuals in response to the state of the environment on a particular day will vary with respect to time of occurrence, perhaps by many days, depending on factors peculiar to each individual, for example, quantity and quality of medical care, the body's resistance to environmental stress, etc. Also, there may be a synergistic effect of consecutive days of high pollution such that the influence of the concentration of pollution occurring on one day is not independent of the concentration on neighboring days. For these reasons the mortality occurring on a particular day cannot be analyzed without considering mortality on adjacent days, and the influence of pollution occurring on a given day cannot be studied without taking into account the levels of pollution on adjoining days. But when the measure of each variable is the average daily value per month, the indexes of the variables reflect the cumulative and lag effects of exposure to the environment and permit a determining of the influence air pollution and temperature have on mortality that is not possible with the daily models. The average daily mortality per month does not distinguish the day within the month when death occurred and includes the spread out effects of environmental exposure. And the average daily value per month of each explanatory variable describes the extent to which the population is subjected to more or less severe environmental stress sustained over a period of many days. Mortality on a given day is related to the state of the environment on many previous days, and the state of the environment on a given day, especially when considered together with the environment of adjacent days, influences mortality on many future days. The use of average daily values per month as measures of the variables provides simultaneous representation of these forces in the analysis.

If this argument is valid there should be evidence of both an immediate and a delayed effect of the environment on mortality; *i.e*, the mortality on a particular day is related to the state of the environment on that day and the preceding day and also to the environmental conditions weeks in the past. Although it is not possible to determine the relationship between mortality on day t and the environment on day $t - k$ (for various k where $k>2$), the mortality on a given day is influenced by the air pollution occurring during a prolonged period of several consecutive weeks prior to the day of death. Many consecutive days, *e.g.*, several weeks or a month, of high pollution should raise mortality on a given day to a higher level than would occur if the past pollution were less because there is an additive and synergistic effect of past exposure, with pollution on each previous day contributing to the mortality on a particular day in the future, and with the effect of a given level of pollution on one day being greater when adjacent days have high pollution. It should be possible to separate the influence, on a particular day's mortality, of the immediate concentration of air pollution and the sustained pollution during previous weeks.

However, the expected improvement in the explanation of daily mortality when the sustained pollution during previous weeks is included does not occur. In fact, there is no statistically significant difference between the average daily mortality per month predicted by the monthly regression equations and the average daily mortality per month predicted by daily regression equations. That is, equally good estimates of average daily mortality per month are obtained by calculation directly from the monthly model or by computing expected daily mortality for each day of the month from the daily regression model and deriving from these an estimate of average daily mortality per month. The difference between the $\bar{R}^2$'s of corresponding monthly and daily models appears to arise not from a misspecification of the daily mortality models, but rather as a result of the process of aggregation relating the monthly models to the daily models. (See Theil, 1954, and Grunfeld and Griliches, 1960, for discussion of this and related aspects of the aggregation problem.) It is not possible to attribute mortality on any given day to a delayed or cumulative effect of past environmental conditions. The apparent influence of the environmental factors on mortality is limited to the immediate increase in mortality that occurs on the day of increased air pollution and extreme temperature and, to a lesser extent, on the following day.

The above property of the daily models is tested by comparing the average of the absolute values of the residuals arising from the monthly regression equation with the average of the absolute values of the deviations of actual average daily mortality per month from the average daily mortality per month predicted by the daily regression equation. For example, let

$\overline{M}_m$ = average absolute value of the residuals in the regression of average daily heart and respiratory disease mortality per month for all ages on average daily value per month of *C*, *S*, *D* (*i.e.*, the regression in Table II)
M_m = expected value of $\overline{M}_m$
$\overline{M}_d$ = average absolute value of the deviations of actual average daily heart and respiratory disease mortality per month for all ages from the average daily mortality per month predicted by the regression of daily heart and respiratory disease mortality for all ages on particulate matter, sulfur dioxide, and degree days (*i.e.*, the regression in Table VII)
M_d = expected value of $\overline{M}_d$

Null hypothesis: $M_m = M_d$
Alternative hyp.: $M_m < M_d$

We are testing the hypothesis that average daily mortality per month is predicted equally well by the monthly and daily models against the alternative hypothesis that the monthly model provides a better prediction (presumably because of a misspecification in the daily model that is overcome in the monthly model). Appealing to the Central Limit Theorem and assuming the condition of independence of the observations are not grossly violated, then

$$\frac{(\overline{M}_m - \overline{M}_d) - (M_m - M_d)}{\sqrt{\dfrac{s_m^2}{30} + \dfrac{s_d^2}{30}}} = Z$$

is approximately distributed as a standard normal random variable where s_m^2, s_d^2 are sample variances of the values included in $\overline{M}_m$ and $\overline{M}_d$, respectively.

Computation of the sample values gives

$$\overline{M}_m = 6.13 \qquad s_m^2 = 20.72$$
$$\overline{M}_d = 6.26 \qquad s_d^2 = 26.51$$

and by substitution $Z = -0.10$. The difference between $\overline{M}_m$ and $\overline{M}_d$ is not significant at a 0.40 level of significance.

Another criterion by which to compare the monthly and daily models is whether the sums of squared deviations of the actual from the predicted average daily mortality per month are significantly different for the monthly and daily models. Such a difference infers the parent disturbance variances are not equal, with the difference presumably reflecting misspecification and inclusion of omitted variables in the disturbance of the model with the larger sum of squared deviations. Space does not permit discussion of the statistical test employed in this latter comparison of the monthly and daily models, but, again, the difference is not significant.

If we consider the regression coefficients in the daily models to be estimates of the immediate response induced in mortality by changes in air pollution, Table VIII gives the expected per cent increase in mortality (in terms of average daily mortality during the study period) during day *t* resulting from a unit increase in the average concentration of particulate matter and a 0.5-unit increase in the average concentration of sulfur dioxide during days *t* and *t* − 1. The per cent increases are conservative in that increases in particulate matter could be greater than 1 unit, *e.g.*, 2 or 3 units (and greater on rare occasions), although a 0.5-unit increase in sulfur dioxide is severe but possible. A difficulty in comparing per cent changes for older and younger ages is that sulfur dioxide is significant for ages 65 and over and not for ages 64 and under in four of the seven categories of mortality in Table VIII, and by assuming $\hat{b}$ of $S = 0$ for these four categories the per cent change for the younger ages is biased downward. However, for "other diseases of the heart, etc.," which have sulfur dioxide significant for all age groups (where significant means at a level of 0.10 or less), both ages 45 to 64 and ages 44 and under show a greater per cent change than those 65 and over for a unit change in *C* and a 0.5-unit change in *S*; and if only a change in particulate matter is considered, then for the categories respiratory and heart diseases, pneumonia, and bronchitis the change is greater for the younger ages, while for the other categories the change for the older is only slightly greater than that for the younger age groups. Thus, both those 64 and under and those 65 and over are affected as has already been pointed out several times. This is true for both the monthly and daily models.

Table VIII. Expected Increase in Mortality for All Ages During Day *t* Resulting from a Unit Increase in the Average Concentration of Particulate Matter (*C*), and a 0.5-unit Increase in the Average Concentration of Sulfur Dioxide (*S*), During Days *t* and *t* − 1

Category of mortality	$\overline{M}$	$\hat{b}$ of *C*	$\hat{b}$ of *S*	$\dfrac{\hat{b} \text{ of } C + (\hat{b} \text{ of } S)/2}{\overline{M}/100}$
Pneumonia	9.40	0.95	3.72	30
Bronchitis	0.81	0.09	NS[a]	11
Vascular lesions affecting CNS	17.10	0.77	5.34	20
Arteriosclerotic heart disease	85.80	3.41	8.29	9
Hypertensive heart disease	8.33	1.09	NS[a]	13
Other diseases of the heart, etc.	18.03	0.75	5.96	21
Respiratory and heart diseases	150.55	7.69	20.68	12

NS[a] = not significant at 0.10 level
$\hat{b}$ of C = regression coefficient of C
$\hat{b}$ of S = regression coefficient of S
$\overline{M}$ = average daily mortality for study period
$\dfrac{\hat{b} \text{ of } C + (\hat{b} \text{ of } S)/2}{\overline{M}/100}$ = % increase

Conclusions

During the 2.5 years of the study there were more deaths the greater the concentration of atmospheric pollution. If air pollution causes the observed variation in mortality, and if particulate matter and sulfur dioxide at least reflect the presence of the harmful environmental factors, then slight or moderate increases in concentration of air pollution during a month can be expected to result in increased mortality from heart and respiratory diseases amounting to several hundred deaths. And this is occurring for levels of pollution that are not considered unusually high and for changes in levels that may indeed pass unnoticed.

Air pollution is an environmental stress which yearly pushes many hundreds prematurely to their death. This is the acute or short-run effect of air pollution. There is also the chronic or long-run effect. This study has been concerned with the acute effect without considering the chronic effect, *i.e.*, without considering the role of continuous exposure to the environment over a period of many years in the evolution of the state of health at time t. The acute effect represents movement along the mortality functions discussed in this paper and the chronic effect helps determine the position of the mortality functions. Regardless of how the state of health at time t came to be, there are acute effects from levels of pollution ordinarily found in urban air.

Although air pollution episodes are not a necessary condition for acute effects, primary concern from a public policy viewpoint appears to be focused on setting air quality standards such that concentrations of air pollution do not approach levels capable of causing the disasters experienced in Donora (1948), London (1952), and New York (1966). This is certainly creditable, however, deaths are occurring when there are no such episodes, but when there are slight and seemingly innocuous increases in concentration from day to day and month to month. Complete consideration of the health effects of air pollution requires including the influence of nonepisodic levels.

Air pollution is a very real health hazard. Kneese (1966), Ridker (1967), and Sterling, Pollack, *et al.* (1967) have discussed the lack of, and need for, estimates of the quantitative relationship between air pollution and health. The present study demonstrates that it is indeed possible to obtain estimates of the response of mortality to the levels of air pollution ordinarily occurring in New York City. Although these estimates are only approximations of the parameters relating mortality to air pollution, and will no doubt become more precise as knowledge of the effect air pollution has on health increases, such estimates are essential if the society is to cope with the problem of air pollution and undertake a rational program of air pollution control.

Acknowledgment

The author gratefully acknowledges the advice provided by Louis M. Falkson, Kenneth G. Johnson, and Walter R. Lynn throughout this study.

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Received for review February 28, 1969. Accepted February 25, 1970. Research supported in part by NIH Training Grant (1 T01 ES 00130-01) from the Division of Environmental Health Sciences and the Center for Environmental Quality Management, Cornell University. Presented at the 96th Annual Meeting of the American Public Health Association, Detroit, Michigan, November 1968.

Strontium-90, Strontium-89, Plutonium-239, and Plutonium-238 Concentrations in Ground-Level Air, 1964–1969

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■ Data are presented on monthly concentrations of strontium-90, strontium-89, plutonium-239, and plutonium-238 in ground-level airborne particulates collected in Winchester, Mass., from October 1963 (for radionuclides of strontium) and May 1965 (for radionuclides of plutonium) to March 1969. The ratio of the activities of strontium-89 to strontium-90 in these samples indicates an influx of strontium-90 following all but the sixth Chinese atmospheric detonation. In 1968, approximately 60% of the strontium-90 present in ground-level air was of post-1963 origin. The ratio of the activities of plutonium-239 to strontium-90 prior to February 1968 was 0.017 ± 0.009. There was a gradual increase in the above ratio later in 1968 which is attributed to debris from the sixth, seventh, and eighth Chinese tests. Levels of plutonium-238 in SNAP-9A debris in ground-level air during 1968 were 80% to 50% lower than had been predicted.

The radionuclides strontium-90, strontium-89, plutonium-239, and plutonium-238 are present in the atmosphere as the result of nuclear weapons tests. In the case of plutonium-238, in addition to the above source, Harley (1964) reported that an injection of this radionculide into the atmosphere took place in April 1964 when 17 kilocuries of plutonium-238, contained in a SNAP-9A power source, burned up south of the equator off the coast of Africa. Information on airborne strontium and plutonium isotopes is of interest in evaluating the potential health hazards of these materials and in investigating the transport processes involved. Analysis of ground-level airborne particulate samples for the radionuclides of strontium has been performed at the Northeastern Radiological Health Laboratory (NERHL) since October 1963. For the plutonium isotopes, radiochemical and alpha spectroscopic analysis has been performed since May 1965. These isotopes include plutonium-239, plutonium-240, and plutonium-238. The energies of the alpha particles from plutonium-239 and plutonium-240 are not sufficiently different to be separated by alpha spectroscopy. Therefore, when plutonium-239 is referred to, it is meant to represent the sum of the activities of plutonium-239 and plutonium-240.

Results of these analyses to April 1966 (for strontium-90) and to February 1967 (for the plutonium isotopes) have been previously reported (Magno, *et al.*, 1967; Shleien and Magno, 1967). Extensive measurements of these radionuclides in air particulates and precipitation have been performed by the Health and Safety Laboratory (HASL) of the Atomic Energy Commission for several years (Volchok, 1969). In addition, the Joint Nuclear Research Center, ISPRA Establishment, Italy, has published data on SNAP-9A plutonium-238 (DeBortoli and Gaglione, 1969).

This paper presents results on ground-level airborne concentrations of the above radionuclides from the inception of the sampling and analysis program at NERHL to March 1969. Shleien (1969), in recent assessment of doses from these radionuclides based on the concentrations presented in this paper, indicates that only an infinitesimal portion of the total strontium-90 dose to bone is due to inhalation of airborne material. On the other hand, the dose from plutonium-239 to the tracheobronchial lymph nodes was reported to be 160 millirem in 50 years, second in magnitude only to the dose from strontium-90 (from ingestion) to the bone. According to the same investigator, the dose from plutonium-238 to this lymphatic tissue was about one-quarter of that from plutonium-239. In this publication, attention will be given to the origin of these radionuclides and to the contribution of various atmospheric nuclear tests and the burnup of the SNAP-9A satellite to the total quantity of the radionuclides present in ground-level air. A summary of reported atmospheric detonations which occurred during the period of this study is given in Table I.

Methodology

Monthly composite particulate samples, representing 12,000 m.^{3} of air, are collected on 8 × 10-inch membrane filters (pore size, 0.8 micron) at a height of 1 m. above the ground. The samples are wet ashed with a mixture of nitric and perchloric acids. The sample is split into two parts for radiochemical analysis.

One-half the sample is analyzed for strontium-90 and strontium-89 as follows (U.S. Dept. HEW, 1967): Strontium carrier is added and the strontium is precipitated from the samples first as the carbonate then as the nitrate. Further purification is made by barium chromate precipitation and hydroxide scavenging. After an ingrowth period, yttrium carrier is added and the yttrium is extracted into TTA (2-thenolytrifluoroacetate) at pH 5.0. The yttrium is stripped from the TTA with dilute nitric acid, precipitated as the oxalate and beta counted for yttrium-90. The strontium is precipitated as the carbonate and beta counted for total radiostrontium. The strontium-89 activity is calculated from the total radiostrontium measurement after correction for the strontium-90 content.

Analysis of the other half of the sample for the plutonium isotopes is briefly described below (U.S. Dept. HEW, 1967): Plutonium-236 tracer is added, the plutonium reduced to the +3 state and coprecipitated with lanthanum fluoride. The lanthanum fluoride is converted to lanthanum hydroxide, dissolved in 7.2 *M* nitric acid and the plutonium oxidized to the +4 state. The solution is passed over an anion exchange resin in the nitrate form. The resin is washed with additional nitric acid and then with 9 *M* hydrochloric acid. The plutonium is then eluted from the resin with a mixture of 0.36 *M* hydrochloric acid and 0.01 *M* hydrofluoric acid, electroplated onto a stainless steel planchet from a sulfuric acid–ammonium sulfate electrolyte. The 5.15 MeV alpha particle of plutonium-239 and the 5.48 MeV alpha particle of plutonium-238 are counted with a silicon surface barrier detector linked to a multichannel analyzer. With the sample electroplated onto a 3.1 $cm.^2$ area, the counting efficiency is ~31% and the resolution 75 KeV (width at half-peak height).

The minimum detectable concentrations are 0.10, 0.40, and 0.003 $fCi/m.^3$ for strontium-90, strontium-89, and the plutonium isotopes, respectively. The strontium-90 represented by the 2σ counting error did not exceed 25% of the corresponding sample value and was approximately 10% in the majority of cases. The corresponding values for strontium-89 are about twice as high. The maximum 2σ counting errors are 50% and 67% of the reported values for plutonium-239 and plutonium-238, respectively, but are appreciably lower as the results increase above the minimum detectable levels.

Results and Discussions

The results of strontium-90 analyses of ground-level airborne particulates from monthly composite samples are presented in Figure 1. Difficulties in sampling and analysis caused the loss of two samples (October 1963 and August 1967), and during a change-over in personnel responsible for collection and analysis of the data, several months of ambiguous data (September, October, November, and December 1967) occurred. Figure 1 illustrates the expected spring maximum which occurs each year and which appears to be extremely reproducible in terms of time of appearance. A line (solid) indicating the expected spring maximum highs, based on the

Table I. Reported Atmospheric Detonations

Date	Source	Comments
October 16, 1964	Chinese (1st)	Low[a]
May 14, 1965	Chinese (2nd)	Low
May 9, 1966	Chinese (3rd)	Intermediate[b]
July 2, 1966	French	70–80 KT
July 19, 1966	French	120 KT
September 24, 1966	French	150 KT
October 4, 1966	French	Intermediate[b]
October 27, 1966	Chinese (4th)	Low-intermediate[c]
December 28, 1966	Chinese (5th)	Few hundred KT
June 5, 1967	French	Low
June 17, 1967	Chinese (6th)	2 MT
June 27, 1967	French	Low
July 3, 1967	French	Low
December 24, 1967	Chinese (7th)	MT range
July 7, 1968	French	Low
July 15, 1968	French	Low
August 3, 1968	French	Low
August 24, 1968	French	2 MT
September 9, 1968	French	2 MT
December 28, 1968	Chinese (8th)	2 MT

[a] Less than 20 KT.
[b] 200-300 KT.
[c] 20-200 KT.

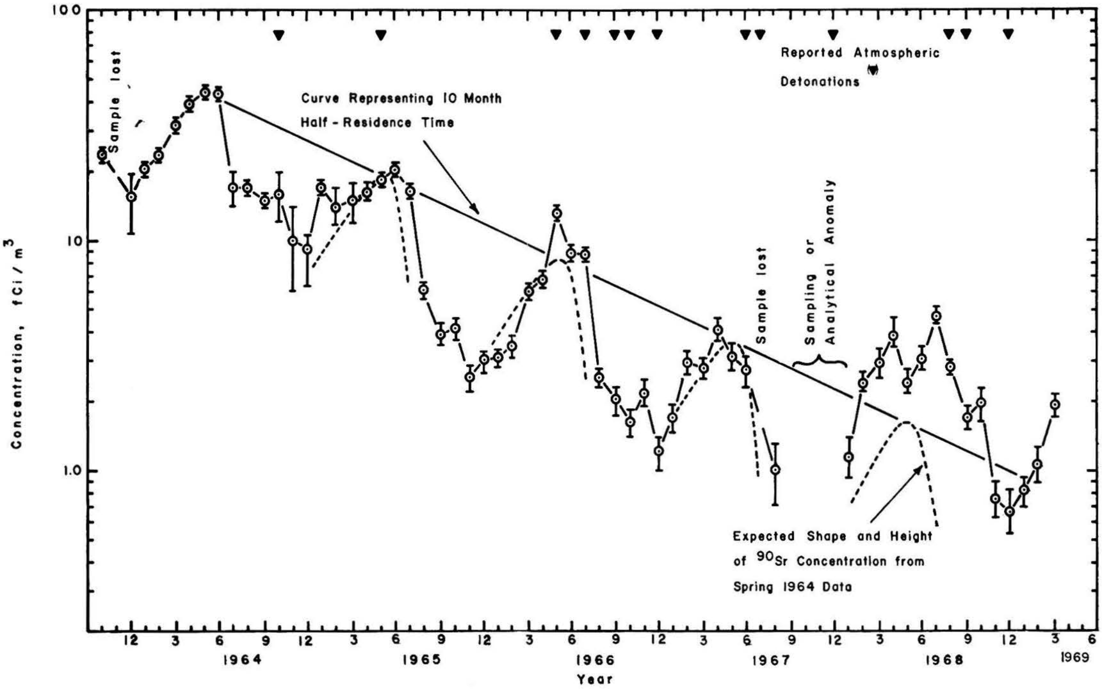

Figure 1. Strontium-90 in ground-level air

strontium-90 concentrations in the spring of 1964 and a stratospheric residence half-time of 10 months (Telegadas, 1969), is shown. The expected strontium-90 curve (dashed), having the shape of the 1964 curve because no fresh intrusion of material occurred until the end of that year, is also shown. The difference in the expected and actual curves indicates strontium-90 of post-1963 origin was present.

A double peak in strontium-90 levels appears in 1968. Although not apparent from this study, Thomas (1969) has noted the presence of fresh fission products during August 1968 and attributes the rise in radioactivity to the rapid movement of debris from the French tests in July 1968. Strontium-90 levels in the latter part of 1968 would be elevated if such an intrusion occurred. Another possibility is an influx of strontium-90 of stratospheric origin, although this is not apparent from the strontium-89 to strontium-90 ratios discussed later.

Strontium-89 concentrations are shown in Table II. Strontium-89 values are indicated only in months where the levels of this radionuclide were above the minimum detectable level. All the appearances of stronium-89 followed Chinese atmospheric tests. This fact, together with the information that, except in the case noted above, the French tests were not measurable at 10° N latitude (Hardy, 1968), appears to make the Chinese detonations the principal source of increases above the expected strontium-90 levels.

The contribution of strontium-90 from a particular test may be estimated from the strontium-89 to strontium-90 ratio. These estimates are also presented in Table II. The theoretical ratios are based on production yield of strontium-90 and strontium-89 from uranium-235 fission (Weaver, *et al.*, 1963) and are corrected for decay time between the nuclear test and the time of collection. In most cases, the contribution of strontium-90 in ground-level air from a recent nuclear test, based on the strontium-89 ratios, appears to be of tropospheric origin. However, the strontium-89 to strontium-90 ratio following the fifth Chinese test appears to be influenced by the presence of strontium-89 of stratospheric origin beginning in March of 1967, as evidenced by the initial decrease and subsequent increase in the strontium-89 to strontium-90 ratio.

Early low yield tests contributed only small amounts to ground-level strontium-90 concentrations. The fifth Chinese test (December 27, 1966) appears to have contributed a substantial quantity of strontium-90. There was no evidence of a fresh strontium-90 intrusion following the sixth Chinese test (June 17, 1967), although complete data are not available.

Table II. Strontium-89 Concentrations and Contribution of Fresh Strontium-90 from Atmospheric Tests

Test and date	Sample collected (month and year)	^{89}Sr concentration (fCi/m.^{3})	Time elapsed since test (days)	Ratio ^{89}Sr to ^{90}Sr		^{90}Sr from test (%)
				Theoretical	Measured	
Chinese, #1 (Oct. 16, 1964)	Nov. 1964	10 ± 3[a]	30	111	1.6	1.5
	Dec.	ND[b]	60	74	ND[b]	...
	Jan. 1965	16 ± 3	91	49	0.8	1.6
Chinese, #2 (May 14, 1965)	June 1965	57.9 ± 2.7	30	111	2.9	2.6
	July	28.2 ± 2.6	60	74	1.7	2.3
	Aug.	2.4 ± 1.1	90	39	0.3	0.8
	Sept.	1.5 ± 1.2	120	33	0.4	1.2
Chinese, #3 (May 9, 1966)	June 1966	13.1 ± 2.8	37	100	1.8	1.8
	July	10.4 ± 1.7	67	67	2.2	3.3
	Aug.	4.3 ± 0.8	108	38	1.7	4.5
	Sept.	1.8 ± 0.7	139	25	0.9	3.6
Chinese, #4 (Oct. 27, 1966)	Nov. 1966	18.7 ± 1.7	19	129	8.5	6.6
	Dec.	6.5 ± 0.8	49	86	5.3	6.2
Chinese, #5 (Dec. 27, 1966)	Jan. 1967	11.9 ± 1.2	19	129	7.0	5.4
	Feb.	15.5 ± 1.1	49	86	5.3	6.2
	March	27.4 ± 1.6	81	55	9.9	18
	April	34.7 ± 1.6	112	36	8.5	23
	May	14.0 ± 1.8	142	24	4.5	19
	June	5.3 ± 0.9	173	16	2.0	13
Chinese, #6 (June 17, 1967)	No evidence of ^{89}Sr in Aug. or Sept. 1967. July sample lost and Sept. through Dec. sampling or analytical ambiguities occurred					
Chinese, #7 (Dec. 24, 1967)	Jan. 1968	6.5 ± 0.6	22	124	5.8	4.7
	Feb.	18.3 ± 1.1	53	81	7.2	11
	March	14.8 ± 1.1	81	55	5.1	9.3
	April	13.1 ± 1.1	111	36	3.4	9.5
	May	3.1 ± 0.7	141	24	1.3	5.5
	June	2.9 ± 0.7	172	16	0.9	5.6
Chinese, #8 (Dec. 28, 1968)	Feb. 1969	2.3 ± 0.5	48	87	2.2	2.5

[a] 2σ counting error.
[b] ND: Not determined.

For the two months following this test, for which results were available, there was no indication of elevated strontium-89 levels. Data from HASL also indicate the absence of strontium-89 from this test (Hardy, 1968). Peirson and Sisefsky (1969) have suggested that this device exploded at a comparatively low altitude (14 km.), but that the bulk of the debris was carried to a high altitude by the rising fireball.

From the differences in projected and actual levels of strontium-90, an estimate of the strontium-90 from atmospheric testing after 1963 can be made. Table III presents the mean predicted (based on a 10-month residence half-time and the mean 1964 results) and measured strontium-90 concentrations in ground-level air. Because of the magnitude of errors in analyses, only the values for 1968 are truly significant, although there are indications of newly injected strontium-90 since 1965. In 1968, 62% of the total ground-level strontium-90 was due to post-1963 tests. Volchok (1969) estimates that 71% of the total reservoir of strontium-90 in 1968 could be attributed to post-1963 debris.

Concentrations of plutonium-239 in ground-level air particulates are presented in Figure 2. The pattern of minimums and maximums is similar to that for strontium-90. The same limitations (sample loss and ambiguity) hold as for the strontium-90 data. The average ratio of the activities of plutonium-239 to strontium-90 for the period May 1965 through February 1968 was 0.017 with a 2σ range of ±0.009. There is a gradual rise in this ratio following this period, the average value being 0.028 from March 1968 to March 1969. This increase in the plutonium-239 to strontium-90 ratio is attributed to the sixth, seventh, and eighth Chinese tests, which were reported to be high yield events.

The ratio of plutonium-238 to plutonium-239 remained relatively constant at 0.04 ± 0.02 from May 1965 to July 1966. A change in the ratio was fairly evident at NERHL in mid-

Table III. Estimated Contribution of Post-1963 Tests to ^{90}Sr

Year	Mean ^{90}Sr (fCi/m.^{3}) Predicted	Mean ^{90}Sr (fCi/m.^{3}) Measured	Estimated contribution post-1963 tests (%)
1964	24.1[a]	24.1	...
1965	10.5	11.3	7
1966	4.6	4.6	...
1967	2.0	2.3[b]	15
1968	0.9	2.4	62

[a] Predicted value based on measured results for 1964.
[b] No data for July, October, November, and December.

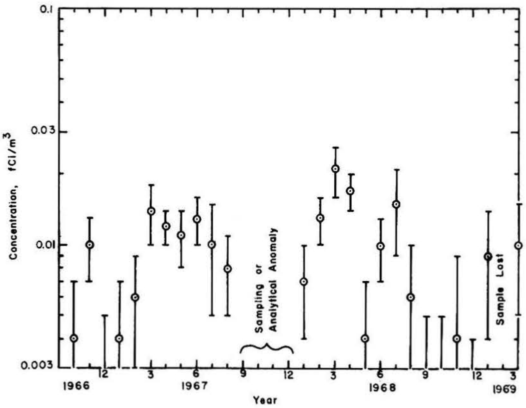

Figure 3. Estimated SNAP-9A plutonium-238 in ground-level air

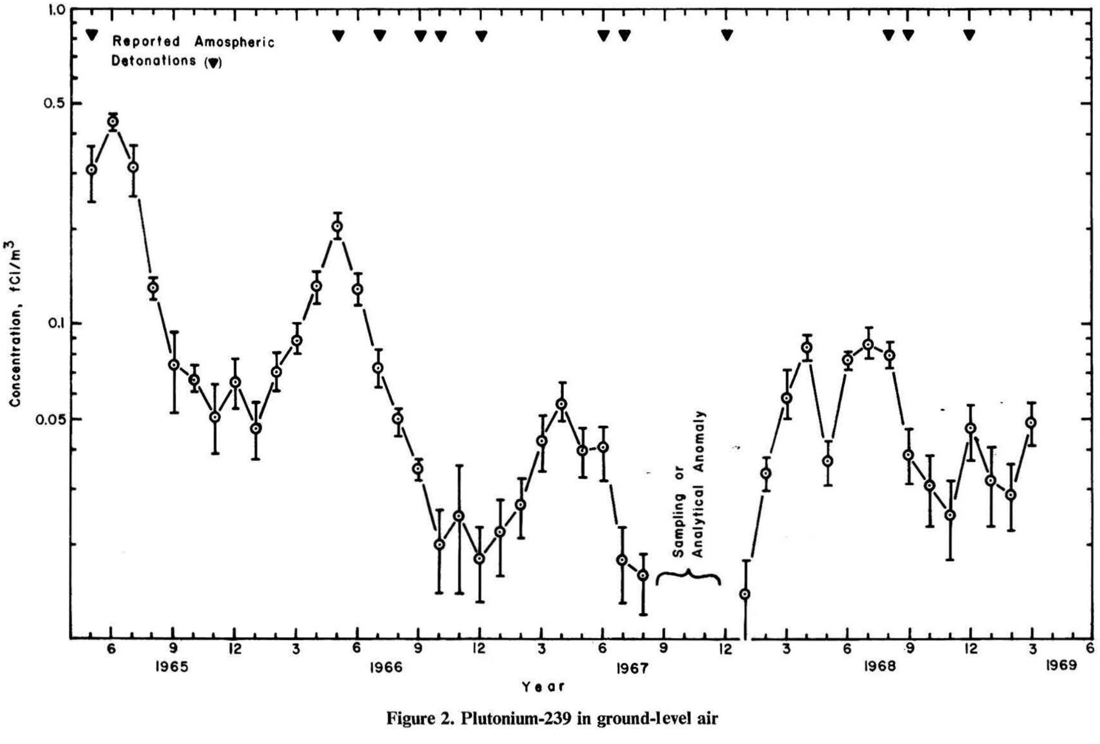

Figure 2. Plutonium-239 in ground-level air

Table IV. SNAP-9A Plutonium in Ground-Level Air (fCi/m.^{3})

Date	Predicted	ISPRA	NERHL
Jan. 1966	0.011	0.001	. . .
July 1966	0.013	0.003	. . .
Jan. 1967	0.015	0.005	0.004
July 1967	0.016	0.015	0.011
Jan. 1968	0.017	0.012	0.014
July 1968	0.018	. . .	0.010

1966 (Shleien and Magno, 1967). This change in ratio indicated a new source of plutonium-238 other than that which was previously present. DeBortoli and Gaglione (1969) announced this change in plutonium-238 to plutonium-239 ratio somewhat earlier in June and July of 1966, the conclusion being that SNAP-9A plutonium-238 had reached ground level in the northern hemisphere.

Figure 3 is a plot of the SNAP-9A plutonium-238 concentrations in ground-level air based on the above ratio of plutonium isotopes prior to influx of the satellite debris. The levels of SNAP-9A plutonium-238 are slightly elevated over the 1967 levels. This elevation is expected, based on prior predictions (Volchok, 1966) of increasing plutonium-238 levels in 1968. These predictions anticipated that plutonium-238 from SNAP-9A would behave similarly to rhodium-102 and cadmium-109 which were used as tracers in high altitude nuclear tests in 1958 and 1962. A comparison of the predicted results, the reported results at ISPRA, and NERHL results is presented in Table IV. In 1968, the NERHL results (3-month averages) are 80% to 50% lower than the predictions.

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Received for review September 24, 1969. Accepted February 9, 1970.

COMMUNICATION

Automated Method for Determining and Removing Silica Interference in Determination of Soluble Phosphorus in Lake and Stream Waters

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■ Values obtained for soluble P in the low μg./l. range in lake and stream waters were found in some cases to be higher than total P values. This error is shown to be due to silica that gives an apparent P reaction with ammonium molybdate. This error is of importance when P is to be determined in the low μg./l. range. A method is presented to permit an automated simultaneous determination of soluble P and the silica interference so that a correction can be made.

In a recent project to define partially the water quality, weed growth, and nutrient content of streams flowing into Canal Lake, Ontario, it was necessary to establish AutoAnalyzer techniques to operate in the μg./l. range for soluble and total phosphorus, perhaps the principle nutrient involved in the eutrophication process (Campbell and Webber, 1969). Soluble P, the fraction that reacts with ammonium molybdate without hydrolysis, is the most frequently determined parameter in water analysis. In developing these techniques, we became aware of a silica interference that appeared to give false soluble P values by the methods used. This interference was illustrated by lower total P than soluble P. Silica is dehydrated during the $HClO_4$ digestion for total P and thus does not interfere with the total P determination. Silica has always been considered a potential interference in P determinations involving the phospho-molybdate complex, but in most cases P is determined in the mg./l. range where Si does not give significant interference except at concentrations over about 100 mg./l. of SiO_2 (Standard Methods, 1965).

The amount of silica in groundwater is controlled by the minerals in contact with the water and should range from about 6 mg./l. in equilibrium with quartz to about 140 mg./l. in equilibrium with amorphous silica (Polzer, 1967). For example, values of 1 to 45 mg./l. of silica have been reported in various lakes and streams in Oregon (Miller and Tash, 1967). Concentrations of silica in this range are sufficient to cause errors in P determinations in the low μg./l. range.

In a manual method of P determination, silica interference has been removed by an extraction into organic solvents at acidity levels that prevent the formation and extraction of the silico-molybdate complex (Sugawara and Kanamori, 1961). Our attempts to automate this procedure were not completely successful. The alternative was to apply a correction to the soluble P values obtained to remove the silica interference. This report describes a method whereby the silica interference is determined and used for correction of soluble P values.

Experimental

Standard units of the AutoAnalyzer system (Technicon Corp., Chauncey, N.Y.) were arranged as illustrated in the flow diagram (Figure 1). If two colorimeters and recorders are not available, single manifolds can be constructed and silica and P run separately rather than combined as illustrated.

A sampling rate of 20 per hour at a 1:1 sample to wash ratio was used. Standards were run about every 40 samples, although baseline drift was negligible.

Silica analyses were conducted using a modification of a method used for monitoring silica in power plant boilers (Rudnik, 1966). Phospho-molybdate and silico-molybdate complexes are formed when the sample is mixed with ammonium molybdate (20 g. per liter) and then acidified with 0.2 N H_2SO_4. The phospho-molybdate complex is completely destroyed with oxalic acid (50 g. per liter) (Standard Methods, 1965). The silico-molybdate complex is reduced with ascorbic acid (20 g. per liter) and the resulting blue color is read at 815 mμ.

One difficulty encountered was in obtaining silica-free water. Glass-distilled water tended to vary in silica content from day to day. This was overcome by using a double ion-exchange column (Illco-Way Ion X Changer, Research Model, Illinois Water Treatment Co., Rockford, Ill.).

The apparent soluble P value which includes the silica interference is obtained with a procedure modified from an automated procedure previously used for soil analysis (Colwell, 1965) and plant analysis (Thomas, Sheard, *et al.*, 1967). It involves the formation of a complex with acidified ammonium molybdate [20 g. $(NH_4)_2MoO_4$ + 225 ml. H_2SO_4 per liter] which is reduced with ascorbic acid (10 g. per liter) to a blue color read at 815 mμ. The modifications used were a 50-mm. flow cell colorimeter instead of a 15-mm. flow cell colorimeter, a 2X range expander, and changes in sizes of pump tubes. These modifications were necessary to reach the low μg./l. range required for the soluble P analysis.

Total P was determined after the samples had been digested with $HClO_4$. Fifty-milliliter samples of water and 2.0 ml. of $HClO_4$ were heated in beakers on a hot plate until the dense white fumes of $HClO_4$ were observed. Then, each beaker was covered with a watch glass and allowed to reflux for 30 min. The $HClO_4$ solution was then diluted to 50 ml. for analysis using the same manifold and technique as for soluble P. Silica did not interfere in the total P determination since it was dehydrated during the $HClO_4$ digestion. The digestion with $HClO_4$ should be carried out in a special stainless steel fume-hood equipped with a water washing device to avoid the dangers inherent in a $HClO_4$ digestion.

Results and Discussion

The relationship between various amounts of silica as determined by the silica analysis and the response of the same solutions in the phosphorus analysis is illustrated in Figure 2. There is a direct relationship between the amount of silica in a solution and the amount of color produced in the P analysis. Thus, this apparent P content which is actually due to silica can be used as a correction. The reverse situation where phosphorus standards were run through both methods yielded normal P results, but the recorder did not deviate from the baseline on the silica analysis. This shows that the oxalic acid in the silica analysis is effectively breaking all of the phospho-molybdate complex present.

By use of the relationship described, corrections in the soluble P analysis were made as follows. All solutions were analyzed for silica and apparent soluble P. An apparent P concen-

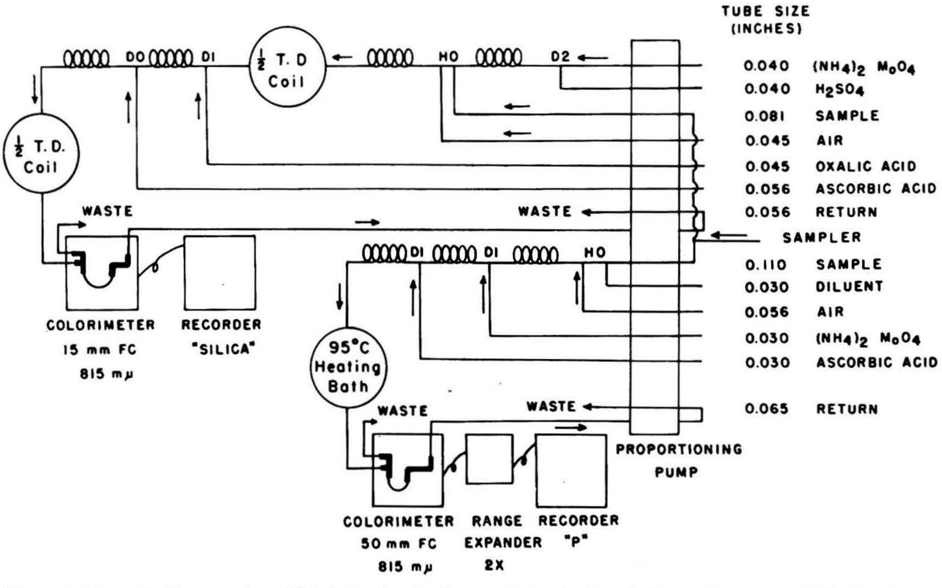

Figure 1. Schematic diagram of manifold design for simultaneous determination of silica and apparent soluble phosphorus

Table I. Analysis of a Series of Water Samples Removed from Canal Lake, July 30, 1968

Location[a]	Sample no.	Si (p.p.m.)	Apparent sol P (p.p.b.)	Sol P correction (p.p.b.)	Corrected sol P (p.p.b.)	Total P (p.p.b.)
L.S.-V (6 ft.)	199	1.34	27	21	6	69.5
L.S.-V (3 ft.)	200	1.48	28	23	5	29.0
L.S.-III (6 ft.)	201	0.70	20	11	9	51
L.S.-III (3 ft.)	202	0.96	21	15	6	23.5
L.S.-IV (3 ft.)	203	0.99	22.5	15.5	7	37
L.S.-II (6 ft.)	204	0.60	27	9	18	57.5
L.S.-II (3 ft.)	205	0.59	38	9	29	69
L.S.-I (6 ft.)	206	0.39	22	6	16	64
L.S.-I (3 ft.)	207	0.35	16.5	5.5	11	32.5
1	208	0.34	14	5	9	27
5	209	0.63	10.5	10	tr	20
4	210	2.64	41.5	41.5	0	15
6	211	0.69	14	11	3	20
7	212	1.26	22	20	2	24
8	213	0.84	13	13	0	19.5
10	214	1.34	30	21	9	21.5
11	215	1.23	26.5	19.5	7	18.5
2	216	1.86	36	29	7	39.5

[a] These refer to various lake and stream locations. Campbell (1969).

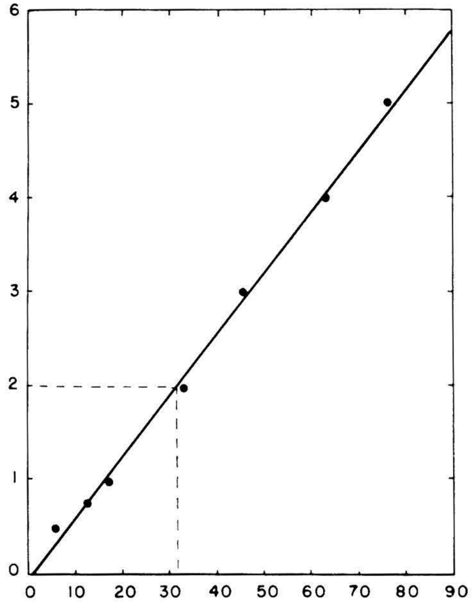

Figure 2. Relationship of silica concentration and apparent phosphorus concentration due to silica

tration that is actually due to silica was determined from the graph illustrated in Figure 2. This apparent P due to silica was then subtracted from the apparent soluble P determination to give a corrected soluble P value. Analytical results using this procedure on 18 water samples taken from Canal Lake on July 30, 1968, are presented in Table I. If only the apparent soluble P and total P had been determined, then anomalies are evident in samples 210, 214, and 215. In these cases the soluble P appears higher than the total P. This is due to the removal of the silica through dehydration during the digestion for total P. Fine granules of silica were visible in all digestion flasks indicating that this had actually occurred. In all cases, the corrected soluble P values have a better relationship to the total P than do the apparent soluble P values.

In studies of streams and lakes, where P determinations are frequently made in the low μg./l. range, it has not been the practice to consider the potential interference from dissolved silica. The results presented here illustrate that there is sufficient dissolved silica present to interfere with low-level P determinations. The methods outlined are suggested as a means of considering silica interference and making corrections for it.

Acknowledgment

The authors appreciate financial assistance for this study from the Department of Energy, Mines, and Resources of Canada, and the Ontario Department of Agriculture and Food.

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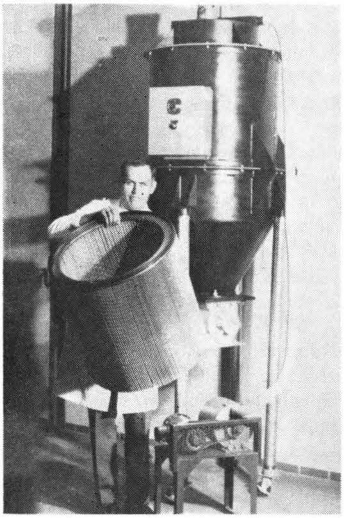

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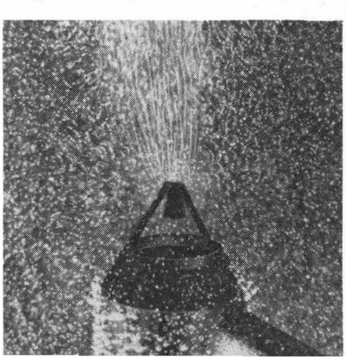

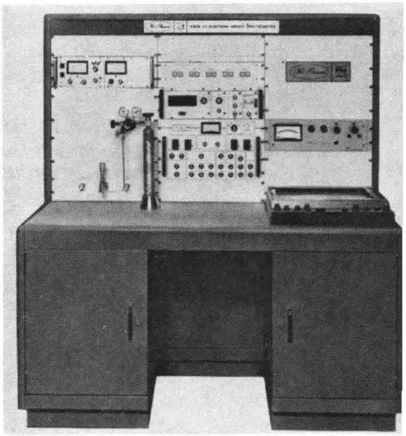

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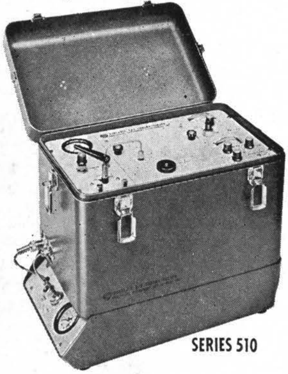

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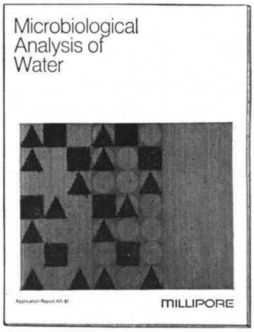

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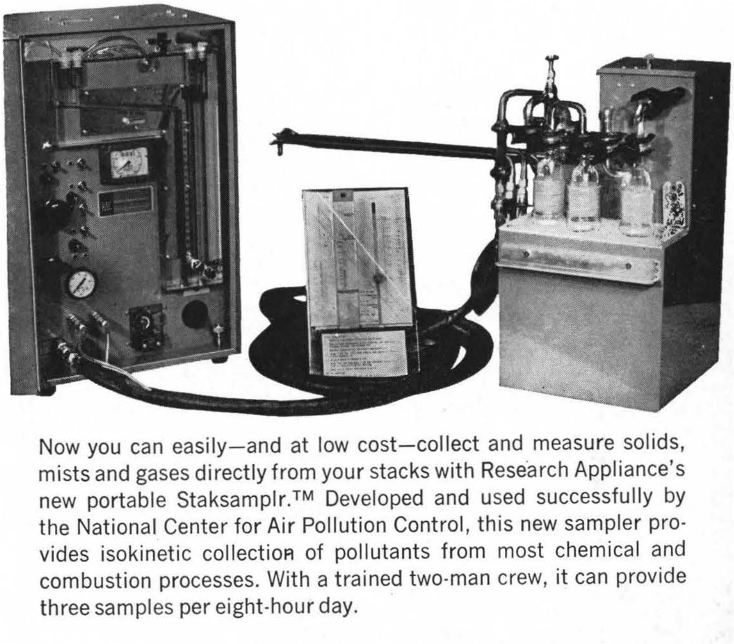

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Waste Conversion for Profits. Proceedings of a conference. v + 105 pages. The Chemurgic Council, 350 Fifth Ave., New York, N.Y. 10001. 1970. $5.50, paper.

This collection of papers presented at the Chemurgic Council's October 1969 meeting emphasizes waste utilization and waste treatment developments in the U.S. food growing and food processing industries. ■

The Environmental Crisis. Edited by Harold W. Helfrich, Jr. x + 187 pages. Yale University Press, 92A Yale Station, New Haven, Conn. 06520. 1970. $7.50, hard cover; $1.95, paper.

A series of lectures originally delivered at Yale University School of Forestry by well-known speakers, among them ecologist LaMont C. Cole, population biologist Paul R. Ehrlich, and Connecticut Congressman Emilio Q. Daddario. ■

Water Quality Improvement by Physical and Chemical Processes. Edited by Ernest F. Gloyna and W. Wesley Eckenfelder, Jr. University of Texas Press, Box 7819, Austin, Tex. 78712. 1970. $15.00, hard cover.

This is the third in a series of water resources symposia. The book contains 4 sections, covering water quality requirements for reuse, designs for solids removal, chemical treatment of liquid wastes, and aspects of sludge handling. Both American and European practices are included. ■

Impact of Air Pollution Regulations on Fuel Selection for Federal Facilities. Report of the Federal Construction Council. viii + 52 pages. Pub. No. 1762, National Academy of Sciences, 2101 Constitution Ave., N.W., Washington, D.C. 20418. 1970. $2.95, paper.

The report was published primarily to assist federal agencies select the most desirable type of fuel to burn in steam power and central heating plants. The availability, quality, and price of coal, oil, and gas are detailed by geographical region in the report. ■

Chemical Ecology. Edited by Ernest Sondheimer and John B. Simeone. 306 pages. Academic Press, 111 Fifth Ave., New York, N.Y. 10003. 1970. $16.50, hard cover.

The book is concerned with the new subject of chemical ecology, based on the application of chemistry and biochemistry to ecological problems. Aspects of the relationships between plants, insects, and fish and their surroundings cover 11 chapters. ■

Inhalation Carcinogenesis. Proceedings of a symposium. xii + 524 pages. Pub. CONF-691001, Clearinghouse for Federal Scientific and Technical Information, Springfield, Va. 22151. 1970. $3.00, paper.

Proceedings of a 1969 conference cosponsored by the U.S. Atomic Energy Commission and the National Cancer Institute. Information presented at the conference (and which is in the book) documents positive correlations between the increased incidence of lung cancer in humans and many common air pollutants. Much of the conference was concerned with the design of inhalation studies. ■

Water Quality Behavior in Reservoirs. Compiled by James M. Symons. xii + 616 pages. PHS Pub. No. 1930, Public Health Service, Cincinnati, O. 45213. 1970. $3.25, paper.

The book contains papers prepared during the course of a PHS project, undertaken in 1962, to discover the effects of impoundments and controlled release on the quality of reservoir water. There is a lengthy literature review and a statement of research needs. ■

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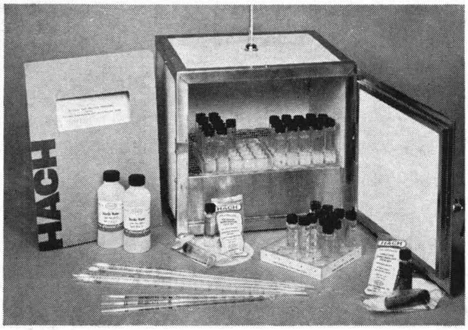

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1. Capital costs are approximately 16 per cent less for secondary levels of BOD removal and 40 per cent less for tertiary treatment.
2. Capability to remove 90 to 95 per cent of organic pollutants including pesticides, phenols, dyes, polyols, TNT and other organics.
3. Land requirements are 85 per cent less.

"Lower land and capital costs mean that we can build more clarification/adsorption sewage treatment plants for the same amount of money. In effect, we can build almost 12 Calgon process plants for every 10 conventional secondary biological plants," Mr. Welton said.

Calgon says an even more important factor is that its process can provide consistent 90 to 95 per cent removal of BOD and suspended solids by simple operating changes such as more frequent reactivation of the granular carbon as compared with irregular removals of 90 per cent at best in biological plants.

"This means," Mr. Welton said, "that when consistent 90 per cent or higher removal of organic pollutants is mandated, a biological plant will have to be supplemented with a process such as granular carbon adsorption at additional capital and operating costs. It appears more logical for financially hard-pressed communities to accomplish this objective in one step and at a single lower cost with clarification/adsorption treatment than in two steps, i.e. secondary biological plus adsorption later and at considerably higher costs."

Calgon says, too, that unlike a biological plant, its process is unaffected by toxic chemicals or by sudden changes in pH resulting from shock loads of acids or alkalies.

"In a biological system, pesticides, herbicides, some phenols and other toxic organics kill the microorganisms with the result that the toxic materials and some of the sewage organics pass through the plant virtually untreated," Mr. Welton said. "And since a biological plant has a high sensitivity to changes in pH, strong acids or alkalies can reduce its effectiveness."

He said this cannot happen in a clarification/adsorption plant.

"Since carbon adsorption is a physical phenomenon rather than biological, a carbon system is unaffected by sudden changes in pH and by toxic wastes. This safety factor is inherent in this patented process," he said.

Calgon says, too, that phosphate removal can be accomplished in its process with the use of precipitating chemicals such as lime or metal salts in the clarification step.

An additional advantage is that the new process reduces the sludge handling problem associated with a secondary biological treatment plant. Unlike a biological system in which microorganisms are constantly dying and producing solids, a carbon system adsorbs the organic materials in the pores of the carbon granules. These organics are then burned off at high temperatures when the carbon is thermally reactivated and purified for reuse.

Calgon also says that its system is esthetically acceptable since the odor problems associated with biological systems are nonexistent as a result of the elimination of secondary sludge. This makes possible the location of clarification/adsorption plants in urban areas.

Inventors of the process are Donald G. Hager, marketing coordinator for environmental products and services in the Water Management Division, and Ronald S. Joyce, research supervisor in the Pittsburgh Activated Carbon Division.

U. S. Patent 3,455,820 summarizes the process in these words:

"The present invention comprises treating raw sewage with a flocculant to cause separation of solids from the liquid, separating the effluent from the flocculated solids, passing the effluent through at least one bed of activated carbon, and periodically backwashing and regenerating the activated carbon."

The inventors state that granular carbon with a surface area of 300 to 1500 square meters per gram and a minimum mesh size of 50 is preferred. A carbon granule of mesh size 50 is comparable in size to the new freeze-dried coffee grains. One pound of this size granule, because of its intricate pore structure, has a surface area of 125 acres. Surface area is a significant factor because adsorption is a surface phenomenon in which molecules of organic materials adhere to the carbon.

Commenting on the process, Hager said regeneration or reactivation of the granular carbon is a key factor since reactivation in high temperature furnaces purifies the carbon for repeated reuse. Carbon losses in such a system average approximately five per cent for each reactivation cycle, he said.

The patent further states that either organic or inorganic flocculants can be used in the clarification step and that solids content of the clarified sewage must be reduced below 100 ppm to assure efficient operation of the granular carbon.

Further information on the Calgon process can be obtained by contacting Mr. Welton at Calgon Center, P. O. Box 1346, Pittsburgh, Pa. 15230. Telephone (412) 923-2345.

Calgon Corporation is a subsidiary of Merck & Co., Inc., the pharmaceutical-chemical manufacturer located in Rahway, New Jersey.

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meeting guide

July 8-10
American Society of Civil Engineers, and University of Massachusetts
National Specialty Conference on Disinfection
University of Massachusetts, Amherst

Technical sessions and papers to be presented will cover such topics as water disinfection (including sewage and industrial wastes, combined sewage overflow, sludge, and recreational waters),effect of waste water disinfection on natural streams, and air disinfection.

July 8-10
University of Colorado, and others
1970 Western Resources Conference
University of Denver

Conference theme will be "Urban Demands on Natural Resources." Speakers will discuss the effect of urbanization on the use and development of natural resources under 5 topics: Air, Water, Raw Materials, Land, and Choices. For details contact: J. J. Schantz, Jr., Denver Research Institute, University Park, Denver, Colo. 80210

July 21-23
Conference of State Sanitary Engineers, Water Pollution Control Federation, and others
National Symposium on Data and Instrumentation for Water Quality Management
University of Wisconsin, Madison

The contribution that collection and use of data can make to bettering the environment is the central theme of the conference. Papers will cover such topics as basic data requirements to evaluate water pollution and quality control programs; and a systems approach to water quality data management. Six concurrent panels will discuss pertinent subjects, including effective approaches to water quality planning and data, operation, evaluation, and interpretation of water quality data, and remote collection, sampling, measurement, and handling of water quality data.

July 21-23
University of Rhode Island, and R.I. State Technical Services
3rd Annual Northeastern Regional Antipollution Conference
University of Rhode Island

Theme of conference is reclamation and reuse of polluted waters, air, and solid wastes. Invited speakers will explore new processing methods that will simultaneously return investment and get rid of wastes. For information: Dr. Calvin Poon, Sanitary Engineering Dept., Univ. of R.I., Kingston, R.I. 02881

July 22-24
Institute of Water Resources, University of Alaska
International Symposium on Water Pollution Control in Cold Climates
University of Alaska, College

The 3-day symposium will be devoted to papers on waste treatment and receiving stream studies in cold climates. For information: R. Sage Murphy, Institute of Water Resources, University of Alaska, College, Alaska 99701

July 26-August 1
International Association on Water Pollution Research
5th International Water Pollution Research Conference
San Francisco

Technical sessions at this year's conference will include workshop/seminars and presentation of papers and discussion. In addition, air tours of California water projects will be available, as well as a film festival, and the international exhibits. The conference will reconvene in Hawaii from August 3–5.

August 19 and 20
Water Quality Research Council
Symposium on Water Pollution and Health
Sheraton Park Hotel, Washington, D.C.

All aspects of water supplies and contamination from the health standpoint will be covered. The conference is open to the public at large. More information: David X. Manners Co., 237 E. Rocks Rd., Norwalk, Conn. 06851

August 24-28
Engineering Foundation, and others
Application of Environmental R&D to Landfill Disposal for Solid Wastes
Deerfield Academy, Deerfield, Mass.

The conference will deal with landfill disposal of solid wastes, degradation of wastes in the landfill, improving efficiency of operations, site selection, ultimate use, and guidelines for sanitary landfills. Professor E. A. Glysson of the U. of Michigan will be conference chairman. Full details from: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017.

August 24-26
Oak Ridge Associated Universities
Conference on Energy and the Environment
Oak Ridge, Tenn.

Conference will deal with the implications for the urban environment and natural resources of various alternative approaches to meeting the nation's future energy requirements. For information: W. W. Grigorieff, Special Projects Office, ORAU, P.O. Box 117, Oak Ridge, Tenn. 37830

Courses

August 3-14
UCLA
Short Course on Remote Sensing of the Environment
UCLA

Course will provide attendees with information on the state of the art and potential benefits of remote sensing. Instrumentation, data use and interpretation will be described. Participants are invited to bring with them any remote sensing data they possess. Course fee: $450. More details: UCLA Extension, 10851 Le Conte Ave., Los Angeles, Calif. 90024

August 10-14
Ohio State University
Short Course on Air Pollution Engineering
Ohio State University, Columbus

Topics to be covered include sampling, plant site selection, atmospheric reactions, design and specfiication of control devices, and emission standards. Case studies and computation sessions will be arranged. Registration fee is $225. For details: T. L. Sweeney, Chemical Engineering Dept., Ohio State University, 140 W. 19th Ave., Columbus, Ohio 43210

August 17-21
UCLA
Short Course on Fundamentals of Pollutant Formation in Combustion Processes
UCLA

Course will deal with combustion thermodynamics and rate processes as applied to combustion in mobile or stationary sources. Modification of combustion conditions to minimize pollution and treatment of exhaust gases will also be discussed. Fee: $310. For details: UCLA Extension, 10851 Le Conte Ave., Los Angeles, Calif. 90024

September 22-25
University of California
Short Course on Management of Solid Waste for Optimum Environmental Control
University of California, Berkeley

Four-day course intended for those concerned with environmental problems will deal with social, cultural, economic, and technological factors governing generation of solid wastes and with practical problems involved in proper management. Registration fee is $200. For details: Continuing Education in Engineering, University Extension, University of California, 2223 Fulton St., Berkeley, Calif. 94720

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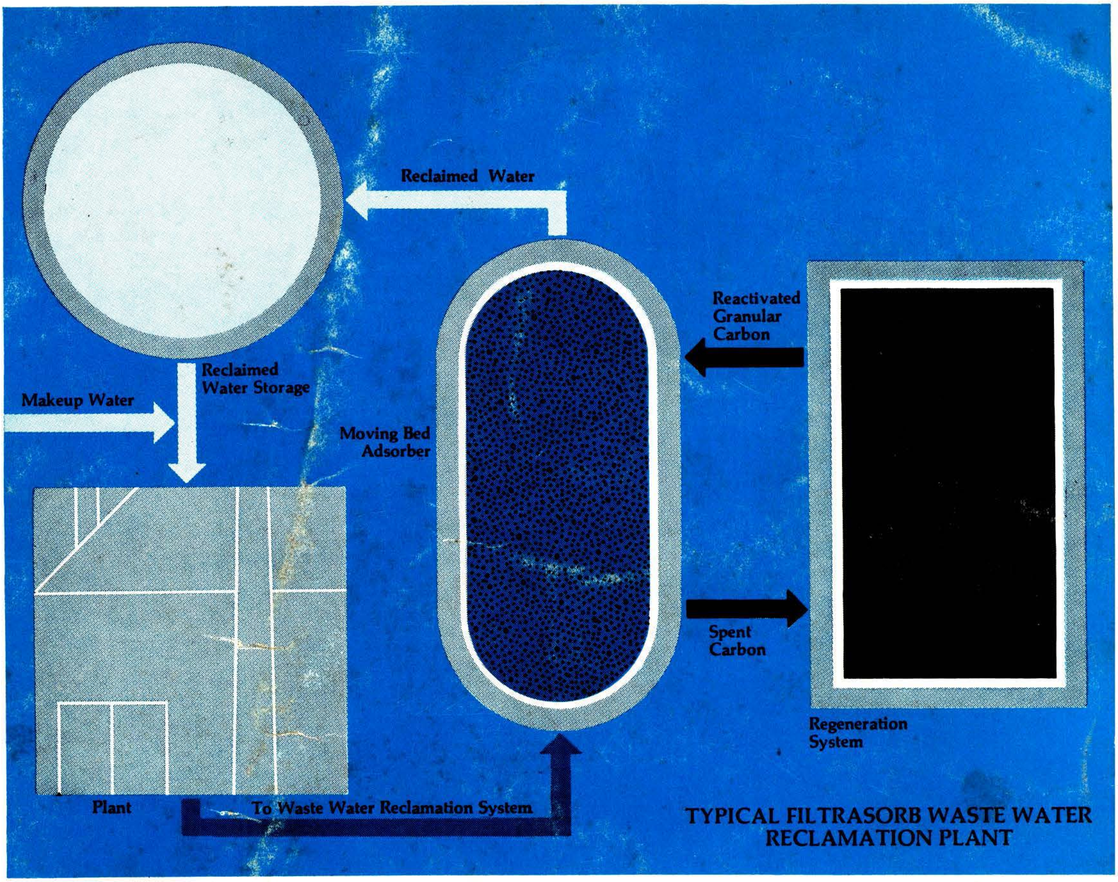

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