

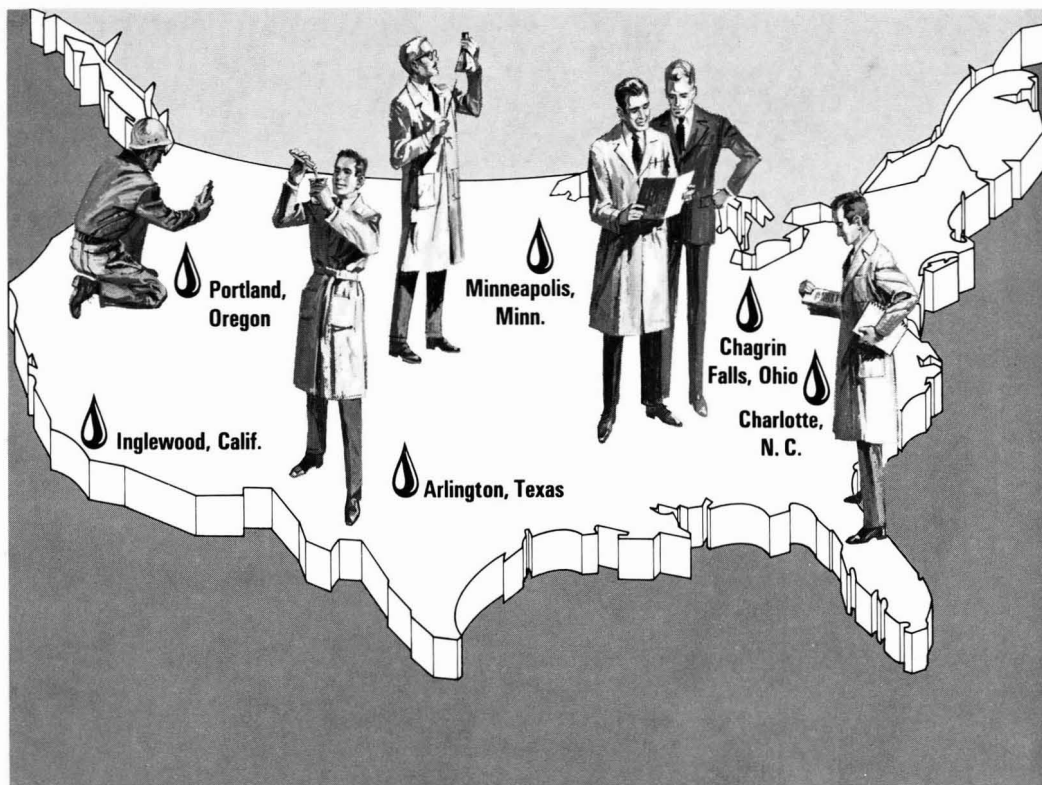
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Feature

- 412 Solid waste treatment technology
by Alex Hershaft, Grumman Aerospace Corp.

Outlook

- 400 Phosphate rock processor curbs fluoride emissions
402 Gulf agency a step ahead of the regional treatment game
404 Watchdogging U.S. environmental spending: the GAO at work
406 New approach to fund raising for public projects
408 Open dumps are giving way to sanitary landfills

Departments

- | | | | |
|---------------------------|-----|----------------------------------|-----|
| Letters | 388 | New literature | 462 |
| Editorial | 393 | Bookshelf | 464 |
| Currents | 395 | Meeting guide | 466 |
| Industry trends | 459 | Professional consulting services | 469 |
| New products | 460 | Classified section | 472 |
| Current research contents | 386 | | |

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Role of SO₂ and photochemical aerosol in eye irritation from photochemical smog 423

W. E. Wilson, Jr., A. Levy, and E. H. McDonald

The presence of SO₂ in irradiated automobile exhaust decreases the eye irritation of such mixtures according to smog chamber test results with a seven-member panel. It was noted that sulfuric acid aerosol does not cause eye irritation but that photochemical aerosol (generated from 1-pentene and nitrogen oxides in the absence of SO₂) does cause eye irritation. The effect of SO₂ is not related to changes in aerosol formation but is due to a chemical interaction which modifies the gas-phase products.

Ozone-induced changes in corn pollen 427

R. A. Mumford, H. Lipke, D. A. Laufer, and W. A. Feder

Corn pollen that has been exposed to the air pollutant ozone may not germinate. A biochemical change, the increase in alpha amino nitrogen, has been observed which can serve as a warning of exposure to ozone. A low level of ozone (3 parts per hundred million) was sufficient to increase free amino acids but did not reduce germination, but higher levels (up to 12 ppm) further enhanced amino acid and peptide accumulation and inhibited germination 40-90%.

Characterization of naturally occurring dissolved organophosphorus compounds 431

R. A. Minear

Dissolved organic compounds (DOP) may represent more than 90% of the soluble phosphorus in a lake, particularly during summer periods of high biological activity. A high level of DOP can be produced by growing certain algal cultures under CO₂-enriched conditions. It has been shown that 20% of the recoverable organic phosphorus is material with molecular weights in excess of 50,000.

Quantitative procedure for evaluating the performance of water and waste water treatment processes at naturally occurring virus levels 438

C. A. Sorber, J. F. Malina, Jr., and B. P. Sagik

A technique is described which can be used to evaluate the removal of virus from water and waste waters treatment procedures at concentrations at which virus can be expected to occur naturally. The technique represents a relatively simple method of virus concentration which is highly reproducible over a broad range of virus levels. The largest sample of water handled was 18 liters, and volumes of 5-10 liters seem to be large enough for most bench and pilot scale studies.

Evaluation of filter materials and impaction surfaces for non-destructive neutron activation analysis of aerosols 441

R. Dams, K. A. Rahn, and J. W. Winchester

Determination of some 35 trace elements in the atmosphere can be made using a nondestructive test procedure—neutron activation spectroscopy, which is useful because of its high sensitivity. Ten filter materials were tested; Whatman 41 is optimum from the standpoints of low blanks, particle retentivity, ease of handling, and commercial availability.

Observations on bactericidal properties of digested sewage sludge 448

J. A. E. Molina, O. C. Braids, and T. D. Hinesly

A major stumbling block to disposal of liquid digested sewage sludge over extended areas of agricultural land is the public health consideration. Evidence reveals the presence of a fecal coliform population in the digested sludge that is resistant to the bacterial agent, *E. coli*. The liquid phase of the digested sludge, rather than the solid phase, contains the toxic agent.

Residues of DDT in lake trout as a function of age 451

W. D. Youngs, W. H. Gutenmann, and D. J. Lisk

Lake trout accumulate approximately 1 ppm of the chlorinated hydrocarbon pesticide—DDT and its degradation products DDE and DDD—each year. Data are presented for 1-yr-old fish with 1 ppm up to 12-yr-old fish with about 14 ppm.

Communications

Device for field determination of selected heavy metals in natural waters

D. M. Coleman, R. E. Van Atta, and L. N. Klatt

The presence of four heavy metals—lead, cadmium, zinc, and iron—in natural waters can be determined in less than 1 hr with an accuracy of ±0.1 ppm. Consisting of a three-electrode polarograph, the device is simple, inexpensive, portable, yet highly accurate; the determinations are made in situ. The device weighs about 5 lb, and can be operated by nontechnical personnel. The total instrument costs less than \$400.

Design of system for removing water-soluble materials from IPC-1478 filter paper 455

B. W. Gandrud and A. L. Lazrus

This filter paper is used extensively in atmospheric sampling of aerosols from aircraft and balloons and is also used in conjunction with sulfur isotope work. However, the paper contains water-extractable contaminants which interfere with analytical results, but now a cleansing procedure is available for obviating this interference. The only limiting factor in the cleansing operation is time. The procedure involves four steps—loading, washing, drying, and unloading of filter paper. Presently, 12 filters take 24 hr.

Mercury uptake by selected agricultural products and by-products 457

M. Friedman and A. C. Waiss, Jr.

Certain agricultural products can be used to remove and recover mercury from contaminated waters. Eight agricultural by-products were examined. The material with the highest sorption capacity is walnut expeller meal (880 mg/g of material) and the lowest is sugar cane bagasse (180 mg/g of materials). Nine other materials were investigated for sorption of mercuric chloride and methyl mercury chloride.

Credits: 395, Stan Miller; 400, 401, Marty Malin; 404, Francis C. Ward, Inc.; 406, Jack Pignatello; 415, Western Body & Hoist Co. Cover: Leroy Corcoran

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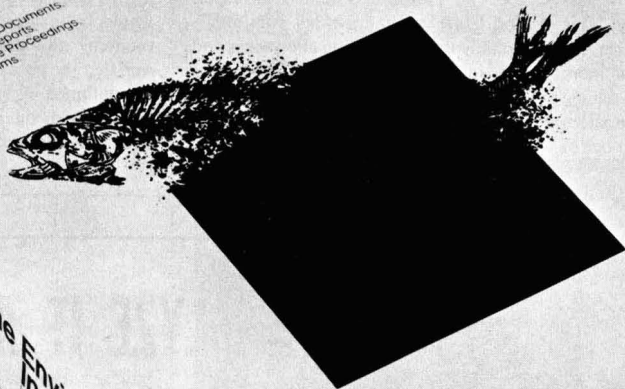
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Coal gasification

DEAR SIR:

The following should be taken into account in evaluating coal gasification (ES&T, December 1971, p 1178) with respect to its long- and short-term environmental implications, its competitiveness with oil in the next 30 to 40 years, and the implications of continuing our nation's present fuels and energy policies.

Of prime importance is the fact that virtually all of the coal that will be gasified will come from strip mines. This strip mining will be conducted in the Great Basin states on a scale far more extensive than that of the strip mining which has laid waste the southeastern coal fields. It should be noted that one of

the major objections being raised to the Four Corners power plant, and the others to follow it in the Rocky Mountain states, is that no account has been taken of the negative environmental impact resulting from the extensive strip mining of coal that will be necessary to meet the fuel requirements of these installations.

At the present time coal is competitive with oil only because of the artificially high price of oil on the domestic U.S. market. This artificial rate structure is the result of a number of federal and state programs and subsidies—notably the oil depletion allowances and the oil import quota. It should be borne in mind that the primary beneficiaries of this rate structure are the domestic subsidiaries of five of the seven

major international oil producers. (These same international majors hold most of the "import tickets," since they were the primary importers of oil when quotas were introduced a decade ago.) The oil industry further enhances its profit margins by virtue of extraordinary tax privileges the result of which is a corporate tax rate of about 4%, as opposed to the 40% tax rate paid by most U.S. corporations such as General Motors.

It is argued that eliminating governmental intervention in the oil industry would be to the detriment of the U.S. economy and national security. It is said that the only way we can be assured of continued oil supplies is to find and use as much oil as possible. At least one responsible economist (Morris Adel-

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man) suggests that the domestic industry could meet this competition. At the present time the various "conservation" programs subsidize production from marginal domestic wells, making it profitable not to produce from the most efficient wells. The logic of using something up so as to be assured of having it when you can't buy it anywhere else has always escaped me.

If we as "environmentalists" are to address the problem of providing increasing amounts of cleaner and cleaner energy, we must deal with energy supplies in the context of the world petroleum industry. It is false and counter-productive to look for immediate (30-40 years on) answers to the energy dilemma in technological innovations such as coal gasification, when it is in economic and political change that the answers are to be found. It is imperative that we in the nation consuming the most energy per capita in the world include in the reordering of our priorities a drastic revision in U.S. energy policies.

Gurdon R. Miller, III
Division of Planning
City of Newark
Newark, NJ 07102

Using waste heat

DEAR SIR:

Your article on waste heat from power plants (December 1971, p 1170) was very interesting, particularly the section dealing with proposals for its beneficial utilization. For some time I have been thinking about this same problem and have conceived an additional means of utilization, not mentioned in your article, which could prove to be both environmentally beneficial and economically rewarding.

In a nutshell, it is to pump heated effluent water through a gridwork of pipe underlying agricultural land, whereby the cooled water may be either safely discharged to a natural water body or brought back for reuse, with the resultant heat rejection serving both to lengthen the growth period of the crops on the land and to enable the production of more warm-weather crops in cooler regions.

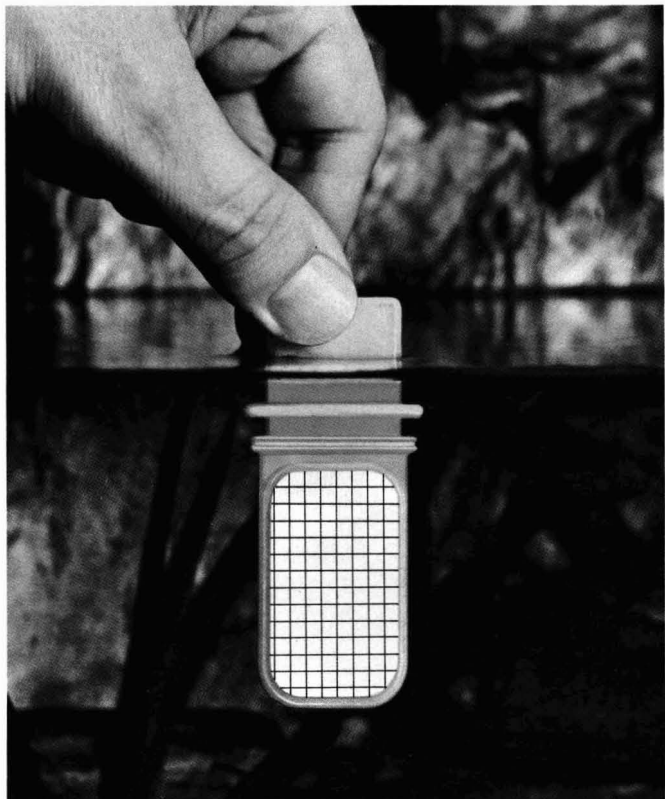
Such a system as this has much to recommend it. First, it is a closed system and therefore not subject to the vast water losses that occur from cooling towers. Second, it would not of itself

(Continued on p 390)



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reduce streamflow, thereby endangering the adequacy of the downstream flow to dilute municipal waste discharges. Third, it would not create any of the potential atmospheric liabilities mentioned in the article—e.g., possible fog, ice formation on roads and power lines, reduction in visibility, or the formation of snow.

Fourth, and most important perhaps, it could permit the return of the water to the natural environment at a much more acceptable temperature, since the underground system could be made as extensive as required to effect the necessary cooling. In fact, the more extensive the system the better, for it would allow greater advantage to be taken of the larger amount of warmed agricultural land. This latter advantage could be a very real economic asset, since many marginal production areas for certain crops could be made sure or safe regions. Some areas could be made to support two or three crops a year, and some could be turned to different, more high-priced crops.

C. B. Pritchard
4203 E. McDonald Dr.
Phoenix, AZ 85018

Benefits of clean water

DEAR SIR:

Your February 1972 editorial, "How clean is clean enough," makes a reasonable plea for benefit studies in pollution control. I too believe benefit-cost studies should be made in pollution control, just as in any other program of resource management.

Recently I made a first estimate of the value of clean water in Illinois. In attacking this problem, I found no theoretical difficulties in making such estimates, thanks to the work in recreation economics of Clawson, Knetsch, and others. Naturally there are practical difficulties in correlating water quality with impairment of indirect uses such as recreation. On the other hand, cost of treating water of different qualities for municipal or industrial use can be readily estimated by qualified engineers.

Recreation benefits were estimated in the following manner: A pollution index, involving six water quality parameters, was evaluated at each water quality sampling station, and then correlated with fisheries sampling data.

Fisheries data were then correlated with potential density of recreational use in visitor-days/acre/year. Total visitor-days for the state were computed using water area as a weighting factor. An average unit value (net of average development cost) was applied to total visitor-days to yield total recreation value.

Estimates were made for three conditions: existing water quality, water quality meeting standards, and wholly degraded water quality. A variant of the procedure was applied to estimate economic value of commercial fisheries.

Benefits of improving water quality are the increased value of recreation, increased value of commercial fisheries, municipal water treatment cost savings, and industrial water treatment cost savings. These totaled \$108,000,000 per year, of which recreation contributed \$78,000,000.

Losses associated with degraded water quality are the lost current recreation values, lost commercial fisheries value, increased cost of municipal water treatment, and increased cost of industrial water treatment. For totally degraded water quality in Illinois these losses

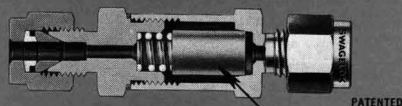
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totaled \$273,000,000 per year, of which recreation contributed \$194,000,000.

Before these data can be compared with cost, total cost must be separated into cost for enhancing quality and cost for maintaining current quality. I have not yet been able to do this. However, a useful comparison can be made between total cost and total value of clean water. The total value of clean water is the sum of gains and losses—\$381,000,000 per year, for Illinois. Available estimates of our annual cost of achieving clean water (including current costs) are significantly less.

This aggregate estimate for Illinois does not prove each pollution control project is individually justified. Each deserves its own evaluation. It gives us hope, however, that with good engineering and judicious investment we can achieve clean water with a net gain for society.

Bruce Barker

*Illinois Department of Transportation
Springfield, IL 62706*

Inflation's not so sweet

DEAR SIR:

I found the article in your December 1971 issue entitled "Hawaii's sugar industry faces tough problems" to be interesting and informative. There are, however, a couple of instances in which dollar figures somehow got inflated even faster than the usual rapid rate.

In one instance, the article says, "Cane brings about \$1.6 billion to the islands each year." Actually, in 1971 the total returns from production of sugar and molasses is estimated to be \$202 million.

At another point, Mr. Berg is quoted as saying, "The industry would be spending some \$10-12 billion in the next five years for pollution control." The figures are correct, but again this is *millions*, not billions.

R. L. Cushing

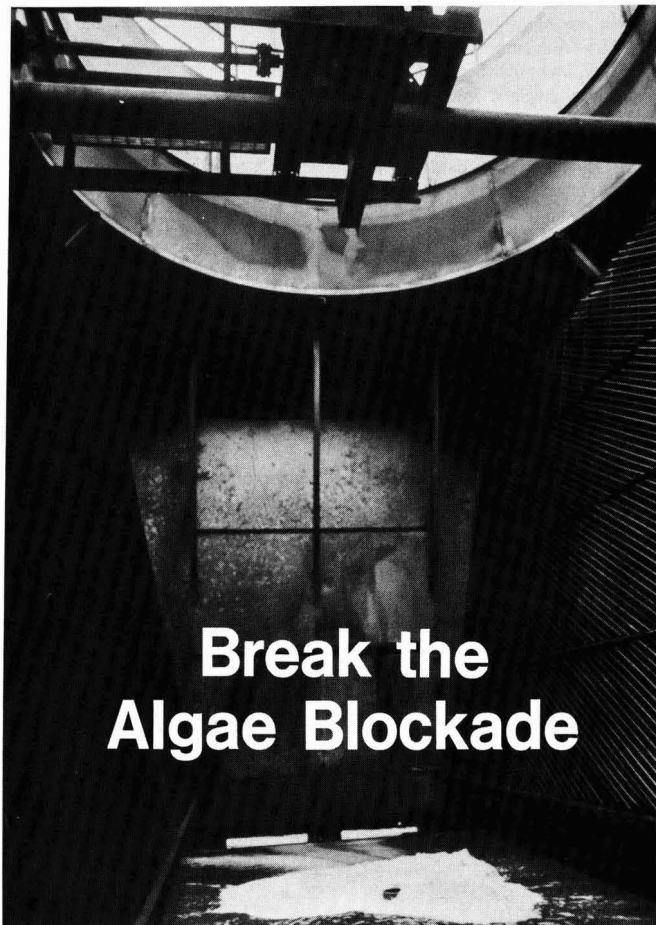
*Hawaiian Sugar Planters' Association
Honolulu, HI 96822*

Textile waste data

DEAR SIR:

Many of the data in the article, "Water uses and wastes in the textile industry," by Porter, Lyons, and Nolan in the January 1972 issue of *ES&T*, first appeared in "A simplification of textile waste survey and treatment," written by Joseph W. Masselli, Nicholas W.

(Continued on p 392)



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Masselli, and M. Gilbert Burford, of the Chemistry Department at Wesleyan University, and published in July 1959, by the New England Interstate Water Pollution Control Commission. We refer specifically to 36 items in Tables II and III, and many of the data on p 40.

Correspondence with Professor Porter reveals that he had given full acknowledgment to this work in his original manuscript, but that in the final editing this reference was removed. We would appreciate appropriate indication in your publication.

M. Gilbert Burford
*Chemistry Department
Wesleyan University
Middletown, CT 06457*

Territorial animals

DEAR SIR:

Your March editorial on environment, interprofessional rivalry, and interdisciplinary teamwork is well taken. There are, of course, many factors which have contributed to environmental degradation. One such factor has been the attempt to employ single-purpose solu-

tions. As you suggest, "the answer, of course, lies . . . in interdisciplinary teamwork."

Universities, through teaching and research, will hopefully contribute to new approaches and solutions. Their past "sins" have to some degree at least been directed by the policies of governmental research funding agencies; therefore the latter's attitudes *must* change if better solutions are to be tried. Specifically, it appears to me that it was not until the IRPOS program (Interdisciplinary Research Related to Problems of Society) of the National Science Foundation, which gave birth to the present RANN program (Research Applied to National Needs), that a researcher could be funded to investigate more than one aspect of a problem. As I read it, bureaucratic agencies tend to subdivide an entity and consider as sacrosanct and inviolable the defined areas of interest of another subdivision, even within an agency—i.e., they are highly "territorial animals." For example, I know of a case where neither of two agencies would even consider funding a look at sewage sludge conditioning and solid waste disposal combined, for the stated

reason that this would involve violation of the other's "territory."

The NSF can shoulder only a small portion of the required interdisciplinary effort. The principal burden is EPA's. They have some new, capable administrators aware of what is required—e.g., Stanley Greenfield—but the task of drastically altering the attitudes of inherited bureaucratic heads is tremendous. The solutions that they must consider in-house as well as "out-house" must in many cases involve several disciplines, including political science, sociology, economics, agriculture, geochemistry, and medicine, in addition to numerous capabilities they now have—from engineering to science to law. It would indeed be instructive to see the results of a thorough objective evaluation of how well this crucial agency is doing itself and with other agencies at what society and your editorial demand—"interdisciplinaryizing."

Roger M. Jordan
*Department of Civil and Environmental
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When to call a spade a spade

Pollution control expenditures are seldom humanitarian gestures; more commonly they are economic necessities

From time to time—possibly often enough to try the patience of our readers—we return on this page to a familiar theme: that pollution control and economics are inseparable topics, have always been inseparable, and are likely to remain inseparable.

One wishes, of course, that it were not so. In fact, as one bathes in the soft bubble bath of soothing, sincere-sounding rhetoric, it sometimes seems that the utopian age of altruism and unselfishness has actually arrived. By this time, top executives of every major corporation in the country must surely have vowed eternal allegiance to the principle of “doing the right thing” by ecology and public health. But when the chips are down, when it comes time to commit money for pollution control, we’ve seen again and again that we’re in the same old ball game.

What is so frustrating about all this is that society’s rules and regulations force the executive’s hand. Even if a corporate official really wants to control pollution—something we do not doubt in the majority of cases—his primary responsibility is still to protect his company’s financial position. To do otherwise is, in many ways, to betray the trust of the shareholders. We are sufficiently capitalistic—despite suspicions aroused in some readers—to believe that a company with exemplary pollution control practices but no profits is really of no net benefit to the country, since it is likely to be soon out of business. As we’ve said before on this page, unilateral action to control pollution on the part of one company in an industry is most likely to result in a competitive advantage to another, and this is in large measure the rationale for tough, evenhanded enforcement action on the part of government (which, incidentally, we still do not have).

Currently, the waters are being muddied even further. Companies have an unfortunate tendency

to announce pollution control spending plans as if their only interest were an altruistic concern to make the world a better place in which to live. In reality, of course, such spending is usually undertaken out of economic necessity—necessity to avoid fines, court cases, or costly enforcement squabbles, or to stay in the competitive marketplace. Even the country’s scrap dealers are now making a big thing of their having been in “resource recovery” for years before anyone ever heard of that current cliché. Come off it, fellers, you’re in the business for profit; if conditions change so that there’s no profit in it, you’ll be out as quick as a flash. And no one could blame you.

Dow Chemical Co.’s chairman Carl Gerstacker made a bit of a splash recently when he said that pollution control was good business. Although his optimism is apparently not shared by everyone, there obviously are instances where there is money to be made, or at least saved. But let’s not kid ourselves that waste can be magically transformed to profit in all situations. If you can do it, Mr. Businessman, more power to you. If you can’t though, you’d best call a spade a spade, and acknowledge that pollution control spending is a net loss to you because you haven’t yet developed the ingenuity to turn it into a winner. But please don’t tell us that you’re doing it for the good of all our souls; we just won’t buy it. The truth by itself is justification enough for our belief that the battle against pollution is at last being waged, albeit not yet won. In the meantime, we should all be working to ensure the effectiveness of the economic and political system as a spur to further progress.

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WASHINGTON CEQ's Train calls for national debate on desirability of growth



CEQ Chairman Train

In a speech to the World Affairs Council (Los Angeles, Calif.) in late March, Council on Environmental Quality Chairman Russell Train said, "states and communities should begin to plan and discuss their short- and long-term alternatives for land use, population growth and industrialization." He pointed out that the questioning of growth is already taking place in many states including California, Colorado, Delaware, Florida, and Oregon. Train also said, "We must learn to adjust to higher density living, learn to share our open spaces and public facilities with more and more people, increasingly forego use of the automobile in favor of public transportation, and give up some cherished habits of privacy and solitude."

EPA: pesticides and implementation plans

After seven months of testimony (which began last August 17) hearings on DDT were closed; a decision will be made by the 15th of next month. At issue were some 32 registrations of products containing DDT. In another move, EPA Administrator William Ruckelshaus ordered an immediate ban on the interstate shipments of a dozen pesticide products containing mercury, products that were used to launder fabrics, on rice seeds, and in antifouling paints. He also proposed rules for expediting hearings on suspension orders, the most drastic regulatory measure that can be taken by EPA, in which interstate shipment of a pesticide is stopped immediately. By the beginning of last month, all state implementation plans with one exception—Alaska were in the hands of EPA. A total of nine states have requested 18-month extensions to implement the national secondary standard (welfare related); six (Conn., Hawaii, N.J., Ohio, Pa., and Mass.) have been granted extensions.

Congress: water bill passage is snagged by differences

The House passed its version of the clean water amendments in late March by a vote of 380-14. The difference between the House and Senate versions, however, must now be resolved in joint conference. All planning effort by industries and municipalities should dovetail with the 1985 no-discharge goal, but still the definition of best practicable technology plagues many. Enforcement provisions follow the blueprint in the clean air amendments; citizen suits are possible but should be held to a minimum. There are five titles to the House version including research and related programs, construction grants program, standards and enforcement, permits and licenses, and general provisions.

Final word: use of PCB's should not be banned entirely

An interdepartmental federal task force finds that if currently available substitutes for polychlorinated biphenyls were used in transformers and capacitors there would be a greatly increased likelihood of fire and explosion, resulting in deaths, injury, and damage to property. Such use (as insulating materials) can be controlled so that it does not significantly contribute to environmental contamination. The task force included representatives from the Office of Science and Technology, CEQ, EPA, and the Departments of Agriculture, Commerce, Interior, and Health, Education, and Welfare. PCB's are widely manufactured in Japan, Italy, France, West Germany, and Russia and possibly in Brazil, Argentina, India, and East Germany. The report is available from NTIS, Springfield, VA 22151 (For more on PCB's, see ES & T, October 1970, p 814).

STATES Stationary source emitters regulated in Ky. and Va.

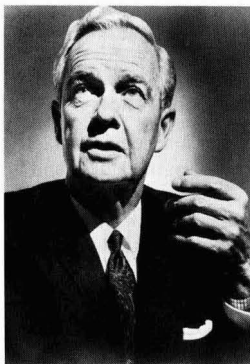
Fifteen Kentucky industries had a deadline last month to apply for an operating permit from the Kentucky Air Pollution Control Commission (KAPCC) or shut down. KAPCC issued cease-and-desist orders to 14 stone quarries and one asphalt plant in March. The firms were ordered to submit reasonable compliance schedules or be fined up to \$1000 per day. The Virginia Air Pollution Control Board, under regulations included in the state implementation plan, requires "stationary sources" to register with the Board by June 30. By that date, they must be in compliance with emission limits or submit satisfactory compliance schedules.

SRI studies Ohio EPA; AEC governs radiation limits

Stanford Research Institute is studying organizational aspects for an environmental protection agency in Ohio. At the same time, both Ohio legislative bodies are considering authorization of a new environmental agency. If the legislature doesn't act, the SRI recommendations will be applied to existing agencies. Last month, the U.S. Supreme Court ruled that states may not establish tougher radiation standards for nuclear power plants than those set by the federal Atomic Energy Commission in the case of *Minnesota vs. Northern States Power Co.* (ES&T, February 1971, p 102).

Arizona regulates smelter SO₂, but not Montana

The Arizona Air Pollution Control Board has renewed conditional operating permits for three copper companies—Inspiration Consolidated, Kennecott Copper, and Magma Copper—since all three companies have submitted satisfactory compliance schedules with a January 1974 compliance completion date. On the other hand, Montana's implementation plan, signed by Governor Forrest H. Anderson, does not mention sulfur dioxide control from its copper smelters at all.



Montana Governor Anderson

Pennsylvania enforces sanitary landfill regulations

A consent decree filed in a Pennsylvania court sets a September 1 deadline for landfill operators in East Deer Township to bring their sanitary landfill into compliance with the Clean Streams Law and Solid Waste Management Act. Other cases are pending as Pa.'s Department of Environmental Resources cracks down on violators (for more on sanitary landfills, see p 408).

N.J. cracks down on dredging, water and air pollution

A New Jersey court, in a riparian right ruling, has ordered Double Creek Development Corp. to restore land illegally dredged in 1970-71 to its natural state. The firm was also fined \$2900 for a lagoon illegally dug in 1958. A bill is presently in the N.J. legislature which would empower the state to make industries clean up their wastes before discharging them into public sewer systems. If passed, it will be the most stringent water pollution legislation in the nation. The Atlantic City (N.J.) Electric Co. recently converted its boilers from coal to crude oil to meet N.J. sulfur dioxide limits.

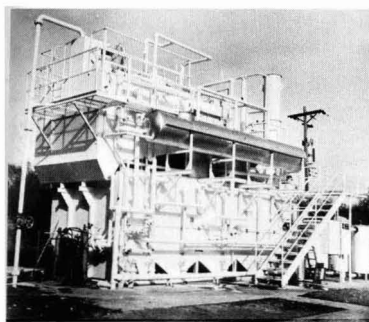
environmental currents

TECHNOLOGY Electric utility tests SO₂ removal process

Savannah Electric & Power Co. and TRIMEX Corp. (Clearwater, Fla.) have completed a nine-month trial sulfur oxide removal process at Savannah Electric's Port Wentworth generating station. Trimex, a mixture of calcium montmorillonite clay, phosphate and borate salts, is fed directly to the combustion chamber of oil-burning boilers where it reacts with sulfur-containing off-gases to yield a mixture of sulfates. Depending on combustion variables and feed rates, SO₂ removals from 60–99% have been achieved. The sulfates can be leached out of the residue and recovered for sale to plant fertilizer makers, according to TRIMEX president Maclin Milner.

Piezodialysis, water machine clean up water

Ionics, Inc. (Watertown, Mass.) is exploring a new desalination technique called piezodialysis (PD). The process, unlike currently used electrolytic dialysis processes, uses pressure to force concentrated salt solutions through a dialysis membrane. Although PD resembles reverse osmosis (RO) in that it uses pressure and membranes, the new process should require less energy because less mass is moved through the membrane. In PD, the residual stream is the desalinated product, whereas in RO, water passes through the membrane, and salt is left behind. Another concept in water processing—a water machine of Chem-Pure Systems (St. Louis, Mo.) is ready to go, according to its designer Sterling R. Kennedy. The M-250 “water machine” uses chemical oxidation followed by reoxygenation to provide primary, secondary, and tertiary treatment of raw sewage at a rate of 250,000 gpd.



Water machine for raw sewage

Land disposal of sewage sludge termed hazardous

Using sewage sludge for plant fertilizer may be a dangerous practice, according to Cornell University scientist Donald Lisk, director of Cornell's Pesticide Residue Laboratory. Lisk warns that some edible plants may concentrate toxic heavy metals present in sludge such as mercury, arsenic, lead, and cadmium which may not harm plants but which could be toxic to animals.

Model predicts CO levels; unit measures stack pollutants

Stanford Research Institute scientists have developed a predictive model that allows city planners to forecast carbon monoxide concentrations in urban air; results indicate that the model can calculate concentration within 3 ppm of actual conditions for large or medium sized cities. Peerless Instruments Corp. (New York City) has developed in stack monitoring techniques for as many as eight pollutants simultaneously with their new equipment. Simultaneous measurement of particulate matter, NO₂, NO, SO₂, CO₂, HCl, hydrocarbons, and H₂S is accomplished by banks of proprietary two-gas analyzers, integrated with sampling and control modules.

Straw reclamation studies are under way

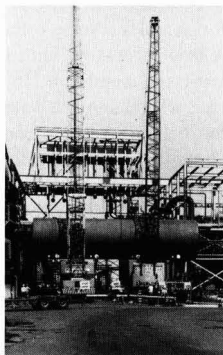
Scientists at Oregon State University at Corvallis are looking into ways to use the estimated one million tons of straw left over annually in the state's Willamette valley by harvesters of grass seed. Until now, growers have been burning the straw, creating an air pollution hazard during the summer months when inversion layers trap smoke in the valley. Open burning will be prohibited in Oregon by 1975.

INDUSTRY Auto makers gear up for emissions showdown

Swedish car manufacturer AB Volvo—the first applicant to submit a documented request for a one-year suspension of the 1975 emission standards for CO and HC—told an EPA panel that they have met “all good faith efforts” to meet the established standards, but that the “state-of-the-art of technology of emission control engineering has not advanced to a level which would justify the 1975 emission standards.” EPA is holding hearings on the request. Volvo’s chief of environmental and safety programs, Lars Larsoen, told the panel “we do not have such technology, and we cannot purchase it.” The EPA panel has until May 12 to make a decision on Volvo’s application. Meanwhile GM, Ford, and Chrysler have also submitted applications requesting the suspension.

Canadian steel tries turn-key approach

Dominion Foundries and Steel Co., Ltd (Dofasco) has put a high-rate, deep bed filtration unit on stream at its Hamilton, Ont., plant. Although deep bed filters have been used in Europe for some time, only 10 installations are operating in North America. To assuage doubts of the Ontario Water Resources Commission about the effectiveness of the units—which may be an economical alternative to low-rate filters where effluent quality does not have to reach near-potable levels, Dofasco contracted for an experimental pilot plant. With successful pilot operations completed, Dofasco let bids for the full-scale plant on a turn-key basis, and awarded the contract to Westinghouse Canada, Ltd. The treatment facility costs about \$4 million, according to Dofasco.



Ecodyne high-rate filters

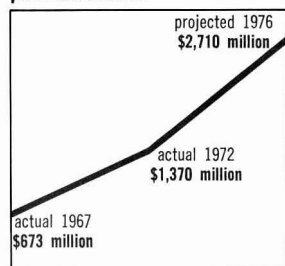
Pipeline company comments on Interior’s report

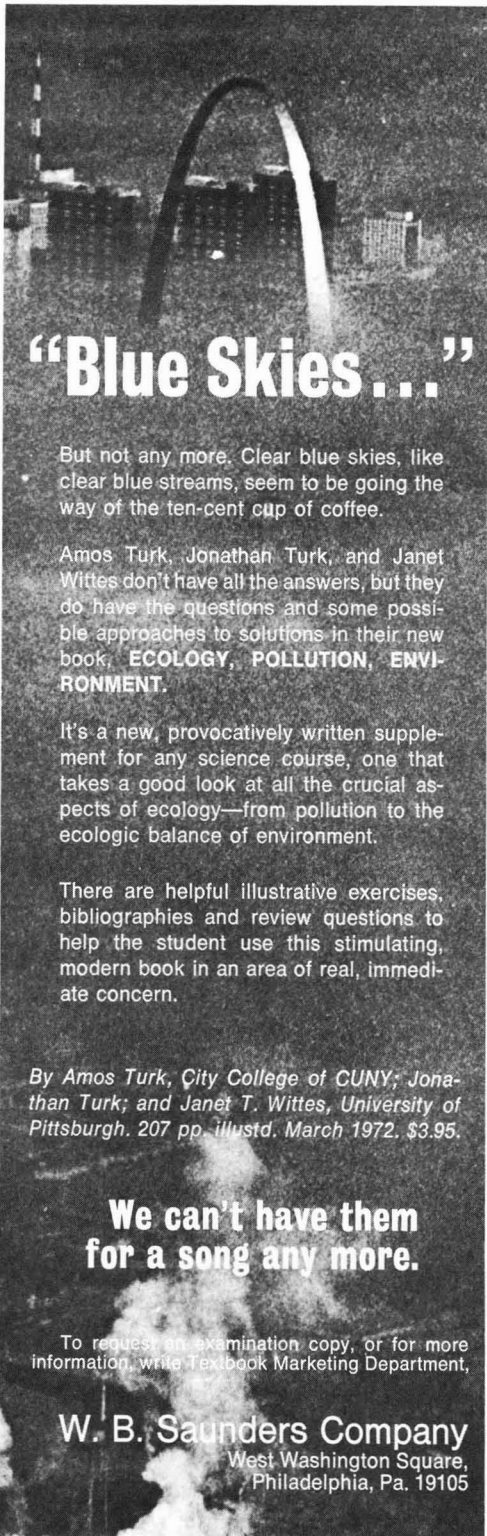
Alyeska Pipeline Service Co. president Edward L. Patton, commenting on the impact statement recently released by the Department of the Interior on the proposed trans-Alaska pipeline system, says that there is no doubt that a pipeline built without regard for the fragile Alaskan environment could result in “severe irreparable damage to that environment,” but he adds that “many of the adverse effects described in the impact statement could only occur if the line were built without proper consideration of the hazards.” Patton says that current estimates place the cost of construction of the line from Prudhoe Bay to Valdez at about \$3 billion. Construction of a similar pipeline through Canada would cost about \$5 billion. “Those figures reflect increased costs due to delays encountered to date,” Patton says.

MCA releases pollution control figures

A survey by the Manufacturing Chemists Assoc. shows that 137 company members will spend \$1.34 billion on capital equipment for environmental improvement in the next four years. The amount more than doubles the \$1.3 billion currently invested for pollution control. By 1976, the total investment is expected to be more than \$2.7 billion. MCA conducted similar surveys in 1962 and 1967 to help assess the progress the chemical industry is making against pollution. In addition to increased spending for capital improvement, MCA’s survey shows that personnel employed in pollution control work increased from 3105 in 1962 to 6868 in 1972. MCA president William Driver notes that the expenditure level “leaves no doubt as to the long-term dedication of the chemical industry in protecting the environment.”

Cumulative capital investment by U.S. chemical companies for pollution control





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Cleanup pays off for fertilizer plant

One plant's need is another plant's poison. At least that's the premise that Farmland Industries goes on. The Bartow, Fla., manufacturer spent nearly a million dollars a couple of years ago to install a fluorine recovery system in its \$22 million phosphate fertilizer plant. After gaining experience, Farmland has decided that the venture "is definitely profitable." During the first full year of the system's operation, Farmland recovered more than 5000 tons (on a 100% basis) of fluosilicic acid (H_2SiF_6)—a by-product it had previously been wasting—and sold every ounce of it.

There's a lot of phosphate in Florida, and most of it is neatly packed into a 40×50 -mile rectangular deposit underlying two west-central counties in the state's peninsula. The deposit—along with a much smaller bed in the northern part of the state accounts for 75–80% of the nation's output of phosphate rock and nearly one third of the total world production.

But where there's phosphate, there's fluorine. Florida's phosphate rock contains 3–4% fluorine, according to E. Wyllys Taylor, executive vice-president of Gulf Design Co., the firm which engineered both the original phosphate complex and the fluorine recovery unit.

Processing phosphate rock liberates substantial quantities of fluorides which must be trapped and neutralized before leaving the plant to prevent air and water pollution. Until recently, most of the fluorides had been largely a wasted material. But what the phosphate industry has been throwing away, the aluminum and steel industries have been busily importing.

Aluminum and steel makers rely heavily on fluorspar—chiefly calcium fluoride—in their process technologies.

Latest statistics from the U.S. Bureau of Mines (BuMines) show that 1.1 million short tons of fluorspar—nearly 85% of the 1.33 million short tons of fluorspar the nation consumed last year—were imported. BuMines estimates that U.S. phosphate plants have the ca-



capacity to replace virtually all current imports of fluorspar with recovered fluosilicic acid.

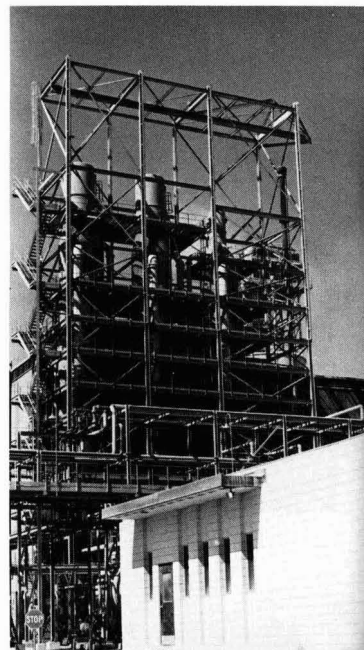
Process technology

Farmland Industries is one of the largest phosphate fertilizer complexes in the country. The original plant had an annual production capacity of 225,000 tons of P_2O_5 to produce 26,000 tons of 54% phosphoric acid, 280,000 tons of granular diammonium phosphate (DAP), and 200,000 tons of granular super triplephosphate. The plant has just been expanded and includes a new fluosilicic acid unit identical to the original.

Farmland Industries does not produce phosphate rock, but receives its supply from strip mines only a few miles away. Rock is digested with dilute sulfuric acid made on the plant site. The end products are phosphoric acid (30% P_2O_5), gypsum, and fluorine-containing off-gases.

Phosphoric acid is evaporated under vacuum in three successive evaporators to a concentration of approximately 54%. Gases from the evaporators pass through barometric condensers, making

Process. Dragline scoops phosphate rock from nearby strip mines (above). Rock is digested to yield 30% phosphoric acid (right) which is concentrated to 54% in evaporators containing fluosilicic acid recovery units (below).



Florida phosphate fertilizer manufacturer snags dirty, fluorine-laden off-gases and turns them into nice, clean money

the evaporation step a closed-loop process.

The fluorine recovery equipment is not complicated and works well. In the case of the Farmland plant, the tops of the evaporators were simply unbolted at a flange and a water recirculation system was installed in the exit gas stream. As the phosphoric acid is successively concentrated in the

Taylor. But equally important as pollution control is the fact that economies of scale may make it possible for phosphate producers to go into the fluorine business.

The Bartow plant can produce some 10,000 tpy of fluosilicic acid (100% basis). Prices for the acid have been trending upward over the past few years in the \$40-50 per ton range.

ping the acid which is still about 80% water.

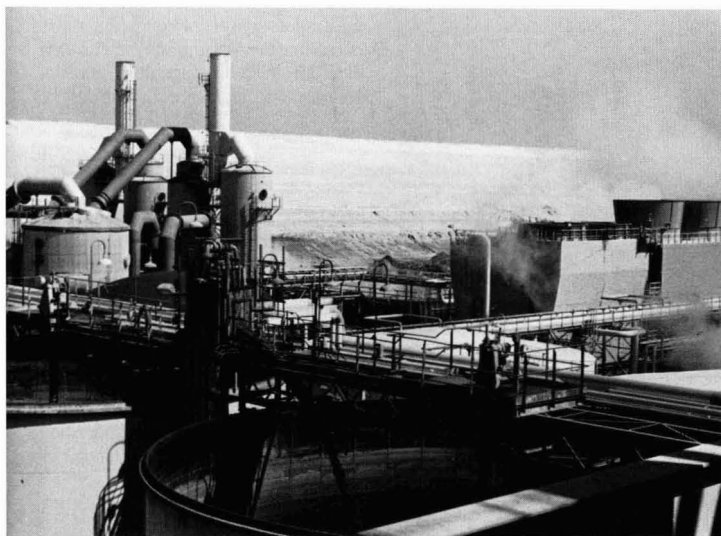
Taylor sees ready markets for large quantities of fluosilicic acid. In the aluminum industry, for example, cryolite (Na_3AlF_6) and aluminum fluoride are mixed with alumina in a reduction cell to produce aluminum metal electrolytically. Stores of natural cryolite are all but depleted and the aluminum industry has been using synthetic cryolite for years. Both synthetic cryolite and aluminum fluoride normally start with hydrofluoric acid and virtually the only material used to produce hydrofluoric acid commercially is "acid grade" fluorspar (better than 97% CaF_2).

The steel industry uses metallurgical fluorspar (less than 97% CaF_2) as a flux. The Basic Oxygen Process, which uses 3-4 times more fluorspar than the open-hearth method and twice as much fluorspar as the electrolytic method, is rapidly replacing other steel-making processes, according to Dr. Allen Cole, director of mining and metallurgy for Gulf Design. He predicts that the world demand for metallurgical fluorspar will exceed 3 million short tons by 1975.

With continued growth in steel and aluminum as well as fluorocarbons and lesser markets for fluorine, competition for fluorspar will be keen in the U.S., which produces only about 15% as much fluorspar as it consumes. The aluminum industry is in a good position to substitute fluosilicic acid for fluorspar in the manufacture of aluminum fluoride and cryolite.

The acidulation of 16 million tons of phosphate rock annually, Cole says, would liberate fluorine equivalent to that contained in 1.2 million tons of fluorspar. Much of that could be recovered as fluosilicic acid, and other fluorine salts.

"Fluorine is now becoming a world article of commerce," says Cole. "Thirty years ago it was said that a nation's consumption of sulfuric acid was a direct index of its industrialization. In the seventies, it appears that we can substitute fluorine as an index of a nation's industrialization." HMM



evaporator units, fluorine-containing off-gases are concentrated in aqueous solution. With the recirculation system, a fluosilicic acid concentration of about 20% is obtained. The concentration is a good one for commercial usefulness and for pollution control. Weaker concentrations would not be as valuable a product. Higher concentrations are possible, but the efficiency of fluorine recovery would fall off slightly, thereby reducing the profitability of the system.

Economics key

Undoubtedly, the fluorine recovery units at Farmland's phosphate complex does its pollution control job well. There are "relatively few" emissions of fluorides to the air or water from the phosphoric acid plant, says Gulf's

At that rate, the Bartow plant could add an annual gross revenue from acid recovery of about half a million dollars. Operating cost for the recovery system, according to Taylor, is relatively low. Additional savings come from the fact that there is a lowering of chemical requirement for neutralizing waste acid.

With the large phosphate plants and the technology now available for recovering sizable quantities of fluosilicic acid available from a single plant site, Taylor says, an economically viable fluoride plant could be constructed adjacent to a phosphate plant. That would reduce costs associated with handling and ship-

In Texas, the Gulf Coast Waste Disposal Authority, a new governmental entity and political subdivision of the state, is now . . .

Managing regional water treatment systems

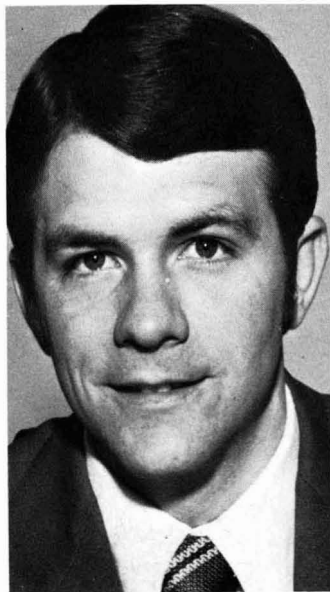
One item in the clean water amendments for 1972 is the requirement of regional planning for waste treatment plants. If the regional officials do not develop such plans for regional treatment of their wastes, then they will not be eligible for federal funds authorized by the nation's new water law.

But Texas legislators are ahead of their federal counterparts. The Gulf Coast Waste Disposal Authority (GCWDA) is one of the newer, if not the newest, regional waste disposal authorities in the U.S. The authority is a political subdivision of the state and it has both the powers to plan and to implement regional waste treatment systems. In addition, GCWDA is eligible to receive construction grant funds from the federal government.

The seed for the authority was planted in 1965 when Texas State Senator Criss Cole, now a judge for the Texas juvenile courts, recognized the need for some sort of super waste treatment agency that would not have to recognize county boundaries. The result, five years later, was GCWDA with boundaries of the authority being the three Texas counties encircling Galveston Bay (see art).

Legislation creating the authority was enacted by the Texas legislature in 1969, and although its general manager, Jack Davis, was not hired till June 8, 1970, now it has both a staff and a board of directors. In addition to Davis, the present staff of 10 includes Mike Eastland, assistant manager for the authority; Joe Watts, director of finances; Charles Hayes, research coordinator; Donald Vacker, chemical engineer; and Larry Crow, planning coordinator. The immediate goal is a central staff of 15-20. Depending on the number and different types of facilities that GCWDA would own and operate, the authority could eventually increase to more than a 100 operating staff in several years.

In addition, the authority has a nine-member board of directors. Three mem-



GCWDA's Mike Eastland
. . .with industrial projects in sight

bers are appointed by the Governor, three by the Commissioner court in each county, and the remaining three by the mayors of each county.

By statute (Texas Civil Statutes Article 7621d-2), the authority was empowered with the ability to levy a tax. It was also empowered with the authority to issue municipal bonds. Although the voters defeated a referendum to permit the institution of this taxing power in the three counties in the general election of 1970, the margin of defeat was slight—54% against, 46% for. Considering the fact that GCWDA was a new governmental entity, the outcome was not all that bad.

"We don't have to have these tax revenues to continue operating," says Mike Eastland, assistant manager for the authority. "We can issue revenue

bonds anytime after legal notice is given. In fact, the authority's first bond issue for \$10.5 million was underwritten last December 28 by Eastman Dillion Securities of New York, N.Y. The 25-year bond issue was sold at a 5.48% interest rate. Earlier, (July 22, 1971), the authority issued \$3.6 million worth of revenue bonds for the city of Houston to assist them in upgrading some of Houston's waste treatment plants.

What it does

Under contract with either industry or a state governmental agency, GCWDA operates, owns, and constructs waste treatment facilities. Thus far, the authority has three industrial projects in sight. The first is under way; it's the one for which the municipal revenue bond was sold. A second is in the contract negotiation stage; signing appears imminent. At press time, the third had suffered a setback because one industry, after considering the pipeline transportation expenses of the venture, had a change of heart.

GCWDA's first project involves treating waste waters of Union Carbide. The contract was signed last October and the municipal bonds now have been sold for this project. The construction will be done in two phases; a primary phase to be completed by July 1973 and the second phase by July 1976. Union Carbide's BOD load was well over 1000 ppm. Union Carbide was passing their wastes through settling ponds, providing some aeration and then discharging them to Galveston Bay.

A primary plant will reduce the burden of pollution to 150 ppm of BOD by the 1973 date. Then, a secondary plus polishing stage in the second construction phase will reduce the BOD burden to less than 50 ppm by the 1976 date.

There is the probability that Monsanto will come into the second phase of this project. Monsanto would provide treatment of its wastes in its own pri-

mary plant but would then send their primary effluent to a secondary treatment facility that is owned by GCWDA. At press time, Monsanto wastes are being analyzed from a treatability and a compatibility standpoint to see if it would be feasible for joint treatment.

In the second project, for which signing of a contract appears imminent, five industrial companies—U.S. Plywood-Champion Paper Co., Atlantic Ritchfield Co. (a refinery), Crown Central Petroleum Corp., Goodyear Tire and Rubber Co., and Petro-Tex Corp. (a petrochemical company)—are planning to combine their waste streams and let GCWDA provide the regional treatment service for their combined wastes. For this project, the authority is negotiating to purchase Champion's existing treatment plant which already provides secondary treatment and good BOD and suspended solids removals. The Champion plant went on line in 1969.

With project two, the authority plans to change the existing plant, to increase the treatment capacity by 10-25%. "There will be some construction," Eastland says. "We will add more clarifiers and aeration basins to increase the capacity of the plant. We will also add sludge-handling facilities including a filter press and an incinerator. Of course, the cost will be prorated among the five companies. The total cost for the second project is \$20-25 million; this figure includes \$10 million for the pur-

chase of the existing plant," Eastland explains.

Earlier this year, the third project was in precontract negotiations but now has been scrapped. This project involved combining waste streams of Ethyl Corp. and Tenneco Hydrocarbons, Inc., and treating their wastes in one plant. Due to the cost of laying a pipeline between the two plants, the industries decided that it would be more feasible for them to perform their own construction and modification to their existing waste treatment plants, rather than to tie in with the authority.

Why go GCWDA?

"When a waste treatment plant is built with municipal revenue bonds, the industry gets a financial break because of the difference in interest rate paid on a municipal bond vs. an industrial bond. Also the treatment facility is taken off the tax rolls," Eastland explains. "What is more, the facility pays no sales tax on the equipment that goes into the plants."

"Because financial advantages accrue to the industry, we must own and control operations at the facility," Eastland continues. "Industry pays the debt service on the bonds that are issued; they also pay the operating cost, and on top of that the authority charges about a 7.5% figure on the average annual debt service as a management fee."

"We don't offer as many benefits to a municipality as we do to an industry because municipalities can issue the same type of revenue bond as the authority. Unless, of course, you combine treatment facilities for municipal wastes, the authority cannot offer a significant financial advantage to a municipality," Eastland elaborates.

"We are trying to follow an evolutionary course here. We start off with small subregional plants and build up to a regional plant. What we are doing is keeping one plant from being built by combining it with another plant. The authority is trying to halt the proliferation of small waste treatment plants." GCWDA has three ongoing municipal projects in which it eliminates the need for three proposed plants by combining the three with existing facilities.

What's ahead?

The reasons for considering regional waste treatment are many and varied. Economies of scale and eligibility for federal funds are only two arguments, but certainly good ones. Permitting one plant to treat wastes from several locations in any one geographic region makes sound economic sense.

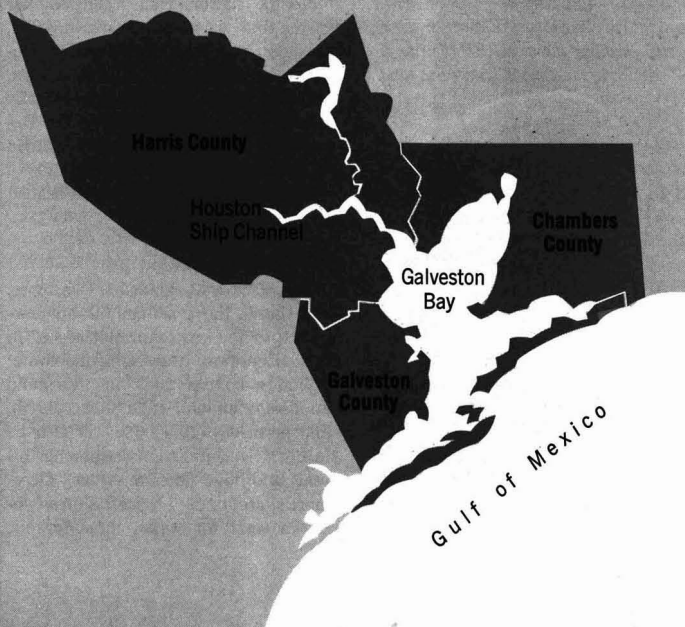
Recently, the Texas Water Quality Board, after public hearings on February 7, ordered industries which discharge their wastes to the Houston Ship Channel to reduce drastically their existing BOD discharges. Presently, there is a collective existing discharge of approximately 100,000 pounds of BOD per day which probably will be lowered to a range of 35,000-50,000 pounds of BOD per day.

The Texas Water Quality Board issues permits. Then, industries of course, had to and still have to file permit applications with the Corps of Engineers. For the Union Carbide project, for example, both sets of permits are being transferred from the industry to the authority.

What is encouraging, at least to the new authority, is that permits issued by the Texas Water Quality Board, its so-called waste control orders, could all one day be turned over to the regional authority—the GCWDA. Then, the authority would get all of the industrial permits issued for the three-county area. The authority believes that should this happen, it will be easier for the authority to institute a monitoring and water-quality management program that would assist in the cleanup of the Ship Channel, Galveston Bay, and the Gulf of Mexico.

SSM

Boundaries of GCWDA



Reorganized last month, the General Accounting Office aims to see if federal programs are meeting the congressionally mandated objectives of laws

Watchdog audits environmental programs

Contrary to popular belief, the General Accounting Office does not just perform financial audits of federal agency activities. In fact, it also performs management audits and reviews program results. Thus, its prime responsibility is to audit and review a department or agency's financial controls and accountability, efficiency of management and use of resources, and effectiveness of program results. The three E's—effectiveness, efficiency, and economy—are what GAO tries to inject into the operations of the executive branch of the federal government.

In 1971, GAO celebrated its 50th anniversary; it is an independent, nonpolitical agency in the legislative branch of the U.S. Government. GAO has brought numerous improvements in management of federal programs as well as major savings in the costs of these programs. It has rightly earned the title of watchdog because of its important supportive role in the legislative oversight responsibility of Congress. Headquartered in Washington, D.C., GAO has some 2900 professional staff members and audit teams covering all 50 departments and agencies of the federal government.

Energy and environmental group

Under the reorganization which became effective on April 3 this year, GAO now is organized along more functional lines so that its various audits can zoom in, focus on, and report on the broad aspects of programs in shorter times than before. There are seven divisions reporting to two assistant comptrollers general. Previously this agency in the legislative branch of government was organized into civil and defense divisions.

Of particular interest to the environmental watcher is the new RED (Resources and Economic Development) division, which includes an Energy and Environmental Program Group, one of four groups in the RED division. The other three cover transportation,

housing, and agriculture and interior agencies. The RED division reports to Assistant Comptroller General A. T. Samuelson.

Henry Eschwege, director of the RED division, says that GAO is no longer just a bunch of accountants. "The emphasis today is to see whether certain programs are meeting the congressionally mandated objectives in recent enacted pieces of legislation," he explains. "This is especially applicable in the environmental area."



Director Henry Eschwege
... heading the new RED division



Assistant Director Edward Densmore
... auditing the EPA progress

Eschwege elaborates that GAO audits can be initiated in one of two ways—by congressional request or internally by GAO. "About 25% of our reviews stem from congressional request; the other 75% is generated internally," the new director says. Eschwege earlier was assigned to the Department of Agriculture audit which, back in 1963, performed a review on the eradication of the imported fire ant, a problem of southern agricultural interests, and pointed out the environmental concern over use of the pesticide dieldrin.

Further down the organizational line, Philip Charam, deputy director of Environmental and Energy Programs, tells *ES&T* that the activities of his group include three audits—one at the EPA, a second at the Atomic Energy Commission, and a third audit for the water and power agencies of the federal government. This last audit covers activities of several departments and agencies—Interior, Corps of Engineers, Tennessee Valley Authority, National Water Commission, and the International Boundary and Water Commission (U.S. Section).

On the environmental fringe, another of the four groups in the RED division, that on Agriculture and Interior programs, headed by M. Hirschhorn, also performs audits on environmentally related matters. For example, the Department of Agriculture audit is headed by R. J. Woods, and the Interior audit—other than water and power—is headed by J. P. Rother.

EPA audit

Like Eschwege, Edward J. Densmore, who heads the EPA audit, is no newcomer to the environmental scene. In fact, Densmore was with the water pollution control audit in 1967, and audits for air and solid waste (1970), and pesticides (1971). He will also be involved with radiation (beginning this year) and noise (later this year). Densmore's group of 17 professionals includes eight for water, three for air,

three for pesticides, one for solid waste, and one for radiation.

Densmore headed the audit team that performed the first major environmental review that GAO ever did for the Congress. That was back in 1969, when GAO issued its (largely critical) review on the construction grants program of the federal government for waste water treatment plants. (For a complete list of completed as well as ongoing audits in the environmental area, see box.)

Densmore explains how some of the GAO work is carried out. He says, "We do two types of studies—surveys and reviews. Generally, surveys can take from 2-3 weeks to 3-5 months on any particular job. GAO rarely issues a report based on a survey. The survey helps us gather information and serves as a basis for getting into detailed review. A report that results from a survey is usually an internal document that we use as a basis for future planning and getting into detailed reviews."

On the other hand, written reports are issued based on findings in reviews. From time to time, written requests from various committee chairmen and individual senators and congressmen are received by the GAO Comptroller General, who is appointed by the President with the advice and consent of the Senate for a nonrenewable period of 15 years. Elmer B. Staats, the incumbent Comptroller General, was appointed in 1965 by former President Johnson.

"As a rule, reviews take from 18 months to two years, but there is great variance in this, depending on the magnitude of the job and the different programs within an agency," Densmore says. "These, of course, result in the public reports that GAO has issued. In addition, we have issued some restricted reports to members of Congress as a consequence of their specific request. These reports are not public documents, and I am not at liberty to give the contents or the source," Densmore explains.

Within the EPA audit are activities of those environmental programs which were transferred to the EPA in the reorganization which was implemented on December 2, 1970. To date, 10 reviews have been completed; three were initiated by congressional request, in this case by the Senate Public Works Committee, and all three were subsequently issued as committee prints. In progress are an additional seven reviews and two surveys.

"The objective of all reviews in the

water program," Densmore explains, "is to look at the administrative aspects of the research and development effort. We are interested in the utilization of people, research facilities, and the use of demonstration grant funds. In this case, the GAO review is a management review—the second E, efficiency. One of the big questions in this review is whether the agency (EPA) has adequate staff to carry out its mission mandated by Congress in specific legislation."

Another ongoing GAO activity is a review of the enforcement aspects of both the air and water pollution control efforts of the EPA. "We are looking at programs of both the state and federal governments," the head of the EPA audit team says. "We will discuss the effectiveness of the enforcement conference procedure and a bit about the number of court cases that have been initiated through the conference hearing procedure." The report on this program was issued on March 23.

"The difference between the GAO and National Academy of Sciences' review of the automobile pollution problem is the fact that ours is non-technical," Densmore comments. "GAO deals exclusively with the administration and management practices. For example, we're interested in learning whether EPA has the people and equipment and procedures for setting automobile standards, testing prototypes, assembly-line testing, and so on."

With regard to new programs for 1972, Densmore says that in the radiation survey, GAO will be taking a look to find out the nature of EPA activity in this area, how much money is being spent on the program and what are the areas that it should look at in more depth. "We will start a noise survey later this year," Densmore predicts.

What's ahead?

Pending legislation, both the water bills (S. 2770 and H.R. 11896) and the national environmental centers bill (see ES&T, June 1971, p 505), assign certain responsibility for oversight studies to GAO. A comprehensive governmentwide review of federal research and development activities relating to environmental quality is specified in Sec. 11 of the environmental centers proposed legislation (S. 1113). The water pollution oversight study shows up in Sec. 517 of the Senate bill. "If the legislation doesn't pass, we still feel that Congress has expressed an interest and we plan to do it on our own," Densmore says. SSM

EPA audit

Reviews completed (10)

WATER

- "Personnel, staffing, and administration of the Federal Water Pollution Control Administration"—April 11, 1969
- "Operation and maintenance of municipal waste treatment plants FWPCA"—July 3, 1969
- "Administration of the construction grant program for abating, controlling, and preventing water pollution"—July 23, 1969
- "Examination into the effectiveness of the construction grant program for abating, controlling, and preventing water pollution"—November 3, 1969
- "Federal grants awarded for constructing waste treatment facilities which benefit industrial users"—May 8, 1970
- "Need for improved operation and maintenance of municipal waste treatment plants"—September 1, 1970
- "Controlling industrial water pollution—progress and problems"—December 2, 1970
- "Alternatives to secondary sewage treatment offer greater improvements in Missouri River Water Quality"—January 6, 1972
- "Water pollution abatement program—Assessment of federal and state enforcement efforts"—March 23, 1972

SOLID WASTE

- "Demonstration grant program has limited impact on national solid waste disposal problem"—February 4, 1972

Studies underway (9) with status of each

WATER (2 reviews)

- administrative aspects of R&D and use of demonstration grants funds, Fall 1972
- combined sanitary storm sewer problem, Fall 1972

AIR (3 reviews)

- enforcement, Fall 1972
- automobile pollution, Spring 1972
- manpower and training, Winter 1972

SOLID WASTE (review)

- disposal practices at federal facilities, Fall 1972

PESTICIDES (review)

- cancellation and suspension of pesticide registration, initiated January 1972

RADIATION (survey)

- radiation program, initiated January 1972

RESEARCH (survey)

- R&D of all federal agencies dealing with environmental quality, initiated January 1972

Financing municipal treatment plants

Maverick New Jersey investment bankers specialize in finding people with money for cities without it but which need hefty chunks of it to abate pollution.

You're the mayor of a small town who won the election last term by promising to hold the line on skyrocketing property taxes. And you've done pretty well. Well enough, in fact, to try again this fall using the same platform.

Today you received a 180-day notice from the EPA, telling you to clean up the the effluent from your town's 50-year-old sewage treatment plant or face the consequences. Your plant operator tells you he can't possibly bring the antiquated facility into compliance, and you know what that means—a new treatment plant, an unpopular bond issue and, yes, higher property taxes.

A way out

Indeed, higher taxes may be the only solution to your problem, but don't give up yet—not until you've considered one of the more successful municipal financing schemes to surface recently. It's called "authority financing." Like most forms of municipal financing, authority financing relies on the sale of bonds—called authority revenue bonds—to bring in the money. But since the bonds are issued by a quasigovernmental, public authority and not the municipal government, they enjoy a number of advantages over conventional municipal bonds.

If, like most small town mayors, you don't feel too comfortable with the intricacies of financing large-scale public works projects, there's at least one company that will help you set up an appropriate financial plan, and guide the project from start to finish. The firm is Munciplex, Inc., a West Orange, N.J., investment banking firm which has recently been bought by the state's largest bond house, Paragon Securities, Inc.

The best part of it all is that Munciplex will do all the spadework free. The company gets no advance fee or retainers for background studies, public relations, or market analyses. You pay them only if your city decides to contract with the firm to sell the bonds.



Munciplex's Rosenberg
pollution control is big business

Munciplex is the brainchild of Fred Rosenberg, a former P.R. man and now the firm's president. Rosenberg decided several years ago that the solution to widespread pollution lay with the investment of private capital in public works projects. "Operating a program of pollution abatement is big business," Rosenberg says, "and should be considered as such."

Munciplex is basically an investment banking house. But basics don't quite describe the feisty little New Jersey company. Although Munciplex makes its money like any investment banking firm—from the discount on bonds placed with brokerage houses or private investors—it goes out of its way to drum up business, a practice foreign to the conservative New York bond houses. And because it offers a package of reports and services including feasibility studies, community education, market research, and public relations free to prospective customers, Munciplex is regarded as something of a maverick in the stolid, sometimes stodgy world of

investment banking, Rosenberg says. But the lack of orthodoxy seems to have paid off. Projects under contract or completed by the first of this year total more than \$75 million, including a 1.6-million gpd sewage treatment plant for the Raritan Township Municipal Utilities Authority and a 1.5-million gpd pumping station for East Rutherford, N.J.

Off the ground

The Munciplex formula is based on the assumption that it takes more than money to build any large-scale public works project. "The big problem is not financing, but getting the project off the ground," Rosenberg says. "We have had no difficulty in underwriting the financing for the project in question." And the most important aspect of getting the project off the ground is communication. "It has been our experience that whenever a project, no matter how well conceived, is placed before the public with little or no attempt at community enlightenment, the first reaction is negative," Rosenberg says. So, realizing that to sell bonds you have to pass bond issues, Munciplex goes all out to prepare the groundwork carefully.

That means discussing types of financing with local officials, projecting costs, interest rates, taxation rates, and other financial variables; appearing at town meetings to educate officials and townspeople, and anything else that may be necessary to assure passage of the bond.

As important as public information is however, the most crucial determination to be made is the type of financing best suited to a particular community for the specific project at hand. There are several ways a municipality may finance large capital improvement projects, according to Munciplex's vice-president Walter Schultz. Traditionally the city will issue general obligation (Go) bonds for major public works projects such as treatment plants, sewers, or water distribution systems. Since the projects benefit the whole community, they are

paid for by property owners in the form of elevated property taxes.

The collateral for such bonds is the "full faith and taxing power" of the local government against the total assessed valuation of the community. GO bonds are attractive to investors in the higher tax brackets because the interest they bear is usually free of federal tax (and local taxes as well, if the investor resides in the state of issue).

Since the bonds are secured by the taxing power of the municipal government—in effect a lien against all real property in the community—they pay investors only modest interest rates and thus save the city considerable money.

But there is a serious drawback to GO bonds, according to Schultz. The borrowing capacity of a municipality is reduced directly by the amount of a bond issue. Thus a municipality which ties up a disproportionately large share of its debt limit in a GO issue for a treatment plant will be unable to finance other capital improvements such as roads, parking facilities, or water mains, which may also be necessary.

There are several other shortcomings of the GO bond, Schultz says. First, both users and nonusers alike pay equally for the service. A treatment plant which benefits only one section of town is paid for by people in another section who do not use it. Furthermore, heavy users pay just as much as light users.

To overcome these inequities, municipalities may issue special or local assessment bonds. The bonds are still a general obligation of the municipality, but they are paid for by assessments charged against properties to the extent that the improvement benefits owners. Issuance of such bonds reduces the ability of a municipality to finance other capital improvement projects, however, in the same way as do GO bonds.

Additionally, special assessment bonds are usually financed for a period not exceeding 15 years, when a period twice that long may actually be more desirable. And while taxes may go up with GO bonds, they are generally a deductible business expense for commercial property owners. Special assessments, on the other hand, do not qualify as tax deductions.

Yet another financing scheme open to municipalities, according to Schultz, is the self-liquidating utility bond. This type of bond is a GO bond which is repaid from service charges levied against users. If user revenues are insufficient, the deficit is a lien against the municipality in the same manner as for any GO bond. Therefore, the bond still reduces the borrowing capacity of a municipality in the same way as the ordinary GO bond.

A municipality's credit rating may also make it difficult to place GO bonds. Bonds are classified by rating agencies such as Standard and Poor Co. or Moody's Investors Service, Inc. on the basis of a municipality's entire financing history. Using Moody's system, for example, bonds are rated Aaa down through Aa, A, Baa, Ba, and so forth, down to C. The lower the rating, the higher the interest rates and the harder the bonds are to sell.

Several municipalities—hard hit during the depression years—find GO bonds hard to place today because they reneged or paid late on one or two issues. Those same communities may be financially healthy today, but they must still pay a premium interest rate to place bonds.

Authority financing

Very often the way around the problems posed by GO bonds, according to Rosenberg, is to create a public authority which can issue revenue bonds.

Bonds are redeemed with money from utility service charges levied against the users. Since the authority is not a municipal institution, deficits cannot result in a lien against the municipality. Similarly the municipality's credit rating is of no consequence and should the authority fail, the municipality's credit rating would be unaffected. It is the investment banker's job to obtain a credit rating for the authority bonds from the major rating houses.

Other advantages, according to Schultz, include the fact that bonds and interest may be extended over a period of time up to 40 years. In some cases, utility charges incurred under authority financing are tax deductible for commercial and industrial firms.

Furthermore, members of an authority board generally outlast the administration which appointed them, making for a degree of political independence which can be highly beneficial to the community. Regional authorities which bridge political or geographical boundaries may also be set up, giving a broader planning base which often proves to be more economical.

While Rosenberg admits that the authority mode of financing is not a "panacea for all problems," he insists that in "most cases" the advantages outweigh the disadvantages. "It is our opinion that in order for the municipal regions and even counties to finance projects of the magnitude that we are discussing today out of their own budgets, or by bonding on the basis of their own credit ratings, with principal and interest to be paid out of the general taxation is a tremendous burden on the individual taxpayer," Rosenberg says. "The bonding necessary would be outlandishly disproportionate to the individual financing structure of the bonding town or country." HMM

Raritan Twp. Municipleplex arranged \$2.2 million worth of financing to build this treatment plant in Flemington, N.J.



Sanitary landfill: alternative to the open dump

Everyone in the solid waste field has heard of Mission 5000—the federal EPA's drive to close 5000 of the country's 12,000 open dumps. Well, after a year, some 1500 dumps have been closed, and the program is being continued. As these dumps are closed, another method must be chosen to take care of the 194 million tons of residential, commercial, and institutional solid waste collected each year in the U.S. Upgrading present facilities alone has a price tag of \$4.2 billion which, if undertaken, would make solid waste disposal the third most expensive of all public services behind education and highways.

As an alternative to open dumping, federal and state officials are recommending sanitary landfills. Essentially, a sanitary landfill is a land disposal area where solid waste is deposited, spread into layers, compacted, and covered daily with earth. This disposal method buries solid wastes to seal off odors and starve off vermin, rats, and other disease carriers—eliminating all unpleasant characteristics associated with open dumps.

The straightforward description of a sanitary landfill makes the operation sound quite simple. Certainly, it is considered the most inexpensive method of waste disposal, and an additional attractive factor is that it reclaims otherwise useless land. However, the design, construction, and operation of a sanitary landfill is an engineering project based

If engineered and operated correctly, landfilling promises efficient, clean, and inexpensive refuse disposal

on various fields of technology—hydrology, geology, engineering, and sanitation.

How to landfill

Sanitary landfilling is carried out by two basic methods: trench and area. In a trench landfill, a cavity or trench is cut into the ground. Solid waste is placed in the trench, spread, compacted, covered with earth at the end of each day's operation, and compacted again. The cycle is repeated daily until the trench is filled; then a thicker layer of earth is placed on the top and compacted for sealing. In general, the trench method is used in areas with a low water table and soil deep enough for trench excavation. It's ideal for flat or gently rolling land.

In the area landfill, refuse is placed on top of the ground, spread, compacted, covered with a layer of earth at the end of the day's operation, and then compacted again. Here again, the cycle is repeated until the area is filled, covered with a thicker layer of soil, and compacted. The area sanitary landfill is most

suitable for canyons, ravines, valleys, or other areas where land depressions already exist. However, in these cases, cover material may have to be hauled in from an adjacent area.

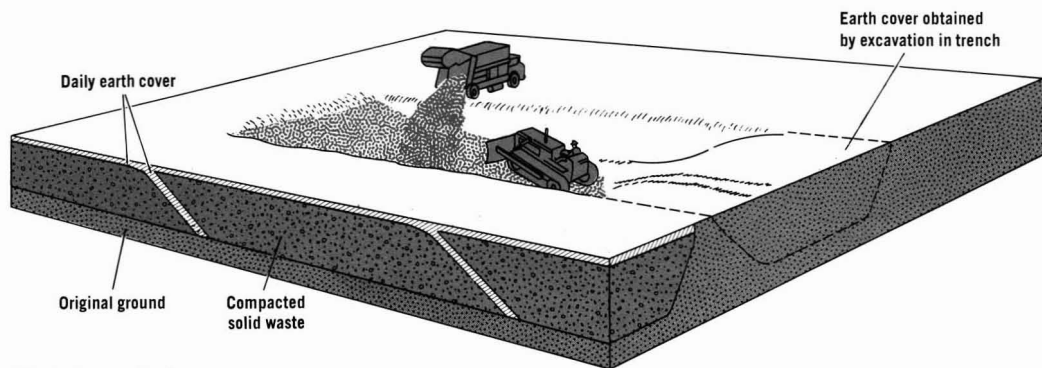
In all methods of sanitary landfilling, the compacted waste and cover material constitute a cell (a cell is completed every day). A series of adjoining cells (from day-by-day operations) all the same height make up a lift. A completed lift is one or more lifts on top of each other.

Leaching

Despite the apparent simplicity of landfill design, there are, in fact, certain problems which can only be avoided by proper landfill design, construction, and operation. Protecting groundwater from leachate is of primary importance. Groundwater or infiltrating surface water moving through the solid waste can produce a solution—leachate—containing dissolved and finely suspended solid matter and microbial waste products. Leachate may leave the landfill as a spring of surface water or percolate through the soil and rock underlying the landfill. In either case, if leachate from a landfill is intermittently or continuously in contact with groundwater or surface water sources, the water can become polluted and unfit for domestic or irrigational use.

Leachate is not produced until all of a sanitary landfill or a sizable portion of it becomes saturated by water entering it

Trench landfills are excavations . . .



from outside. Precipitation, surface water runoff characteristics, evapotranspiration, the location and movement of groundwater, and solid waste all determine leachate characteristics.

The most obvious means of controlling leachate production and movement, say EPA officials, is to prevent water from entering the landfill to the greatest extent practicable. Leachate can be controlled by

- locating the landfill at a safe distance from streams, lakes, wells, and other water sources
- avoiding site location above subsurface stratification that could lead the leachate from the landfill to water sources (for example, fractured limestone)
- using an earth cover that is nearly impervious; grading the fill to promote rapid runoff; and providing suitable drainage trenches to carry surface water away from the site.

Decomposition gases

A problem associated with solid waste decomposition is gas production; in landfills all types of wastes are decomposing. Gases produced include methane, carbon dioxide, nitrogen, and hydrogen sulfide. Methane and carbon dioxide are the major landfill decomposition gases. Methane can be a hazard if it accumulates in enclosed spaces; however, it is explosive only when present in air at concentrations between 5-15%. Oxygen is not usually present in a landfill, but methane may vent into the atmosphere and accumulate in buildings or other enclosed places on or close to a landfill. Mineralization of groundwater can occur if carbon dioxide dissolves and forms carbonic acid.

Landfill gas movement and accumulation can be controlled if sound engineering principles are applied to the landfill—permeable vents and impermeable barriers. No problems will occur if

the gas can be vented to the atmosphere. If landfill cover is impermeable to gas movement, methane can move laterally. Gravel vents, trenches, or vent pipes will allow methane to be released harmlessly into the atmosphere. Fine-grained soils, clays, or synthetic liners used in the bottom of the trench or landfill area restrict gas (or leachate) movement.

Settling will occur at a sanitary landfill as a result of waste decomposition, filtering of fines, superimposed loads, and its own weight. Decomposition (as well as mechanical settling) is the most significant cause of settling and is greatly influenced by the amount of water in the fill. Studies have indicated that approximately 90% of the ultimate settlement will occur in the first five years. For example, several Los Angeles (Calif.) area sanitary landfills, 90-110 ft deep, have settled 2.5-5.5 ft in three years. Because every landfill settles, its surface should be periodically inspected, and soil added and graded where necessary.

Two minor problems associated with landfill operation include blowing litter and dust. However, "litter fences" can be temporarily erected around the site, and sprinkling the road or landfill area (but not the refuse) can drastically reduce dust problems.

Public opinion

One of the major obstacles to sanitary landfill construction is public acceptance. Many potential landfill sites which are environmentally acceptable are vigorously opposed by citizens, particularly those who live near the site. In many communities, public acceptance of a landfill site is the most important factor in deciding whether it will be used.

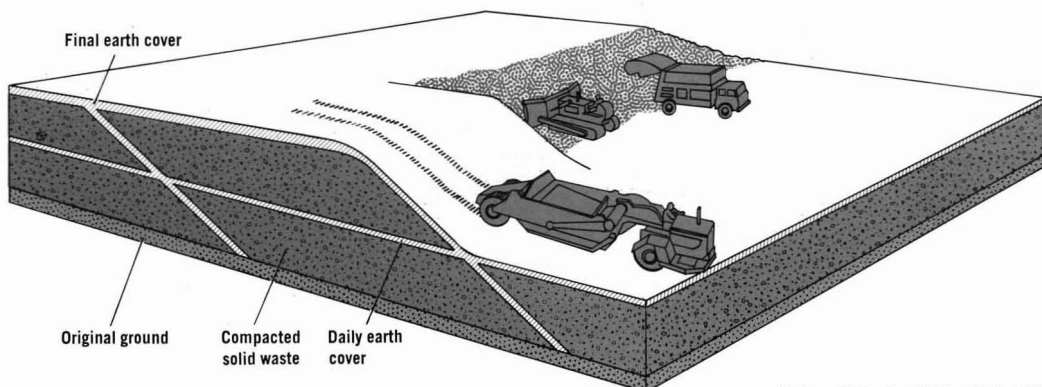
As a result, an active public relations and education program is often necessary for community approval. In many areas, people who are aware of the end use of the landfill see no problem living

with it. For example, homes in the Mission Canyon area of Los Angeles (Calif.) were intentionally built to overlook a large sanitary landfill, because owners knew that a golf course would be constructed on the completed fill. In cases such as Mission Canyon, filling arroyos, canyons, gullies, and other natural depressions give the land a productive use it would never otherwise have had. In spite of the attractiveness of end uses, public acceptance of a landfill site "is always a big hurdle," says John Talty, EPA's director of Processing and Disposal Division, Office of Solid Waste Management Programs. "Another major problem," explains Eugene Wingerter, technical director of the National Solid Waste Management Association (NSWMA), "is getting communities to coordinate disposal needs with the sites available to satisfy those needs." One community may have a shortage of available land while an adjacent community may have land which could be reclaimed through a well-planned sanitary landfill. An outstanding example of regional cooperation includes San Francisco and Mt. View, Calif., and private industry. About two years ago, San Francisco was faced with a critical shortage of landfill space; however, Mt. View (30 miles away) had a large amount of unusable land. Through mutual cooperation, a regional solid waste disposal program was created. Seventeen hundred tons/day of San Francisco refuse are now trucked to 500 acres of formerly unusable land which will eventually become a park and marina. This public-private partnership provides San Francisco citizens service at low cost and high quality. The operation is serviced by private contractors and guided by local municipal agencies.

Technology

Many decisions must be made before a sanitary landfill can be constructed

... while area landfills are not





Unsanitary. *The country's 12,000 open dumps cause many environmental problems*

and operated properly. A sanitary landfill can be constructed on virtually any terrain, but the designer must consider the topography, geology, and hydrology for maximum land use and minimal environmental dangers.

Depressions, such as canyons and ravines, are more efficient than flat areas from a land-use standpoint since they can hold more wastes. There are also numerous man-made topographic features—strip mines, worked out stone and clay quarries, open pit mines, and sand and gravel pits—which can be economically reclaimed by utilizing them as sanitary landfills. Sarpy Co., Neb., and Big Springs, Tex., reclaimed gullies with sanitary landfills, and Frostburg, Md., uses an old strip mine for landfilling.

The ultimate use of the completed landfill site should be decided during the initial planning stage. In most cases, the end use will influence the design and operation of a landfill. In fact, buildings can be built on landfills if some undisturbed ground is left.

With proper planning, landfills also can be built in areas with high water tables, although this is usually not recommended. Orange County, Fla., has a high water table, making solid waste disposal a problem. Landfilling is being done in trenches having dry bottoms; the water table is lowered by drainage canals. The ultimate use of the land includes undisturbed woodland, park areas, camping grounds, recreation areas, golf course, industrial park, and areas for modular or mobile homes.

Sanitary landfills can also be constructed in high water table areas by mounding the solid waste and cover material. In Virginia Beach, Va., a geographic location with a flat terrain, a 65-ft hill has been created to provide an amphitheater, soap box derby ramp, and landscaped park, now in its final development stages.

Monitoring is essential in landfill operations to ensure no water pollution or undesirable gas movement. Monitoring for potential water pollution or

groundwater contamination is done by drilling peripheral wells in strategic locations around the fill. By monitoring these waters, any groundwater pollution (and lateral gas movement) is detected.

Water pollution can also be prevented by collecting and treating leachate. Two landfill sites in Pennsylvania use synthetic liners to collect leachate which is then treated by conventional methods. In Seattle, Wash., leachate is treated in an aerated lagoon.

End uses

There are many ways in which a completed sanitary landfill can be used. A park or green area is established for the pleasure of the community. A completed sanitary landfill can be utilized for pasture or crop land. In this case, final soil cover should be thick enough so that roots or cultivating do not disturb its bottom foot.

Construction is a possibility, although in this case the design must be centered around the final use. Completed landfills are often used as ski slopes, toboggan runs, coasting hills, ball fields, golf courses, amphitheatres, playgrounds, parks, tennis courts, botanical gardens, and riding rings.

The Heckimovich sanitary landfill near Mayville, Wis., serving a population of 18,000–20,000, may eventually be developed into a recreational area. A privately owned operation near Denver, Colo., may be converted into a golf course when completed.

EPA efforts

EPA is undertaking in-house studies of sanitary landfills as well as numerous research and demonstration projects. Presently, the push is toward sanitary landfills; however, EPA wants to look further into leachate generation, control, and treatment; gas generation and control; settlement; and decomposition to come to grips with any problems.

The solid waste research division (SWRD) (located in Cincinnati, Ohio) of EPA's Office of Research and Monitoring has leased 10 acres of land and

constructed a sanitary landfill field test facility in Boone County, Ky. "The intention of the Boone County field site," explains Norbert Schomaker, research civil engineer with SWRD, "is to have full capability of quality control in constructing a landfill, placing various probes and monitoring devices, and performing actual routine weekly monitoring. We felt we would be right on the spot during actual cell construction, placement of solid waste and probes, and have a good quality control item." Laboratory tests will be compared to and correlated with actual field conditions.

EPA engineers lined the trench and are collecting and analyzing leachate, monitoring gas production, temperature, moisture, and settlement. The site will be monitored for three years, and SWRD plans to complete two more experimental cells before the end of the summer.

Demonstration and research projects under EPA auspices include recycling leachate over the fill, developing treatment methods for leachate, leachate attenuation in the soil, leachate generation, settlement characteristics, milling landfill refuse, and slurry injection into landfills.

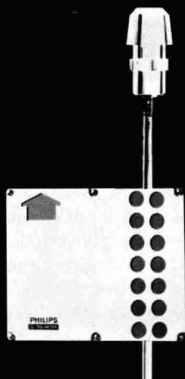
Guidelines and regs

EPA does not yet have enforcement or regulatory authority over solid waste disposal or sanitary landfills. At present, the agency can only recommend; however, no community that permits open dumping is eligible for EPA grants. In this way, at least some pressure can be applied to convert dumps to sanitary landfills.

Last year, EPA and NSWMA jointly published recommended guidelines for sanitary landfill construction and operation. Unfortunately, many municipalities incorporate such recommended standards into law without looking at their particular situation. EPA is presently preparing revised guidelines that will appear in the Federal Register in the near future.

Besides the fact that sanitary landfills are an improvement over open dumping, costs run way below those of most other solid waste disposal methods. Generally, landfill capital and operating costs run $\frac{1}{4}$ to $\frac{1}{3}$ of the costs of other solid waste disposal methods. Getting rid of solid waste and reclaiming waste land for a minimal fee is indeed attractive, although whether the method constitutes recycling is, of course, debatable. CKL

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Advances in research and commercial solid waste handling offer many processing choices and herald an era of sophistication in management

SOLID WASTE

Treatment technology constitutes one of three fundamental aspects of solid waste management; the other two—waste generation and waste management operations—are mentioned in this article only in passing.

However, the tendency to solve solid waste management problems by substantial investment in treatment hardware persists, and important decisions continue to be made with less than complete information. This survey attempts to draw the reader's attention to recent advances in equipment and techniques.

Storage and removal

The most substantial innovation in on-site refuse storage has been introduction of paper and plastic bags in place of conventional metal and plastic cans. Bags are neat and odor-free, and collection is quieter and faster.

On-site compaction devices are available in many varieties (Table I). The smallest fits under a kitchen counter, while larger, commercial units pack refuse into standard bags and cans or into closed metal containers.

Collection, the costliest aspect (75-80%) of refuse management, has long been the most neglected. Recently, however, more effective packer bodies, auxiliary and automatic collection vehicles, improved transfer stations, and pneumatic ducts and pipelines have been developed.

In the first major innovation in packer bodies, the "Shark" vehicle replaced the conventional packer mechanism. A large endless horizontal screw crushes large objects and compresses the load in one continuous operation. Auxiliary or satellite collection vehicles are designed to alleviate traffic congestion. These

vehicles, consisting of metal containers, are mounted on a scooter or pickup truck chassis, or pulled as a train by a power unit, and periodically transfer their load to a large "mother" truck.

Automatic collection vehicles, a major breakthrough in collection technology, are gradually replacing conventional equipment in Scottsdale, Ariz. The driver operates (from his cab) a boom that picks up a special container or a precompacted package and dumps it into the packer body behind.

Over 60 transfer stations have been built in the U.S. for long-distance hauling of municipal waste by large trailer vans, railroad cars, or barges. A typical modern station is equipped with a compacting mechanism, and the addition of shredders is being considered. The feasibility of transporting solid wastes by rail has been studied by the American Public Works Association. However, negotiations between railroads, municipal sanitation authorities, and county officials with jurisdiction over routes have not been successful.

In spite of technological advances, manned collection of refuse is still plagued by substantial problems of on-site storage, removal to the curb, meeting collection schedules, high labor costs, hazardous and noisy operation, and traffic obstruction. Eventual replacement of manual collection by pneumatic ducts and slurry pipelines appears increasingly more attractive.

With pneumatic duct systems, refuse is deposited in gravity chutes and propelled through a network of 20-in. ducts to a central collection depot by an airstream produced by an air exhauster. Installations are planned at a number of U.S. sites, including the Martin Luther King Hospital in Los Angeles, Calif.,

the Disney World Amusement Park in Florida, and a major housing project in New York, N.Y.

For longer distances and/or heavier loads, slurry pipeline systems become more cost-effective. A slurry pipeline system requires fragmentation of refuse at the point of introduction and pumping stations at suitable intervals.

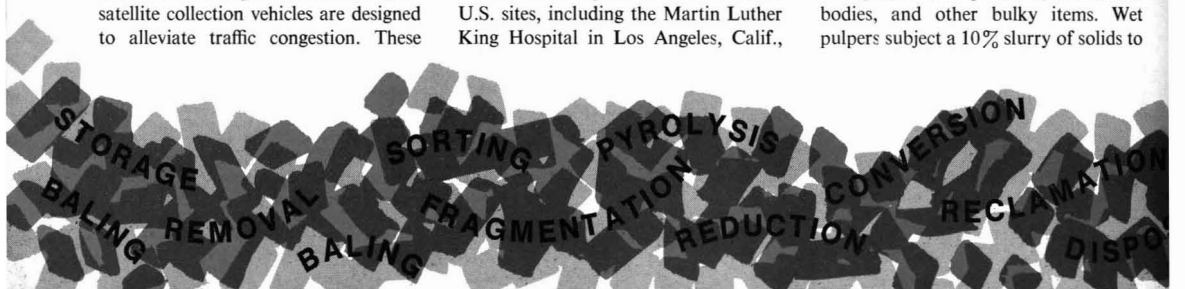
In the Garchey system, used in parts of Western Europe, refuse and waste water are mixed in a 5-gal. container under the kitchen sink and transported as a slurry to an underground collection chamber. There, excess water is drained into the sewer, and wet residue is transferred pneumatically to a central processing plant.

Fragmentation and sorting

Reducing the average size of refuse fragments, also known as fragmentation, comminution, or presizing, enhances homogeneity, packing, and handling quality, and is thus a useful preliminary step for subsequent processing.

Most common fragmentation equipment includes hammer mills, shredders, shears, and wet pulpers (Table II). Other devices with essentially similar functions are ball mills, cage disintegrators, chippers, crushers, cutters, disk mills, drum pulverizers, grinders, hoggers, and rasp mills.

Hammer mills employ rotating hammers that apply tensile, compressive, and shearing forces to fragmentize a wide mix of refuse. Shredders use overlapping fingers operating at different speeds to tear and shear fibrous and ductile materials. Shears are used primarily to break up timber, automobile bodies, and other bulky items. Wet pulpers subject a 10% slurry of solids to



feature

Alex Hershaff

*Grumman Aerospace Corp.
Bethpage, NY 11714*

treatment technology

repeated impacts of hardened high-speed members.

A significant contribution to refuse fragmentation has been made by a demonstration project in Madison, Wis., where a 150-ton/day hammer mill grinds municipal refuse into an inoffensive product that can be landfilled with only partial cover and in half the space of unprocessed refuse.

Sorting refuse into its constituent materials, also known as separation or segregation, is essential in recovery operations but also is useful in other processing steps, where it permits optional adjustment of operating conditions to each category of refuse.

Sorting relies on differences in the physical characteristics of refuse materials, including size, shape, specific gravity, brittleness, elasticity, color, reflectance, magnetic susceptibility, electric conductivity, absorption of electromagnetic radiation, and radioactivity.

Sorting is aided considerably by fragmenting refuse to enhance the cleanliness of individual particles, and by screening to promote dimensional uniformity. In addition, recovering valuable components can be facilitated by tagging these materials, for example, imparting a recognizable coding characteristic (magnetic or radioactive) that does not affect the material's performance. Sorting techniques may be categorized loosely as: manual, dimensional, dynamic, electric and magnetic, optical, and "exotic."

Manual sorting from conveyors is still the most common method, employed at nearly all composting plants and some incinerators. Mechanical methods have been developed recently by adapting proved techniques from the mineral processing industry. Dimen-

sional separation, perhaps the simplest sorting operation, is accomplished typically by passing refuse over a series of vibrating screens.

Dynamic sorting techniques rely on combinations of characteristics that affect the motion of refuse particles (size, specific gravity, inertia, shape, and elasticity). The devices include the stoner, fluidized bed separator, Osborne dry separator, air classification unit, vortex classifier, ballistic separator, secator, and inclined conveyor. A number of other techniques (flotation, heavy medium separation, hydropulping) and devices (jigs, Wilfley tables, spiral classifiers) require an aqueous slurry or pulp and are not generally applicable to solid waste processing.

The stoner, an inclined perforated table that vibrates at different reciprocating speeds in the incline direction, causes heavier particles with greater inertia to migrate upward. Simultaneously, air flows up through the perforations, lifts lighter particles, and propels them toward the lower end of the incline.

The fluidized bed separator is similar to the stoner but employs a fluidized medium, such as ferrosilicon or iron powder, in place of pressurized air. The Osborne dry separator uses pulsed air to separate materials of different density.

The air classification unit consists of zig-zag shaped columns and cyclone separators and relies on differences in specific gravity and aerodynamic characteristics of materials. A stream of air flowing up through the columns carries lighter particles to the top, where they are removed by cyclones, while heavier particles fall to the bottom.

In the vortex classifier, refuse particles are introduced into a radially inward flowing air vortex. The resulting drag

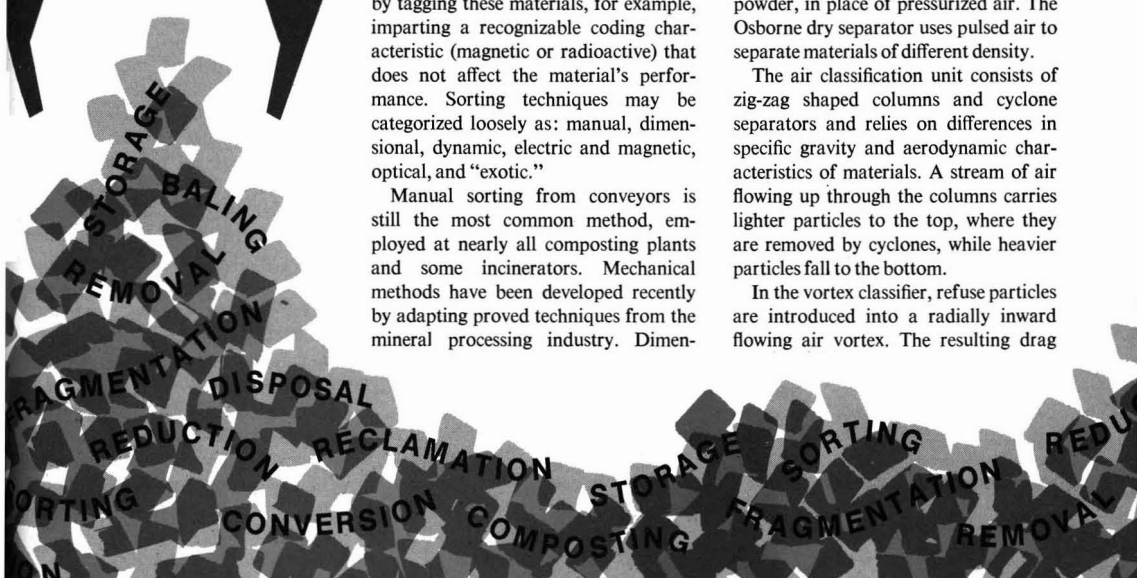
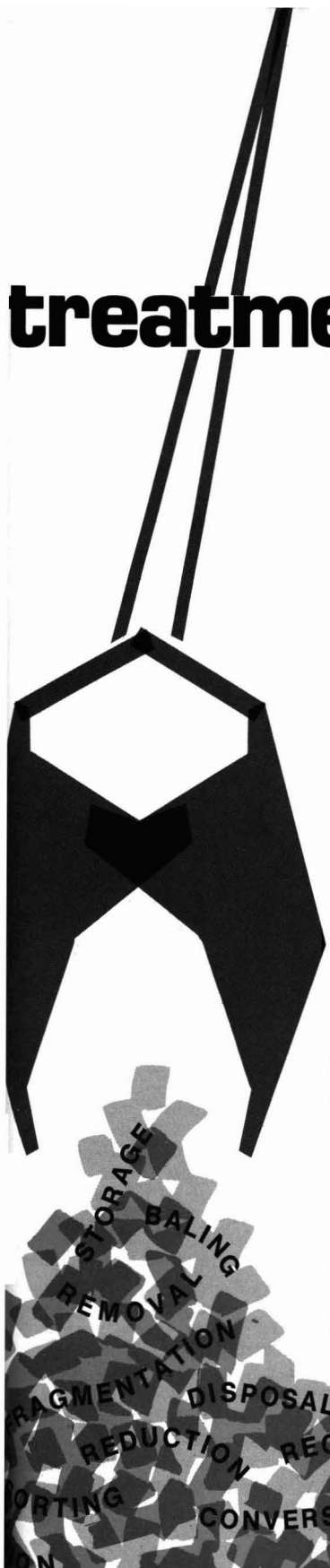


Table I.

Storage and removal**COMMERCIAL**

American Solid Waste Systems Co.
 Compaction Equipment Co.
 Compactor Corp.
 Cushman Motors Div.
 Dempster Bros., Inc.
 EDM, Inc.
 Elgin Leach Corp.
 Envirogenics Co.
 Environmental Equipment Corp.
 E-Z Pack Co.
 Garwood Industries, Inc.
 Gulf Oil Co.
 Hagie Manufacturing Co.
 Hercules, Inc.
 Heil Co.
 Hobbs-Pak Div.
 Industrial Services of America, Inc.
 I.P.&D. Patents & Devel. Corp.
 M-B Co.
 M & E Sales, Inc.
 Mid Equipment Corp.
 Mil-Pac Systems, Inc.

Mobil Oil Co.
 Nat'l Compactor & Tech. Sys., Inc.
 Pak-Mor Manuf. Co.
 Perfection-Cobey Co.
 St. Regis Paper Co.
 Swiftainer Industries Co.
 Truck Equipment Corp.
 Tubar Waste Systems Div.
 Union Carbide Corp.
 Waste Techniques, Inc.
 Wayne Engineering Corp.
 Western Body and Hoist Div.
 Whirlpool Corp.
 Westvaco Corp.

RESEARCH & DEVELOPMENT

A. B. Centralsug (Sweden)
 Amer. Pub. Works Assoc.
 City of Scottsdale, Ariz.
 MIT
 Stanford Research Inst.
 University of Pa.

produces a centripetal acceleration on each particle until equilibrium is reached (a function of specific gravity and aerodynamic drag). The ballistic separator sorts materials on the basis of their ballistic trajectories. The separator bounces the particles off a plate onto a rotating pulley, bringing elastic differences into play as well. The last device drops the refuse onto an inclined conveyor belt, where denser and more elastic particles bounce down the incline, while the lighter and less elastic ones are transported upward on the conveyor.

Magnetic and electric sorting techniques, including magnetized belts and pulleys, rely on differences in the magnetic susceptibility and electrical conductivity of materials, and thus are particularly suited for separating metals.

In the case of optical separators, any refuse particle that differs in color or shade from a selected background triggers a short blast of air that deflects it into a separate chute. More "exotic" sorting concepts utilizing X-ray, microwave, infrared, and spectrographic sensors are under development at the Massachusetts Institute of Technology.

Major sorting operations must rely on several techniques acting in series or parallel, and in either a binary or multichoice mode. A large installation for sorting municipal refuse at the recently closed composting plant of the Metropolitan Waste Conversion Corp. in Houston, Tex., removed paper by air classification, extracted steel cans by magnetic separator, and aluminum cans manually; rags were removed by a mechanical rag picker or by hand; and finally, glass was sorted by a stoner.

A sorting system developed by the Bureau of Mines Metallurgy Research Center at College Park, Md., separates incinerator residue into clear and colored glass fractions, ferrous and nonferrous metal fractions, and a residue of ash and sand. The equipment consists of a series of vibrating screens, magnetic separators, and an air classifier. A process capable of extracting paper, glass, metal, and plastics from municipal refuse is currently under development by the Franklin Institute (Philadelphia, Pa.).

Bulk reduction

Bulk reduction, or densification, of solid waste is becoming increasingly important as potential landfill space disappears under pressure of suburban growth. Long-favored conventional incineration is now encountering serious

Table II.

Fragmentation and sorting**COMMERCIAL**

Black Clawson Co.
 Denver Equipment Co.
 Eidal International Corp.
 Environment One Corp.
 Eriez Magnetics
 Hazemag (USA), Inc.
 Heil Co.
 Jeffrey Manuf. Co.
 Joy Manuf. Co.
 Logemann Bros. Co.
 Metropolitan Waste Conversion Corp.
 Ore Sorters, Ltd.
 Raymond G. Osborne Laboratories, Inc.
 Sortex Co. of North America
 Syntron Div.
 Triple/S Dynamics, Inc.
 Warner Brake and Clutch Co.
 Williams Patent Crusher & Pulverizer Co.

RESEARCH & DEVELOPMENT

Franklin Institute
 MIT
 Stanford Research Institute
 U.S. Bureau of Mines

Table III.

Bulk reduction**COMMERCIAL**

American Baler Co.
 American Menmax Co.
 American Solid Waste Systems Co.
 American Thermogen, Inc.
 Combustion Engineering, Inc.
 Combustion Power Co.
 Copeland Systems, Inc.
 D and J Press Co.
 Dorr-Oliver, Inc.
 Dravo Corp.
 Ferro-Tech Industries, Inc.
 General Electric Co.
 Harris Press & Shear Corp.
 Joseph Martin Co.
 Logemann Bros. Co.
 Lombard Corp.
 Reclamation Systems, Inc.
 Rust Engineering Co.
 Sira Corp.
 Tezuka Kosan Co., Ltd. (Japan)
 Torrax Systems, Inc.
 UGI Corp.

RESEARCH & DEVELOPMENT

Amer. Pub. Works Assoc.
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 City of St. Louis, Mo.
 University of Hartford
 West Virginia University

competition from advanced forms of incineration as well as high-pressure baling and pyrolysis.

Baling. Compressing solid waste is the most direct method of bulk reduction. The degree of compaction is governed by pressure applied, manner of application, and waste composition. Low-level compaction of solid waste has been practiced in the U.S. for a number of years with stationary compactors, packer vehicles, and landfill tractors.

Large-scale, high-pressure compaction and baling of municipal waste were popularized in 1967, by Tezuka Kosan Co. Ltd. (Japan) by a process compressing refuse into sterile bales that could be clad in asphalt or concrete and used as building blocks. Eventually, the company's credibility became badly damaged by early unwarranted claims. Since then, over 50 U.S. firms have entered the refuse-baling field with equipment or management services (Table III).

A continuously operating press, manufactured by American Baler Co. (Belevue, Ohio) recently passed a satisfactory demonstration phase in San Diego, Calif. The refuse is shredded, charged into a vertical chute, and dropped into the compression chamber. Successive charges are compressed by repeated strokes of the horizontal ram until the desired thickness is reached, and the bale is banded and removed for storage and shipment.

Harris Press & Shear Corp.'s (Cordele, Ga.) baler employs three rams operating consecutively along three octagonal directions to compress each successive batch of refuse. A solid waste processing facility using the Harris baler was opened a year ago in St. Paul, Minn., by American Solid Waste Systems Co.

The Lombard Corp. (Youngstown, Ohio) press compresses refuse into 16-in. contiguous layers, which are then banded into a bale. A \$1 million baling facility employing two Lombard presses was opened two years ago in East Cambridge, Mass., by Reclamation Systems, Inc. (Boston, Mass.).

In a strict bulk reduction role, high-pressure baling offers a number of advantages over conventional incineration:

- accepts all types of waste, including noncombustibles and plastics
- yields greater volume reduction on the basis of total municipal waste stream
- capital and operating costs are, respectively, $1/10$ and between $1/3$ - $1/2$ of corresponding incineration costs
- requires less maintenance and operating skills

- generates no significant air or water pollution

- produces a residue easier to handle, transport, and landfill

- affords nearly full future recovery of waste materials.

Incineration. Major drawbacks of incineration include high construction, maintenance, and pollution control costs, frequent "downtime" to replace refractory lining and grate elements damaged by excessive temperatures and corrosive gases, and incomplete combustion. Development efforts have focused on incinerating bulky wastes, suspension of the waste charge, improved emission control, high-temperature incineration, and waste heat recovery.

One approach to suspension firing, vortex incineration, burns shredded refuse as it is blown tangentially into the combustion chamber. Residence time is reduced, heat released is an order of magnitude higher, excess air requirement is lowered, and pollutant emissions are reduced substantially.

Fluidized bed incineration is a form of suspension firing. Refuse is shredded, preheated, and burned in a turbulent bed of hot silica sand held in suspension by a powerful upward stream of air. Advanced development in this field is being pursued at West Virginia University (Morgantown, W.Va.).

Improved incinerator emissions control is perhaps the most concrete near-term advance in incineration technology



Removal. Automated collection vehicles allow the operator to remain in the cab while picking up containers and dumping the contents into the packer body behind

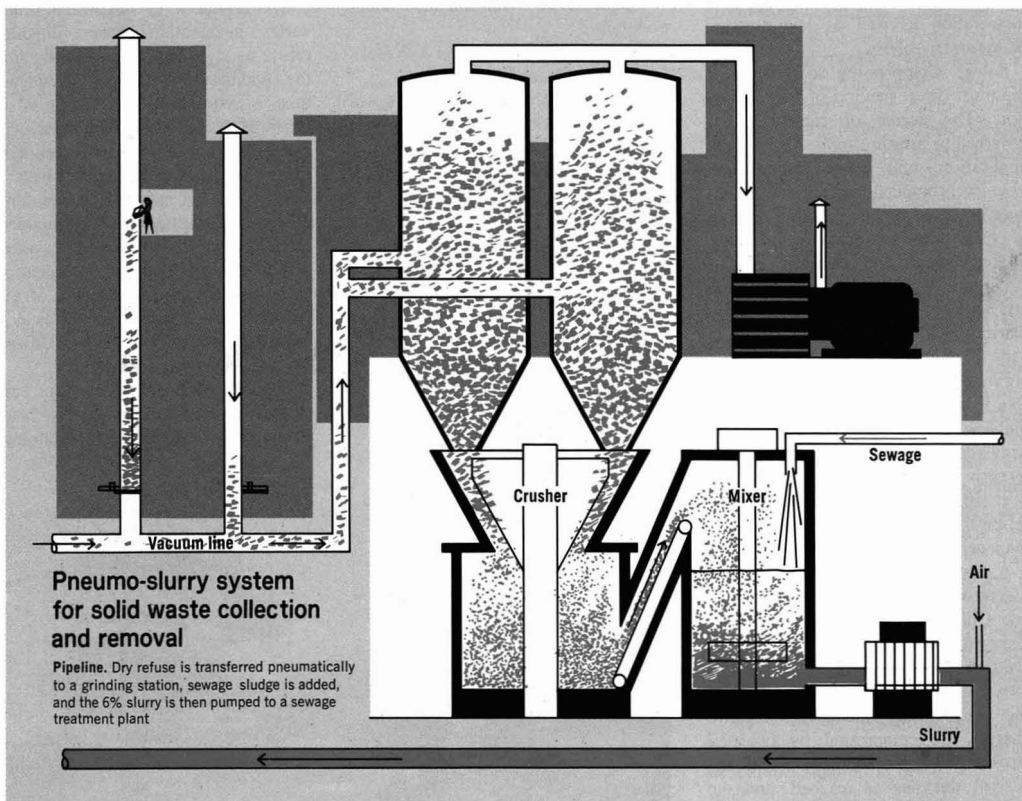
Incinerating bulky solid wastes, such as logs, crates, furniture, mattresses, and large appliances, requires either fragmentation, followed by conventional incineration, or batch incineration in specially designed furnaces. Three bulky waste furnaces are currently operating in Detroit, Mich., and Stamford, Conn.

Suspension firing is another incineration method where fuel is supported in fluid medium rather than conventional metal grates. It promotes more uniform temperature distribution, improves fuel and oxygen interaction, higher combustion rate, greater heat output, and reduces operating temperature and amount of excess air required. Suspension firing has been used widely in power and heating furnaces and for combustion of sewage sludge and certain industrial wastes, but its application to incineration and pyrolysis of municipal wastes is still under development.

(since the necessary equipment is available). Principal incineration pollutants, fly ash and carbon monoxide, are controlled by high-energy scrubbers, bag filters, and electrostatic precipitators.

High-temperature incinerators, also known as slagging incinerators, operate at 2700-3100°F. Their principal advantages are: acceptance of practically all municipal waste, bulk reduction up to 97%, complete combustion of all combustible materials, potential utilization of solid residue, and reduced air pollutant emissions. Disadvantages include: need for auxiliary fuel and fluxing agents, more rapid deterioration of refractory materials, and higher NO_x emissions.

The first U.S. high-temperature incineration pilot plant was built in 1966 by American Thermogen, Inc., in Whitman, Mass. Mixed municipal refuse undergoes partial pyrolysis and eventual combustion in the lower portion of the



furnace. Auxiliary heat is provided by oil burners; molten, noncombustible residue is quenched in water to produce an inert frit. Effluent gases burn in the upper portion of the furnace, heat a steam-generating boiler, and are purified by a wet scrubber before release. American Thermogen is constructing a slightly larger unit in Fort Meade, Md., while a 2000-ton/day facility is planned for Malden, Mass.

The Dravo/FLK system (Table III) feeds shredded refuse into a primary combustion chamber, while molten residue and gaseous effluents are discharged at the bottom. A 100-ton/day plant is operating at the Volkswagen works in Wolfsburg, West Germany. In the Torrax process, refuse is charged at the top of a vertical "gasifier" furnace, while preheated air enters at the bottom. The material in the top of the furnace is pyrolyzed, the charred pyrolysis residue drops to the bottom and is incinerated, and the molten incineration residue is drawn off and quenched. Gaseous combustion and pyrolysis effluents are burned in a secondary combustion chamber, cooled, and purified prior to release.

Three other high-temperature incinerators, the Ferro-Tech system, Sira Process, and University of Hartford (Conn.) method are currently undergoing development.

The two most common designs for waste heat recovery installations involve steam generation by a boiler located immediately after a conventional refractory furnace, or by water-bearing pipes imbedded in the furnace walls (water wall). The furnace/boiler combination is simpler and cheaper to construct, but requires 150–200% excess air introduced to prevent refractory lining damage. The second design, with more efficient heat transfer, requires only 50–100% excess air and reduces the required air pollution control equipment. Both systems make unnecessary special cooling of effluent gases to protect this equipment. Heat recovery can offset a fraction of incineration costs, if the variable heat output can be matched to a customer's variable demand.

Heat recovery with boilers is practiced in U.S. incinerators at Providence, R.I.; Atlanta, Ga.; Merrick, N.Y.; Miami, Fla.; Oyster Bay, N.Y.; Boston, Mass.; Chicago (Southwest), Ill.; and

Oceanside, N.Y. The first operational waterwall incinerator in America was constructed in 1967 at the Norfolk Naval Station (Va). Subsequent installations have been completed at Braintree, Mass.; Hamilton, Ont.; Montreal, Que.; and Chicago (Northwest), Ill. (ES&T, March 1971, p 207).

An interesting variation of incineration heat recovery involves the combustion of a $1/10$ mixture of milled refuse and pulverized coal in Union Electric's power plant suspension-fired boiler furnace (St. Louis, Mo.).

A novel waste heat recovery system is the CPU-400 (400-ton/day Combustion Power Unit), a fluidized-bed refuse incinerator that drives a turbine electric generator (Combustion Power Co., Menlo Park, Calif.), (ES&T, August 1970, p 631).

Conversion

Salvage of useful components from a solid waste stream consists of conversion, reclamation, or secondary utilization (Table IV). Conversion is defined as the chemical or biochemical transformation of a waste material into a useful product. More promising chemi-

cal conversion processes include pyrolysis, hydrogenation, wet oxidation, and hydrolysis; the biochemical processes take in composting, anaerobic digestion, and biological fractionation. Waste heat recovery is a special form of conversion. Reclamation entails removing components from the waste stream and physically reprocessing them into a form suitable for reuse. Typical applications are salvage of paper, glass, and metal scrap.

Secondary utilization involves using unaltered waste material in a new role, for example, employing municipal refuse to alter topographic features for recreational purposes, or incorporating glass cullet and fly ash in construction materials.

Pyrolysis. Destructive distillation or pyrolysis is a process for breaking down organic substances by applying heat at 1100–1800°F in the absence of oxygen. Depending on composition and operating conditions, municipal refuse could yield char, tar and pitch, light oil, organic acids and alcohols, ammonium sulfate, and gases. These products can be separated and sold or used as fuel.

A number of commercial enterprises have attempted to market their own pyrolysis systems. Thus far, no major municipal facilities have been built, but several are under serious consideration. The Lantz converter, an air-tight, insulated, cylindrical retort revolving on a slight incline, has been operating at the Ford Motor Co. plant in San Jose, Calif., since 1968. Monsanto's totally enclosed Landgard system is being considered for a 1000-ton/day plant on Staten Island, N.Y. (ES&T, April 1971, p 310). The Union Carbide Refuse Converter System converts mixed municipal wastes without prior treatment into marketable fuel gas and an inert residue that represents a 95–98% volume reduction. After Union Carbide's successful experience with a 5-ton/day pilot plant, the city of Mt. Vernon, N.Y., plans to construct a 150-ton/day demonstration plant.

An important advantage of pyrolysis is its ability to tackle plastic and rubber wastes, which are the bane of incinerators and are not readily amenable to other processing techniques. Pyrolysis of plastics, developed by Union Carbide's Chemicals and Plastics Division, converts polyolefins, polyvinyl chloride, polystyrene, and their copolymers into waxy solids, viscous liquids, or gases, depending on operating temperatures and residence time.

Pyrolysis of tires, pioneered by Fire-

stone Tire and Rubber Co. (Akron, Ohio) and the Bureau of Mines Coal Research Center (Pittsburgh, Pa.), produces a char that can be used as a filtering medium, an asphalt filler, or a smokeless fuel. A process developed jointly by Cities Service Co. and Goodyear Tire and Rubber Co. converts scrap tires into carbon black used in producing new tires.

Composting. Aerobic digestion or composting is a controlled process, where aerobic bacteria convert cellulose waste into a relatively inert humus-like material. The procedure generally requires shredding of the waste materials, removing the 25% noncompostable fraction (metals, glass, plastics, and rubber), adding water or sewage sludge, digesting for 4–6 days at 140–160°F, and curing to reduce the moisture content. There is a 30–50% bulk reduction, and the product is suitable for a soil conditioner, a base for fertilizer, or manufacture of wallboard.

Of the 20 plus composting plants built in this country since 1951, all but two or three have been shut down by shortage of markets for the products and by technical difficulties. In Europe, India, and other parts of the world, composting is more successful, reflecting a greater demand for natural fertilizers and soil conditioners.

The first U.S. composting plant, built in 1951 in Altoona, Pa., currently operates with a Fairfield-Hardy process. The compostable fraction of municipal refuse is ground in a wet pulper and turned in a digestion tank by augers

suspended from a rotating arm, while air is blown through pipes at the bottom.

The Metro process, developed by the Metropolitan Waste Conversion Corp. (Wheaton, Ill.), sorts and fragments the incoming refuse. After moisturization with sewage sludge, the material is propelled through the digestion tank by an agitating machine, while air is blown through holes in the bottom.

A comprehensive study of windrow composting was conducted by the U.S. Public Health Service and Tennessee Valley Authority with a 60-ton/day pilot facility in Johnson City, Tenn. Incoming refuse was sorted by hand and magnetically to remove noncompostable materials. The remaining fraction was ground, moisturized with sewage sludge, and digested in windrows—long banked rows turned periodically and aerated by wind action. This process is much cheaper than mechanical digestion, but takes six to seven weeks, rather than four to six days and requires a much larger land area.

The most recent, and perhaps most promising, addition to the composting industry has been the 150-ton/day Ecology, Inc., plant built in Brooklyn, N.Y. (ES&T, November 1971, p 1088). Raw refuse is shredded, and ferrous metals are removed magnetically. The remaining fraction, including noncompostable components, is shredded again and introduced into the three-story digester. Here, the refuse moves over 180-ft stacked platforms by variable-speed harrows, while nutrient content, mois-

Reduction. Three rams in this baler operate consecutively along three octagonal directions to compress 60 tons of refuse each hour into 2500–3000-lb bales



Table IV.

Conversion

COMMERCIAL

Cities Service Co.
Ecology, Inc.
Environ-Chem Systems, Inc.
Fairfield Engineering Co.
Firestone Tire and Rubber Co.
Garrett R&D Co.
Goodyear Tire and Rubber Co.
International Disposal Corp.
Metropolitan Waste Conversion Corp.
Pan American Resources, Inc.
Union Carbide Corp.

RESEARCH & DEVELOPMENT

Dartmouth College
Denver Research Institute
General Electric R&D Center
Glasgow University (Scotland)
Ionics, Inc.
Louisiana State University
New York University
Oregon State University
Rensselaer Polytechnic Institute
San Diego State College
University of California
University of Illinois
U.S. Bureau of Mines

Table V.

Reclamation

COMMERCIAL

Bigelow-Liptak Corp.
Black Clawson Co.
Ecoplastics, Ltd.
Garden State Paper Co.
Hercules, Inc.
Ilicon Corp.
Imperial Chemical Industries
Kiryoku Co. (Japan)
Owens-Illinois, Inc.
Reynolds Metals Co.
Rust Engineering Co.
Waste Conversion Corp.

RESEARCH & DEVELOPMENT

Aluminum Association
American Iron and Steel Institute
Arthur D. Little, Inc.
Aston University
Battelle Memorial Institute
Clemson University
Eastman Kodak
Franklin Institute
Glass Containers Manufacturers' Institute
IIT Research Institute
N.Y. State Environ. Facil. Corp.
New York University
Sokisui Products
Syracuse University
Texas A&M University
TRW, Inc.
University of Michigan
University of Texas (Austin)
University of Toronto
U.S. Dept. of Agriculture
U.S. Bureau of Mines
U.S. Dept. of Interior

Table VI.

Mining and mineral

Franklin Institute
IIT Research Institute
Penn. State Univ.
Stanford Univ.
Univ. of Illinois
Univ. of Notre Dame
Univ. of Utah
Univ. of Wisconsin
U.S. Bureau of Mines
Va. Polytech. Institute
West Virginia University

Table VII.

Disposal

COMMERCIAL

American Hoist & Derrick Co.
Caterpillar Tractor Co.
Clark Equipment Co.
D & J Press Co., Inc.
Hyster Co.
J. I. Case Co.
Rex Chainbelt, Inc.

RESEARCH & DEVELOPMENT

Amer. Pub. Works Assoc.
City of Madison, Wis.
City of Riverview, Mich.
City of Virginia Beach, Va.
City of Wheeling, W.Va.
Council on Envir. Quality
Dillingham Environmental Co.
Engineering Science
Franklin Institute
Geological Reclamation Operations & Wastes Systems
Grumman Aerospace Corp.
Gulf South Research Institute
Harvard School of Public Health
Hawaii Dept. of Transport
Los Angeles County
Maryland Dept. of Health
Material Disposal Corp.
Metropolitan Sanitary District of Chicago
MIT
N.Y. State Environ. Facil. Corp.
Offshore/Sea Development Corp.
Ralph Stone and Co.
Reclamation Systems, Inc.
University of California
University of Rhode Island
U.S. Dept. of Interior
West Virginia University

ture, aeration rates, and temperature are controlled carefully. After digestion, the rough compost is screened, dried, fortified with nutrients, granulated or pelletized, and packaged.

Other processes. Other chemical and biochemical conversion processes—hydrogenation, wet oxidation, hydrolysis, anaerobic digestion, and biological fractionation—apply only to cellulose waste, require prior removal of any metal, glass, or plastic fraction, and appear particularly attractive for treating agricultural wastes.

Hydrogenation converts cellulose waste into fuel oil by heating the material under pressure with water and carbon monoxide. One ton of refuse yields up to two barrels (84 gal.) of low-sulfur fuel oil. Wet oxidation converts cellulose waste into carbon monoxide, carbon dioxide, a mixture of organic acids, and a solid fibrous sludge by heating the material under pressure with water and oxygen.

Hydrolysis converts cellulose waste into fermentable sugars by heating the material with an acid at an elevated temperature. The sugars can then be fermented to produce ethyl alcohol, citric acid, animal fodder, and other useful substances. Anaerobic digestion employs anaerobic bacteria to convert cellulose waste, at an elevated temperature and in an oxygen-free atmosphere, into methane, carbon dioxide, hydrogen sulfide, and a solid residue. Methane can be used as fuel, while solid residue can serve as soil conditioner or landfill cover.

Biological fractionation is a generic term for a number of biochemical processes that employ microorganisms to convert cellulose waste into glucose and other useful products, such as single cell protein.

Reclamation

Reclamation is the base of an \$8 billion salvage or secondary materials industry dealing with the extraction and sale of valuable components from industrial and commercial wastes. Reclaiming mineral and agricultural wastes is slowly getting under way. On the other hand, reclaiming residential waste is stymied by lack of economical sorting and cleaning processes and neglect of environmental considerations in current product design practices.

Metal reclamation in general and automotive salvage in particular account for the bulk of activity in the salvage industry. In past years, ferrous scrap accounted for 50% of annual U.S. steel

production; the trend from open hearth to basic oxygen furnaces has generally reduced demand for scrap. Recovery rates for nonferrous metals are 52% for lead, 45–50%, for copper, 30% for aluminum, and 18–20% for zinc for an annual total of 3 million tons.

About 9 million automobiles, trucks, and buses are junked annually in the U.S. After replacement parts and other valuable components have been removed, the stripped hulks are landfilled or processed into steel-making scrap by baling, shredding, shearing, or incineration. Most commonly, the hulk is simply compressed for ease of shipment by a hydraulic baling press. Shredders, the most significant development in this field, process a hulk into small fragments which can be separated magnetically into pure ferrous scrap and contaminants. Shears, a relatively new innovation, cut the hulk into a 2 × 2 × 20 ft log, which is then compressed and cut into high-density slabs by a guillotine shear. Incinerating hulks to remove combustible contaminants is increasingly confined to the smokeless incinerator developed by the U.S. Bureau of Mines.

Salvage of metal cans from municipal waste is minimal, however. About 2% of discarded "tin" cans are reused as "precipitation iron" in the beneficiation of copper ore, before ultimate disposal, while reclamation of aluminum cans amounts to less than 5% of the annual production.

The glass content of municipal waste has grown in recent years with increasing popularity of nonreturnable containers, while collection at reclamation centers accounts for only 2–3% of the annual production. Numerous attempts at using cullet in road pavement and construction materials, including bricks, facing panels, and tiles, have yielded encouraging results (Table V).

Although plastics constitute only a minute fraction of today's municipal solid waste, their amount is expected to rise rapidly in the future, and their treatment and disposal are troublesome. Plastic waste reclamation is minimal and consists almost entirely of reprocessing industrial thermoplastic waste. At present, there are no practical techniques for reclaiming mixed plastic waste from the municipal solid waste stream. A number of institutions have developed plastics that degrade upon exposure to solar ultraviolet radiation or dissolve when a protective coating is breached.

Landfilling and incinerating tires and

other rubber products suffer from severe limitations similar to those of plastic goods. Reclamation of rubber scrap is favored, however, by its ease of processing over crude or synthetic stock and by the minor importance of scrap quality. Tire reclamation practices include recapping, pyrolysis, carbonization, and incorporation in asphalt pavement.

Paper products constitute the largest component (45–50%) of municipal waste, but most reclaimed scrap comes from commercial sources. The most significant recent innovation in the processing and reclamation of residential paper scrap has been a deinking process (Garden State Paper Co., Garfield, N.J.) that makes possible reprocessing discarded newspapers into new high-quality newsprint stock. The company now accounts for nearly 5% of all U.S. newsprint consumption and paper reclamation. Some residential paper waste is used in wallboard and boxboard production.

About 30% of the 1.2 million tons of textile waste generated annually in the U.S. is reclaimed, generally as wiping rags for industrial use. Cotton waste is used in manufacturing fine writing and roofing papers.

Several major solid waste salvage systems have been proposed during the past few years. One of the earliest was developed by the Bureau of Mines Metallurgy Research Center (College Park, Md.) to separate and extract useful substances from incineration residue (ES & T, July 1971, p 594).

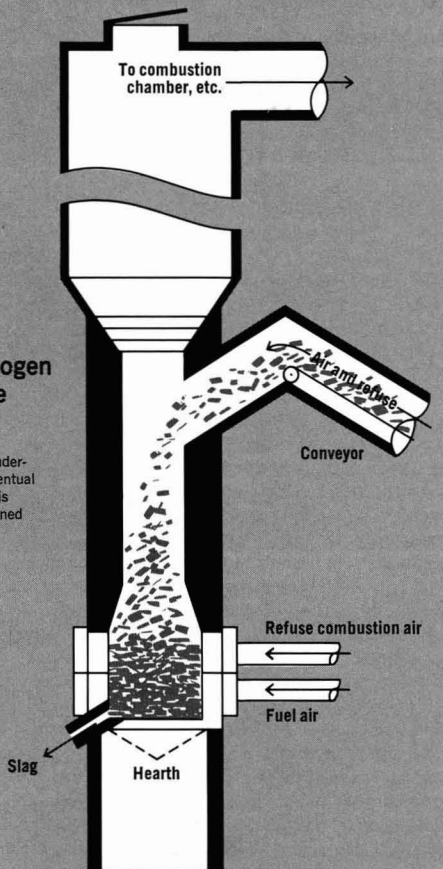
A related project at the IIT Research Institute (Chicago, Ill.) involves reclaiming residue from high-temperature incineration. Molten residue is separated into metallic and ceramic fractions at temperatures above 2800°F. The ceramic fraction can be processed into glass wool, sewer pipe, tiles, and structural blocks, while the metallic fraction can be used in manufacturing assorted metal objects.

A comprehensive, 150-ton/day solid waste processing plant was built a year ago by Black Clawson Co. (Middletown, Ohio) in Franklin, Ohio. The system accepts mixed municipal waste, except bulky items, and yields paper fiber, ferrous and nonferrous metals, a mixed glass fraction, and a combustible fraction burned in a fluidized bed furnace (ES & T, October 1971, p 998).

A 500-ton/day facility designed by Hercules, Inc. (Wilmington, Del.) for New Castle County, Del., is awaiting funding (ES & T, September 1970, p 729).

American Thermogen high-temperature incinerator

High-temperature. Refuse undergoes partial pyrolysis and eventual combustion, molten residue is recovered, and gases are burned and purified before release



Residential refuse will be mixed with sewage sludge and composted in a Fairfield digestion unit. Noncompostable organic components will be pyrolyzed. Inorganic residues will be sorted and reclaimed. Industrial and commercial wastes will be handled in a similar fashion, following a preliminary reclamation stage.

A demonstration project, designed a year ago by the Aluminum Association (New York, N.Y.) and Rust Engineering Co. (Birmingham, Ala.) to process 500 tons of refuse per day, would comprise two waterwall incinerators and one pyrolysis unit, each with a capacity of 200 tons/day. Some 60% of the refuse would be burned to generate steam. The incineration residue would be sorted to recover clear and colored glass, ferrous and nonferrous metals, and ash (ES&T, February 1971, p 109).

Also, the Environmental Facilities Park, proposed by New York State Environmental Facilities Corp., would receive all solid wastes collected in a city or several surrounding counties

and channel the various fractions to adjacent processing and manufacturing plants in accordance with expected market conditions. A typical site might comprise a central unloading, fragmentation, and sorting plant, a steel mill, a general metal processing plant, a glass container factory, a paper mill, and a pyrolysis or incineration facility.

Mining and agriculture

Mining and mineral processing wastes are generated in the U.S. at four times the rate of municipal waste, but receive less attention because they accumulate in sparsely populated areas. They include over 400 million tons of mine waste (other than overburden), nearly 300 million tons of mill tailings, 150 million tons of washing plant rejects, over 40 million tons of processing waste, and 50 million tons of slag and fly ash.

The Bureau of Mines has developed a number of processes for reclaiming mining and mineral wastes in conjunction with research institutions (Table VI), and some of these are now ex-

ploited commercially. The bureau has also succeeded in stabilizing copper, lead-zinc, and uranium tailing piles against water and wind erosion by chemical and vegetative techniques. About 20% of the fly ash generated annually by the U.S. electric power industry is utilized in various applications, while nearly all bottom ash is crushed and used for road fill and antiskid agent.

Agricultural wastes are generated at the rate nearly 10 times that of municipal waste and consist of 75% animal manure and 25% logging debris, crop residues, and food processing waste. The most common and obnoxious method of "disposal" of agricultural wastes is open burning. Animal waste may also be treated by aerobic digestion in aeration ponds, and occasionally can be used for composting and land fertilization. Efforts by the U.S. Dept. of Agriculture to cope with the problem are directed both at waste curtailment and utilization. The first approach includes development of crops that yield minimal residues or of cropping sequences that dispose of previous residues by tillage for succeeding crops. Attempts at utilization have proceeded either along the route of conversion processes described earlier or of reclamation projects (ES&T, December 1970, p 1098).

Disposal

Ultimate disposal of solid wastes generally takes place on land, as obstruction of waterways has been banned nearly everywhere and as ocean dumping has been restricted to certain types of waste. Also, the critical solid waste disposal problem facing most major metropolitan areas has less to do with the existence of sufficient disposal sites than with the political and economic obstacles to their utilization (Table VII).

Recent advances in solid waste disposal on land have been made in: landfill stabilization, land spreading, mine filling, and topographic alterations. The recent proliferation of sanitary landfills increased concern for environmental dangers of land disposal. These include generation of carbon dioxide, methane, ammonia, and hydrogen sulfide through aerobic and anaerobic decomposition; leaching of these and other contaminants by rainfall into nearby waterways and groundwater supplies; and eventual subsidence of the surface as a consequence of these two factors and mechanical consolidation. Solutions to problems of accumulating explosive and odorous gases include inserting vents and constructing bag barriers.

ENVIRONMENTAL PROBLEM-SOLVING

Efforts to prevent leaching contamination have been expanded beyond sloping of the landfill cover to placement of an impermeable lining for the site. The leachate is then collected and treated before discharge.

Mechanical consolidation in landfill subsidence can be minimized by shredding refuse and/or compaction by balers or by landfill compactors (modified tractors equipped with large blades and knob-studded steel wheels).

Land spreading of waste is an old form of composting that is well suited for treating and disposing of high organic content wastes from dairies, slaughterhouses, canneries, and paper mills, and shows considerable promise in reclaiming surface soils stripped by mining operations. The waste is applied to the top layer of soil by plow-furrowing, spray irrigation of a waste slurry, or other techniques. The material is then decomposed by soil organisms, and the residues are adsorbed on soil particles and utilized as plant nutrients.

Advantages of using strip mines for waste disposal include: existence of access roads, availability of overburden for cover, reclaiming otherwise useless land, and restoring a potential mine when raw mineral resources become depleted. A number of such proposals were all defeated by economic considerations and objections by local residents.

Solid waste disposal also presents opportunity for topographic engineering. In Wheeling, W.Va., a gap between two hills is being bridged by deposited refuse in preparation for constructing a major parkway. Recreational complexes designed around mounds of solid waste are in planning or construction phases at Virginia Beach, Va., Riverview, Mich., and Brookhaven, N.Y.

In theory, oceans offer a nearly unlimited capacity for assimilation of most wastes. In practice, this is prevented by the failure to control, treat, and distribute the wastes properly and the frequent concentration of toxic substances in the food chain. Disposal of municipal solid waste at sea can take the form of surface dispersion, bottom deposition, and wetfill. Waste discharged by surface dispersion should be either inoffensive or totally assimilable by the marine ecosystem.

Bottom deposition requires that the waste material either be denser than seawater (64 lb/ft³), or placed at a depth (~1000 ft) where the hydrostatic pressure can compact the material suffi-

ciently to render it negatively buoyant. Without ocean bottom currents, wastes do not disperse significantly and degrade very slowly. Suitable densities can be achieved by baling refuse before deposition. The Marine Sciences Laboratory of the Department of the Interior at Sand Hook, N.J., has emplaced stacks of tires, automobile hulks, large derelicts, and broken concrete slabs at several sites along the bottom of the Atlantic shelf to provide anchorage and shelter for marine life. Wetfill, or sanitary landfill in shallow or marshy coastal areas, has been a fairly well-established practice, responsible for some 17% of the land area of New York City. Appropriate allowance must be made to preserve major marine breeding grounds or migrating bird refuges, and adequate diking and sealing are essential to prevent pollution of adjacent waters.

Additional reading

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Alex Hershaft is currently employed by the Research Department of Grumman Aerospace Corp. as an in-house consultant on environmental matters. Dr. Hershaft is the founder of the Environmental Technology Seminar, Inc., a Long Island (N.Y.) professional society of scientists and engineers concerned with environmental matters.

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Role of SO₂ and Photochemical Aerosol in Eye Irritation from Photochemical Smog

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■ Measurements were made with irradiated auto exhaust and pure organic compounds to determine the influence of SO₂ and photochemical aerosol on eye irritation. Auto exhaust and mixtures of nitrogen oxides and a variety of organic compounds were irradiated in a 610-ft³ smog chamber. Response-delay and intensity measurements of eye irritation were made by seven-member panels. Exposure was through ports in the irradiation chamber. The addition of SO₂, although it increased aerosol formation, produced a decrease in eye irritation with many of the hydrocarbon/NO_x systems studied. Sulfuric acid aerosol, produced by the photooxidation of SO₂ in clean air, does not cause eye irritation. However, photochemical aerosol, generated from 1-heptene and nitrogen oxides in the absence of SO₂, does cause eye irritation. This was demonstrated in one run in which the photochemical aerosol was removed by rapid stirring. It is concluded that the effect of SO₂ is not related to changes in aerosol formation but is due to a chemical interaction which modifies the gas-phase products.

Numerous studies have investigated the influence of SO₂ on aerosol formation (Wilson et al., 1969; Wilson, 1971). A lesser effort has been devoted to other aspects of the interaction between SO₂ and photochemical smog although the effect of SO₂ on reaction rates and on NO_x and oxidant concentrations has been examined (Wilson and Levy, 1968-70; Wilson et al., 1972). This study was undertaken to determine if there was a relationship between eye irritation and SO₂ concentration. In this study, eye irritation measurements were made during several experiments with Battelle's 610-ft³ smog chamber to determine the role of SO₂ and photochemical aerosol in eye irritation.

Experimental

Eye irritation was measured by the response-delay and the intensity methods according to standard Battelle procedures (Levy and Miller, 1970) similar to that used by the Los Angeles County Air Pollution Control District (Brunelle et al., 1966). After 6 hr of irradiation, panels of seven subjects were exposed to the contents of the smog chamber through eye ports in the chamber wall. The panelists, volunteers from the Battelle staff, were screened to eliminate hypersensitive and insensitive subjects. The primary measurement of eye irritation (response-delay) was made by determining the time to irritation—i.e., the duration of exposure prior to onset of irritation. This measurement is reported in the tables as "equiv sec" (antilog of the average of the logs of the individual response-delay times). The maximum exposure time was 360 sec. The subjects also reported their response in terms of the severity of the eye irritation. The irritation was judged to be "severe," "moderate," "slight," or "equivalent to clean air."

The techniques used to measure eye irritation and the validity of the data has been reviewed by Wayne (1967) and discussed in more recent articles (Heuss and Glasson, 1968; Altshuller et al., 1969; Levy and Miller, 1970). A statistical analysis was made of the 100 runs performed at Battelle Columbus for the National Paint, Varnish, and Lacquer Association (Levy and Miller, 1970). Results of this analysis, as yet unpublished, indicated a correlation of 0.96 between reaction time and subjective severity and supported the division of eye irritation into the four categories of severity. The analysis further indicated that an individual panelist's response to the same chemical system, measured over a period of two years, was constant to $\pm 25\%$.

For this study the comparisons were made with identical panelists within a time frame of a few days. In each case the presence or absence of SO₂ or organic aerosol resulted in a change in severity class. The differences in eye irritation reported may therefore be considered highly significant without recourse to statistical interpretation.

SO₂ was measured by a coulometric technique using a Beckman 906 analyzer whose calibration was checked with permeation tubes. Oxidant was measured with a Mast ozone meter whose response to ozone was calibrated with neutral KI solution (Mast and Saunders, 1962). A dichromate scrub-

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Table I. Effect of SO₂ on Eye Irritation
Solvent, 4 ppm; NO, 2 ppm

Hydrocarbon Type	Concn ^c	NO _x ^a , concn ^c	SO ₂ , concn ^c	Equiv sec ^d	Eye irritation ^b	
					Severity index ^e	Subjective severity ^f
Propylene	9	1.5	<0.002	51	8.6	Severe
	9	1.5	1.5	109	7.0	Moderate
1-Heptene	21	1.5	<0.002	64 ^g	8.2	Severe
	21	1.5	0.1	92 ^g	7.4	Moderate
	21	1.5	0.75	170 ^g	5.3	Moderate
	21	1.5	0.75	125 ^h	6.5	Moderate
Olefin-aromatic mixture ⁱ	23.8	2	<0.002	110	7.0	Moderate
	23.8	2	0.02	112	7.0	Moderate
	23.8	2	0.05	108	7.0	Moderate
	23.8	2	0.3	108	7.0	Moderate
Exhaust from Fuel A ^j	12	1.2	<0.002	147	5.9	Moderate
	12	1.2	0.1	212	4.1	Slight
Exhaust from Fuel A ^j	8	1.1	<0.002	175	5.1	Moderate
	8	1.1	0.3	246	3.2	Slight
	8	1.1	0.75	246	3.2	Slight
	8	1.1	0.75	246	3.2	Slight
Exhaust from Fuel B ^k	8	1.2	<0.002	159	5.6	Moderate
	8	1.2	0.75	139	6.1	Moderate

^a NO_x = NO + NO₂.

^b Measured by panels of 7 or 14 people after 6 hr of irradiation unless indicated otherwise.

^c Concn in ppm (v/v) except for hydrocarbon where ppmC is given.

^d Equiv sec—antilog of the average of the logs of the individual times.

^e Based on [(360 - response time)/360] × 10.

^f Av panel response from the four categories: severe, moderate, slight, equiv to clear air.

^g Measured after 300 min irradiation.

^h Measured after 420 min irradiation.

ⁱ Composition of mixture 45% 1-butene, 7% 2-methyl-2-butene, 8% 1-heptene, 23% toluene, 7% 1,3,5-trimethylbenzene, 10% methylbutylbenzene.

^j Composition of Fuel A: 65% paraffins, 10% olefins, 25% aromatics.

^k Composition of Fuel B: 40% paraffins, 5% olefins, 55% aromatics.

ber, changed daily, was used to remove SO₂ interference (Saltzman, 1965; Miller et al., 1971) and oxidize NO to NO₂ (Wilson and Kopczynski, 1968). Light scattering was measured with an integrating nephelometer and aerosol mass was inferred from empirical light-scatter-aerosol-mass relationships (Charlson et al., 1969). Extensive tests have shown that conversion of NO to NO₂ is better than 95% complete for 4-8 hr and that all measurable SO₂ (<0.002 ppm) is removed for at least 8 hr. Scrubbers were used on all runs so that any effect on oxidant would be canceled. The Mast response was corrected for the contribution of NO₂ and NO.

Role of SO₂

In early studies at Stanford (Doyle et al., 1961) it was reported that on the addition of SO₂, slightly increased eye irritation was observed in smog chamber studies with ethylene and cyclohexene and slightly decreased eye irritation with propylene, isobutylene, 2-methyl-2-butene, and butadiene. In studies at Battelle (Wilson and Levy, 1968-70; Wilson et al., 1972), it was observed that the addition of SO₂ causes a reduction in the maximum oxidant produced in smog chamber studies with propylene, 1-butene, 1-heptene, 2,2,4-trimethylpentane, and a mixture of olefinic and aromatic compounds. With toluene, however, there was a slight increase in the maximum concentration of oxidant. The effect of SO₂ on oxidant formation, therefore, depends on the type of hydrocarbon and perhaps the hydrocarbon/NO_x ratio.

The effect of SO₂ on eye irritation is shown in Figure 1. More details are given in Table I. With the addition of SO₂ a reduction in eye irritation was observed in the runs with propylene, 1-heptene, and exhaust from Fuel A which had a composition of 65% paraffins, 10% olefins, and 25% aromatics. The addition of SO₂ had little effect on the eye irritation observed in runs with exhaust from Fuel B (40% paraffins, 5% olefins, and 55% aromatics) or with the olefin-aromatic mixture.

For runs with added SO₂, a reduction in the maximum oxidant concentration was observed with the olefins and the olefin-aromatic mix. Apparently the effect of SO₂ on eye irritation is related to the different interaction with olefinic and aromatic compounds but is not directly related to the reduction in oxidant.

Additional information on the role of SO₂, shown in Table II, was obtained in a study of the reactivity of solvents in photochemical smog (Levy and Miller, 1970). With toluene,

Figure 1. Eye-irritation index

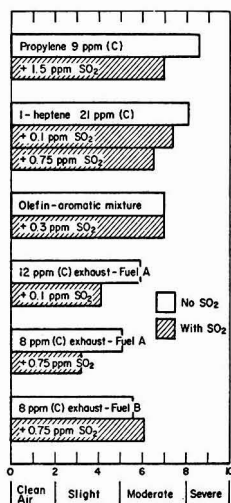


Table II. SO₂-Solvent Experiments
Solvent, 4 ppm; NO, 2 ppm

Solvent	SO ₂ , concn ^b	Eye irritation ^a			Aerosol, log units, Sinclair-Phoenix	Oxidant, max concn ^b
		Equiv sec ^c	Severity index ^d	Subjective severity ^e		
Clean air	0	292	1.9	Clean air	0.1	...
	1.6	298	1.7	Clean air	2.6	...
Toluene	0	89	7.5	Moderate	3.0	0.35
	1.3	96	7.3	Moderate	3.1	0.36
Mineral spirits (7.5% aromatics)	0	245	3.2	Slight	1.4	0.40
	1.5	196	4.6	Slight	2.8	0.43
Isophorone (cyclic ketone)	0	156	5.7	Moderate	3.2	0.71
	1.7	151	5.8	Moderate	3.1	0.63
Methyl oxide (unsaturated ketone)	0	86	7.6	Moderate	0.1	0.78
	1.8	82	7.7	Moderate	3.1	0.66
Methyl isobutyl ketone	0	134	6.3	Moderate	0.1	0.43
	1.8	216	4.0	Slight	1.1	0.36

^a Measured by panels of 7 or 14 people after 6 hr of irradiation unless indicated otherwise.

^b Concn in ppm (v/v) except for auto exhaust where ppmC is given.

^c Equiv sec—antilog of the average of the logs of the individual times.

^d Based on [(360 - response time)/360] × 10.

^e Av panel response from the four categories: severe, moderate, slight, equiv to clear air.

isophorone, and mesityl oxide, the addition of SO₂ had no effect on eye irritation although in the case of mesityl oxide there was a large increase in aerosol. In the case of mineral spirits, the slight increase in eye irritation, which is barely statistically significant, may be related to the increased aerosol. The effect of SO₂ on oxidant is similar to that noted above. A decrease in oxidant occurred when SO₂ was added in runs with nonaromatic compounds.

The interaction of SO₂ with photochemical smog is a complex process and depends on many factors including the relative humidity (r.h.) and the type of hydrocarbon (Wilson and Levy, 1969). With the 1-heptene-NO₂ system at 40% r.h. at 90-95°F, the addition of SO₂ causes a decrease of maximum oxidant and a slowing down of the reaction. Evidence of the latter effect is the increase in the time to the maximum oxidant concentration observed with added SO₂—e.g., no SO₂, 250 min; 0.1 ppm SO₂, 280 min; 0.75 ppm SO₂, 375 min. Decrease in eye irritation might be due merely to a slowing down of the reaction rather than to a change in composition of the products formed. To test this hypothesis, eye irritation was measured twice during the run with 0.75 ppm SO₂ added. Eye irritation measurements were made at 300 min for each of the three runs in the series. This was after the maximum oxidant concentration had been reached for the no SO₂ and 0.1 ppm SO₂ runs but before the oxidant maximum for the run with 0.75 ppm SO₂. (For all other runs the oxidant maximum had been reached prior to the eye irritation measurements at 300 min.) Two hours later, after the oxidant maximum, the eye irritation from the 0.75-ppm SO₂ run had increased but was still lower than that observed from the other two runs. This indicated that in the 1-heptene-NO₂ system the decrease in eye irritation with added SO₂ is due to a change in product formation.

If the reactive hydrocarbon component of a polluted atmosphere were composed primarily of olefins with only a minor aromatic component, it is possible that the presence or absence of SO₂ might result in a noticeable change in eye irritation. The effect of small changes within the range of ambient SO₂ concentrations is less certain. There appears to be little difference in the 0.1-0.75-ppm range with auto exhaust. With

1-heptene, however, there is a larger decrease in eye irritation with 0.75 than with 0.1 ppm SO₂, although in all cases the addition of SO₂ changed the eye irritation from "severe" to "moderate."

Toward the end of this study a specific ozone detector, utilizing the chemiluminescent reaction between ozone and ethylene was built (Warren and Babcock, 1970). The difference between ozone, measured by this instrument, and total oxidant, measured by the Mast oxidant meter, gives an indication of nonozone oxidant. The effect of SO₂ on nonozone oxidant from irradiated 1-butene-NO₂ is shown in Figure 2. The peak ozone and peak oxidant concentrations occur at very nearly the same time. The added SO₂ has a greater effect on total oxidant than on ozone and significantly reduces nonozone oxidant except at the peak. If the nonozone oxidant were a potent eye irritant, such as a peroxyacetyl nitrate (PAN), the effect of SO₂ in reducing eye irritation would be explained. Since PAN's are formed primarily from olefins, the lack of an SO₂ effect with aromatic systems would also be explained.

Role of Aerosol

In many of the experimental studies, eye irritation has been observed only with higher concentration of pollutants than are found in the atmosphere. It has been suggested that the lower irritation observed in smog chamber studies may be due to the lack of aerosol particles which are normally present in polluted atmospheres but are removed from the air used in smog chambers. The Stanford studies (Doyle et al., 1961) were designed to determine if the aerosol formed from SO₂ would cause increased eye irritation. However, with the addition of SO₂, several, possibly competing, influences are involved: there is a chemical interaction between SO₂ and photochemical smog; the photooxidation of SO₂ produces sulfuric acid mist; and SO₂ may possibly accelerate the photochemical formation of hydrocarbon and nitrate aerosols (Wilson et al., 1972).

An alternate method for studying the effect of photochemically generated aerosol on eye irritation is to remove the aerosol by stirring. The stirring normally used in smog chamber operations can lead to a substantial decrease in aerosol over

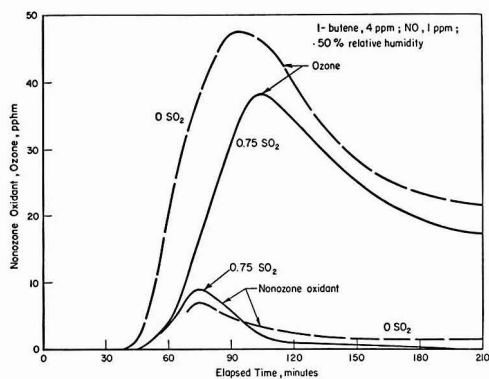


Figure 2. Comparison of ozone and nonozone oxidant profiles with and without SO₂.

that observed when the stirring fan is turned off after the lights are turned on (Wilson et al., 1971). Table III gives eye irritation measurements and other data from one set of runs in which a portion of the photochemically generated aerosol was removed by mild stirring. The 50% decrease in eye irritation response time in the run with 50% more photochemical aerosol indicated an appreciable increase in eye irritation—i.e., a change from “moderate” irritation to “severe” irritation.

It would be desirable to have sufficient data to perform a statistical interpretation. However, since each of the seven panelists reported increased eye irritation, the results strongly suggest that the aerosol formed during the photochemical reaction of 1-heptene and nitrogen oxides does contribute to eye irritation. A positive correlation between aerosol formation and eye irritation has also been observed in studies of irradiated auto exhaust (Doyle and Renzetti, 1958). In the solvent-SO₂ studies, the addition of SO₂ to mesityl oxide resulted in the formation of aerosol with no change in eye irritation. With mineral spirits, aerosol was present without SO₂ and was increased by the addition of SO₂. In this case there was a slight increase in eye irritation.

The possible eye irritation from sulfuric acid mist, generated by the photochemical oxidation of SO₂ in clean air, has been checked. The eye irritation from a run with 0.75 ppm SO₂ initially (yielding approximately 100 μg/m³ aerosol) was not statistically different from clean air. Similar results were obtained in the solvent study with 1.6 ppm SO₂ yielding approximately 600 μg/m³ of aerosol. These results, of course give no information on the possible eye irritation due to sulfuric acid absorbed on pre-existing particulate matter.

The results of Stanford studies (Doyle et al., 1961) led to the conclusion that “the aerosols formed did not increase, but on the average decreased, the eye irritation effects of the olefin-nitrogen oxide systems” (Altshuller and Bufalini, 1965). This study suggests that in contrast to sulfuric acid mist, which does not cause eye irritation, other types of photochemical aerosol may cause eye irritation. Therefore, in studies of eye irritation, care should be taken to ensure that photochemical aerosol formation is not inhibited by stirring during irradiation (Wilson et al., 1971) and that the aerosol is not removed during transfer of the irradiated air sample to the subject’s eyes. In addition, this study suggests that the reduction in

Table III. Effect of Aerosol Concentration on Eye Irritation

Initial Composition 1-Heptene/21 ppmC, NO/0.75 ppm, NO ₂ /0.75 ppm Aerosol Mass Loading and Eye Irritation		
	No stirring	Stirred at 270 rpm
Aerosol, μg/m ^{3a}	133	84
Eye irritation ^b		
Equiv sec ^c	64	112
Severity index ^d	8.2	6.9
Subjective severity ^e	Severe	Moderate

^a Estimated from light scattering measurements with an Integrating Nephelometer (Charlson et al., 1969).

^b Measured by panels of 7 or 14 people after 6 hr of irradiation unless indicated otherwise.

^c Equiv sec—antilog of the average of the logs of the individual times.

^d Based on [(360 - response time)/360] × 10.

^e Av panel response from the four categories: severe, moderate, slight, equiv to clear air.

eye irritation observed previously (Doyle et al., 1961) was due to the influence of SO₂ on the gaseous components of smog and was unrelated to the presence of aerosol.

The possible participation in eye irritation of fly ash and other inorganic particulate matter and the particulate matter emitted directly in auto exhaust are unknown. Comparing eye irritation measurements from the following smog chamber studies would be useful in determining the role of aerosols in eye irritation: auto exhaust, with and without particulate matter removed; simulated smog, with and without fly ash added; and simulated smog, with and without photochemically generated aerosol completely removed by stirring.

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Ozone-Induced Changes in Corn Pollen

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Free amino acids of corn pollen increased 50% following exposure to ozone at 3 ppm. Higher levels further enhanced amino acid and peptide accumulation and inhibited germination 40-90%. Total α -amino N, free amino acids, and ethanol-soluble peptides increased in proportion to ozone exposure. Amino acid accumulation was greatest for α -alanine, glutamic acid, and proline. Reducing and neutral sugars bound to ethanol-soluble peptides decreased. No change in the titer or composition of the sulfur-containing F3 histone was observed. The data suggest that ozone induces the autolysis of structural glycoproteins and stimulates amino acid synthesis.

In Boston and Los Angeles, peak summer concentrations of ozone (O_3) reach levels of 20 and 100 parts per hundred million (pphm), respectively (Cooke et al., 1969; Feder, 1970). Plants exposed to comparable levels of O_3 show both structural abnormalities (Thomas, 1951; Rich, 1964; Darley and Middleton, 1966) and an accumulation of amino acids and carbohydrates in the leaf (Dugger and Ting, 1970). In addition, germination of corn, petunia, and tobacco pollen is reduced, the decline is manifest both in intact plants and in isolated pollen ozonated after removal from untreated plants (Feder, 1970). In the higher plants, fertilization is accomplished by transfer of the germinative nucleus from the pollen grain to the ovule, the transfer is effected by growth of the pollen tube from the germinated grain to the ovule via the stigma and style. Since normal growth of the pollen tube is required for

fertilization, inhibition of tube development adversely affects the reproductive potential of the plant. Feder (1970) observed a reduction in the rate and magnitude of tube elongation following ozonization, at low levels of exposure the inhibition could be reversed by a return to normal environment. Since germination requires the production of protein-polysaccharide complexes from nitrogenous stores and polysaccharide depots (Stanley, 1971; Van der Woude et al., 1971), levels of amino acids and peptides have been determined in ozone-treated pollen to establish if these metabolites could serve as sensitive indices of damage from atmospheric pollutants.

The reversible inhibition of growth observed by Feder (1970) following the removal of pollen from an ozone atmosphere, suggested that a regulator of pollen tube formation was rendered temporarily nonfunctional by oxidation of an ozone-sensitive site. In this respect, the basic protein of the cell nucleus, the histones, are presumed to regulate the expression of the genetic potential of the cell by interaction with specific regions of DNA (Farmbrough et al., 1968). One of these basic proteins, the F3 histone, includes an oxidizable thiol group (Ord and Stocken, 1968). Since thiols are readily oxidized by ozone, the distribution and composition of pollen histones has been monitored during the course of ozonation in vivo.

Experimental

Corn (*Zea Maize*, var. Harvard Hybrid-dwarf) was grown in greenhouses during winter months when ozone was not detectable. Plants were grown on a steam-sterilized sandy loam, fertilized with a 15-15-15 commercial mix. The day length was maintained at 12 hr with fluorescent lighting. Growth was normal for this variety when maintained at a day temperature of 85-90°F and a night temperature of 72°F. Weekly inspections revealed no damage from pathogens or insects. The ozonated corn was grown in greenhouses in which the ozone level was maintained at 3, 6, and 12 ppm of O_3 for 5.5 hr/day for 60 days with a Welsback Ozonator Model RB-2. The

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Table I. Effect of Ozone on the Free Amino Acid Pool of Corn Pollen

O ₃ , pphm	Stage	μMoles α-amino N/0.5 gram ^a
0	ungerminated	25
3	ungerminated	38
6	ungerminated	40
12	ungerminated	49
0	germinated	12

^a α-Amino nitrogen determined on ethanol-extractable material.

ozone concentration was continuously monitored on a Mast Ozone Meter. The pollen was harvested daily, as soon as mature (at dehiscing). The tassels were shaken gently into a bag, the pollen separated from other plant debris and weighed. The untreated pollen and ozonated samples were washed by centrifugation at 3000 × g in 20 ml of a medium consisting of 0.25M sucrose, 0.25M tris buffer pH 8.0, and 10⁻³M MgCl₂ (STM medium). The supernatant was discarded and the pellet stored at -20°C.

Pollen was germinated in a petri dish on a flattened and split dialysis membrane in contact with nutrient agar and placed in a lighted growth chamber at 27°C for 2 hr. The medium consisted of sucrose (114 grams), CaCl₂ (30 mg), boric acid (100 mg), and Difco Agar (7 grams) made to 1 liter with distilled water and autoclaved. The germinated pollen was scraped from the dialysis tubing, suspended in 20 ml of STM medium and centrifuged at 3000 × g for 20 min. The supernatant was discarded and the pellet stored at -20°C. The 50-pphm O₃ sample was prepared by a single 2-hr exposure. This sample was spread uniformly on dialysis membrane on agar in a petri dish and ozonated in a plexiglass ozonating

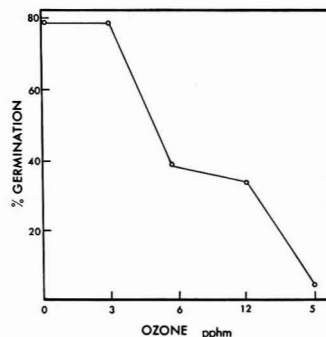


Figure 1. Effect of varying amounts of ozone on corn pollen germination

chamber, equipped with a GE ozone source. The amount of ozone was controlled by adjusting the input voltage to the bulb. The ozone was generated in a separate chamber and mixed with scrubbed air so the rate could be maintained at a 1./min at 27°C.

The pollen was thawed and homogenized in 20 ml of STM medium, then ground for 4 hr in a ball mill with stainless steel balls (2-mm diam) at 0°C. The process of cell breakage was followed microscopically. The fragmented cells were filtered through two layers of Miracloth (Chicopee Mfg. Co., New York, N.Y.), and the filtrate was centrifuged at 4000 × g for 30 min. The supernatant was lyophilized and extracted with 70 ml of 95% ethanol at 80°C for 30 min. The hot solution was filtered through a fine frit and concentrated to 5.0 ml in a flash evaporator at 50°C. Further extraction of the lyophilized supernatant or the pollen residue failed to increase the amino acid, carbohydrate, or peptide recovery significantly.

The free amino acids and peptides were isolated by ion exchange chromatography on a column of Dowex 50 × 8 (H⁺), 1 × 20 cm. The uncharged carbohydrates were removed from the column with water, and the free amino acids, peptides, and

Table II. Effect of Ozone on Amino Acid Composition of Corn Pollen

Amino acid	Ungerminated								Germinated	
	O ₃ , pphm								0	
	0		3		6		12		Per 0.5 gram	Per μmole α-amino N ^a
Asp	trace ^b	trace	0.28	0.73	0.16	0.40	0.57	1.16	0.14	1.14
Thr	0.79	3.18	1.3	3.42	1.15	2.87	1.47	3.00	0.52	4.35
Ser	1.14	4.56	2.9	7.63	2.19	5.47	2.20	4.48	1.13	9.41
Glu	0.98	3.99	0.56	1.47	0.57	1.43	2.67	5.44	0.23	1.87
Pro	23.5	94.0	27.4	72.1	29.3	73.15	32.0	65.3	6.95	57.9
Gly	0.76	3.02	0.52	1.36	0.64	1.60	0.93	1.88	0.31	2.60
Ala	0.79	3.16	1.49	3.92	1.44	3.60	5.0	10.20	0.57	4.88
Cys/2	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace
Val	0.76	3.02	0.74	1.84	0.70	1.75	0.75	1.53	0.40	3.33
Met	0.29	1.14	0.14	0.36	0.17	0.43	0.17	0.35	0.08	0.66
Ile	0.36	1.45	0.42	1.10	0.40	1.0	0.42	0.86	0.26	2.19
Leu	0.53	2.12	1.01	2.65	1.03	2.57	0.75	1.53	0.62	2.19
Tyr	0.19	0.74	0.35	0.92	0.28	0.71	0.25	0.51	0.20	1.66
Phe	0.54	2.16	1.05	2.76	1.72	4.30	0.93	1.88	0.41	3.42
Lys	trace	trace	trace	trace	0.12	0.30	0.30	0.61	0.07	0.60
His	trace	trace	0.19	0.50	0.35	0.86	0.75	1.53	trace	trace
Arg	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace

^a Values in μmoles × (10⁻³).

^b Trace indicates less than 0.06 μmole/0.5 gram.

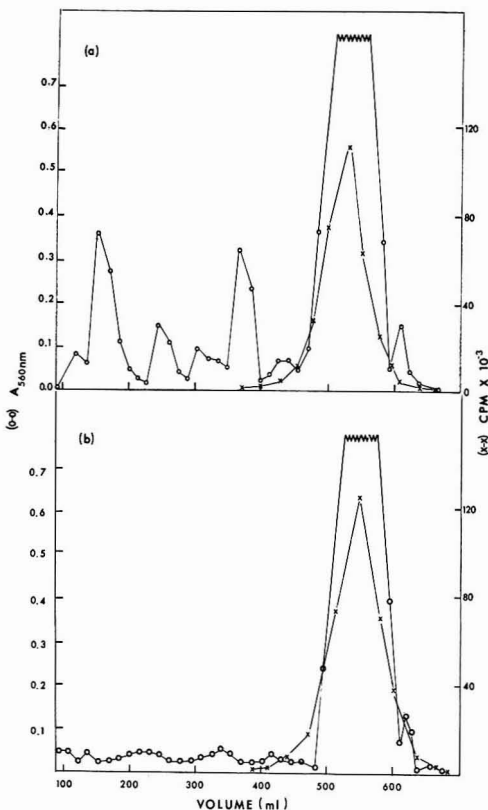


Figure 2. Chromatography of ungerminated corn pollen ethanol-soluble peptides and amino acids on a Bio Gel P-2 column (2 × 150 cm)

Extract contains added ^{14}C -leucine as an amino acid marker. Peptides and amino acids were eluted with 0.02M pyridinium acetate, pH 4.3, at room temperature; (a) ozonated at 12 pp hm, (b) no ozone exposure

glycopeptides were eluted with 1M ammonium hydroxide. The ammonium hydroxide was removed by three cycles on a flash evaporator at 50°C with addition of 1% piperidine. Peptide and amino acids present in the ethanol extract were separated by column chromatography on Bio-Gel P-2 (2 × 150 cm). Elution was carried out with 0.02M pyridinium acetate buffer, pH 4.3; the sample contained ^{14}C -leucine as an internal standard for identification of the free amino acid peak. Histones were isolated from pollen chromatin by the method of Farmbrough et al. (1968). Separation of individual histones was effected by chromatography according to Farmbrough and Bonner (1966). Amino acids in each fraction were determined after hydrolysis in sealed tubes in 6N HCl at 105°C for 18 hr in an atmosphere of N_2 .

Radioactivity was measured with a Packard Model 3320 Tri-Carb Scintillation Spectrometer using the naphthalene-dioxane system of Bray (1960). Amino acid analysis was performed according to Spackman et al. (1958). Reducing sugars associated with glycopeptide fractions were assayed with ferricyanide (Park and Johnson, 1949). Neutral sugars were assayed by the phenol-sulfuric method (Dubois et al., 1956). Glucosamine, a ninhydrin-positive sugar, was determined with the amino acid analyzer. Pentoses were assayed by the

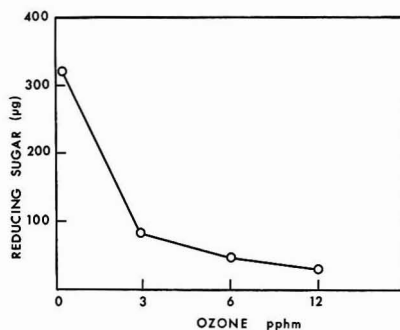


Figure 3. Effects of ozonation on reducing sugars bound to Dowex-50 cation exchange resin

orcinol method (Mejbaum, 1939). Total free amino acids were determined as α -amino N (Rosen, 1957) using leucine as a standard.

Results

Amino Acid Analysis. In the course of a decline in germination, the total free amino acids showed a significant increase on ozonation (Figure 1 and Table I). At 12-pp hm O_3 , amino N increased from 25 to 49 μmoles per 0.5 gram pollen. In the absence of O_3 the level declined to 12 μmoles during an equivalent period of germination. The free amino acid composition of corn pollen is presented in Table II. In general, levels increased with ozone concentration, especially at the 12-pp hm level. At lower doses, only certain amino acids were enhanced. At 12 pp hm, for example, the amino acids which increased (in $\mu\text{moles}/0.5$ gram) were alanine 0.79 to 5.0; proline 23.5 to 32; aspartic acid <0.06 to 0.57; threonine 0.8 to 1.2; serine 1.1 to 2.2; and glutamic acid 0.99 to 2.7. Valine, methionine, isoleucine, leucine, tyrosine, and phenylalanine increased slightly. Total α -amino N values compared with summed ninhydrin values obtained from the amino acid analyzer showed recovery was quantitative.

Ethanol-soluble peptides and free amino acids were fractionated by chromatography on Bio-Gel P-2 (Figure 2). The results showed that the ungerminated pollen contained small amounts of ethanol-extractable peptides compared to ozonated samples. The elution patterns of untreated germinated samples were identical to those of ungerminated, unozonated material. The peaks at 170 and 380 ml represent material of mol wt 2000 and 500, respectively, as determined from the yield of α -amino N on hydrolysis.

Reducing Carbohydrates. While the ungerminated and germinated samples contained high amounts of reducing sugars bonded to peptides, exposure to 3 pp hm of O_3 resulted in a fourfold decrease in peptide-bound hemiacetals, followed by a lesser rate of decline (Figure 3). Similarly, ozonated samples showed a threefold decrease in peptide-bound neutral sugars which include hexoses and uronides involved in glycosidic linkages (Table III). These changes were characteristic of specific glycosyl residues, rather than the carbohydrate pool in general. Pentoses bound to peptides and free glucosamine, for example, remained constant with ozonation.

Histones. Chromatography of the basic proteins on a carboxylic cation exchange resin, IRC-50, established the identity of the corn pollen histones with those of calf thymus and pea cotyledons (Farmbrough et al., 1968) Well-defined peaks cor-

Table III. Effect of Ozone on Carbohydrates Retained as Glycopeptides on Dowex-50^a

O ₃ , pphm	Stage	Per 0.5 gram	Per mg peptide
0	ungerminated	380	118
3	ungerminated	110	22
6	ungerminated	140	27
12	ungerminated	145	23
0	germinated	405	253

^a Determined by phenol-sulfuric assay on ethanol-extractable material.

responding to the F1, F2a, F2b, F3a, and F3b components were observed. Histones from ozonated pollen were indistinguishable from controls with respect to the number or amount of individual components. The amino acid composition of the arginine-rich and thiol-bearing pooled F3 histones is presented in Table IV. Although the cysteine and the disulfide (half cysteine) titer was unaffected by exposure to ozone, a decline in the levels of tyrosine and phenylalanine and an increase in valine and serine was recorded. The amino acid composition of the remaining histones, F1, F2a, and F2b, was essentially the same in the presence and absence of ozone.

Discussion

The results indicate an increase in α -amino N during development of the corn pollen grain in the presence of ozone. Similar findings were obtained with petunia pollen (Lipke et al., 1970) and with excised cotton leaves (Dugger and Ting, 1970). The biochemical changes were evident before development was affected, since a low level of ozone (3 pphm) sufficient to increase free amino acids did not reduce germination (Figure 1 and Table II). The ozone-dependent decrease in germination with higher exposure levels was accompanied by increased titers of specific members of the free amino acid pool. The increase in serine, for example, suggests either pathways of serine synthesis are stimulated or serine utilization is inhibited. In addition to serine, alanine, glycine, and threonine levels increased on ozonation. Inhibition of the tricarboxylic acid cycle by ozone would result in the accumulation of pyruvate and phosphoglycerate, which in turn would eventually appear as the above amino acids via transamination. The failure of the pollen tube to grow would contribute further to the accumulation of amino N via an arrest of protein synthesis.

Possible explanations for the increase in peptides and free amino acids must consider at least two types of injury, one occurring at low exposure levels which is reversible, and a second, more severe lesion appearing at higher doses accompanied by a more permanent developmental arrest. At low levels of O₃ the effects mentioned above may be operative. In samples ozonated at high levels, on the other hand, peptides and amino acids may accumulate as a result of the activation of cathepsins and other hydrolytic enzymes from lysosomes or similar bodies as a result of ozone action. Electron microscopy supports the latter proposal, showing autolysis of cell wall glycoprotein at the exine-intine interface following ozone treatment at 12 pphm (Harrison and Mumford, 1971). With respect to the increase in free proline, this amino acid serves as a precursor of hydroxyproline residues in the wall glycoprotein. More recent studies, to be reported elsewhere, show that

Table IV. Amino Acid Composition of Corn Pollen Histone F3^a

	Pphm O ₃		
	Ungerminated	Germinated	Ungerminated
	0	0	12
Asp	7.2	7.4	7.3
Thr	4.2	4.4	5.1
Ser	4.4	4.0	7.2
Glu	11.0	11.4	8.4
Pro	4.3	4.0	4.2
Gly	11.2	11.5	12.6
Ala	9.4	9.1	9.8
Cys-SH	0.24	0.18	0.22
Cys/2	trace	trace	trace
Val	3.2	3.5	5.6
Met	0.11	0.11	0.15
Ile	2.5	2.7	3.1
Leu	6.2	6.0	6.5
Tyr	2.0	1.7	trace
Phe	2.9	2.8	0.4
Lys	18.9	18.5	19.5
His	1.4	1.6	1.2
Arg	10.1	10.5	10.2

^a Compositions expressed as moles per 100 moles of total amino acids recovered.

the peptide pool formed as a consequence of ozone action is enriched with respect to proline and hydroxyproline.

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Characterization of Naturally Occurring Dissolved Organophosphorus Compounds

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■ By growing pure algal cultures of *Chlamydomonas reinhardtii* under CO₂-enriched conditions, high levels of soluble organic phosphorus were obtained with accompanying low residual orthophosphate. Concentration and characterization techniques developed with the pure-culture dissolved organic phosphorus compounds were applied to natural lake water samples with only slight modifications. Molecular Sieve studies showed that up to 20% of the recoverable organic phosphorus is high-molecular-weight material (mol wt \geq 50,000). In most cases, a sizable percentage of the high-molecular-weight fraction appeared to be deoxyribonucleic acid (DNA) or its fragments. Special culture studies employing dual chamber vessels divided by 0.22- μ membranes substantiated the natural origin of the soluble organic phosphorus compounds in general and specifically DNA and other high-molecular-weight components.

Phosphorus is present in natural waters in both dissolved and particulate forms, the complete distinction between which is operational (Olsen, 1967). The greater proportion of particulate phosphorus in natural waters is associated with biological matter (Hutchinson, 1957; Pomeroy, 1963; Rigler, 1964) though not all organically bound particulate phosphorus is readily solubilized or rapidly degraded to orthophosphate (Grill and Richards, 1964; Foree and McCarty, 1968; Jewell and McCarty, 1968). Some of it will accumulate as refractory forms in bottom deposits where slow release may occur.

Dissolved organic phosphorus compounds (DOP) are present in natural waters and can represent significant proportions of the total phosphorus content of the water. Rigler (1964) has reported that 15–30% of the total phosphorus in lakes can be present as dissolved organic forms. At times, these compounds may represent greater than 90% of the soluble phosphorus in a lake, particularly during the summer periods of high biological activity. Yet, the mechanisms of release and/or formation of these compounds in the complex natural environment is not clear because the nature of these compounds is ill-defined.

In addition to little being definitely known about the chemical nature of soluble organophosphorus compounds, there has been evidence that the operational distinction between orthophosphate and other forms may much less closely approximate the conceptual distinction than previously was thought. It has been reported that current analytical techniques may overestimate orthophosphate concentration by one or two orders of magnitude. (Kuenzler and Ketchum, 1962; Rigler, 1968; Chamberlain and Shapiro, 1969).

The interrelationships of the various phosphorus forms in natural waters are referred to collectively as the phosphorus

cycle. The highly dynamic nature of this cycle has been established for some time as the result of radiophosphorus tracer studies (Coffin et al., 1949; Rigler, 1956, 1964; Harris, 1957; Hayes and Phillips, 1958; Watt and Hayes, 1963). Thus, the instantaneous concentrations of the various forms are complex functions of chemical, physical, and biological parameters and are likely pseudosteady-state values in dynamic equilibrium.

Figure 1 illustrates the possible pathways to and from the DOP pool. Although it is likely that all of these mechanisms are involved to some extent, the buildup of DOP in natural waters has been associated with the presence of phytoplankton blooms for many years. Pratt (1950) and Anita et al. (1963) attribute the DOP buildup to healthy algae. Others, such as Ansell et al. (1963) have stated that this buildup results from unhealthy and dead algae. Recently, Kuenzler (1970) has demonstrated that pure axenic marine algal cultures are capable of direct excretion of organic phosphorus compounds, the amounts excreted varying with the particular species and with the environmental conditions imposed. Others have reported the buildup of DOP in axenic algal cultures in the absence of light under both aerobic (Jewell and McCarty, 1968) and anaerobic (Foree and McCarty, 1968) conditions.

Better understanding of the exact nature of dissolved organophosphorus compounds should provide insight into determining their source and mechanism of origin, their exact role in the phosphorus cycle, and assist in clarification of orthophosphate analytical determinations since the extent to which hydrolyzable organic phosphorus contributes to the apparent orthophosphate measurement on a natural water sample is unknown. There is evidence that this contribution may be quite large (Rigler, 1968; Chamberlain and Shapiro, 1969).

Experimental

Samples. Two sources of DOP were used in this study. Pure algal cultures of *Chlamydomonas reinhardtii*, a green alga, were grown in large-volume batch cultures under axenic conditions, 24-hr illumination, constant temperature of 25°C and 2% CO₂-enriched atmosphere. The growth medium, listed in Table I, was completely inorganic with the exception

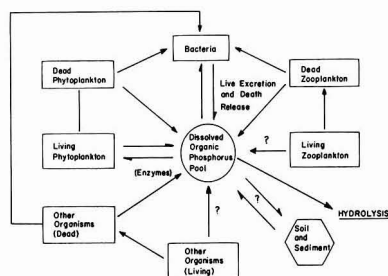


Figure 1. Summary of various possible input and output mechanisms for the DOP pool in natural waters

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Table I. Basic Growth Medium used for *Chlamydomonas reinhardtii* Cultures

Salt	Medium concn	
	mg/l.	mM
NaNO ₃	8.5	0.5
MgSO ₄ ·7H ₂ O	24.65	0.1
KH ₂ PO ₄	27.2	0.2
NaOH	6.4	0.07
NaCl	175	3.0
FeSO ₄ ·7H ₂ O	6.2	0.0224
Na ₂ EDTA	6.5	0.0224
NaOH	2.7	0.067
H ₃ BO ₃	1.854	0.03
ZnSO ₄ ·7H ₂ O	0.287	0.001
MnCl ₂ ·9H ₂ O	1.98	0.01
Na ₂ MoO ₄ ·2H ₂ O	0.242	0.001
CuSO ₄ ·5H ₂ O	0.0499	0.0002
Co(NO ₃) ₂ ·6H ₂ O	0.291	0.0001

of sodium EDTA. A schematic of the culture system is shown in Figure 2.

Natural water samples were taken from three separate lakes. One lake was sampled four times over a five-month period, while single samples only were taken from the other two lakes. The characteristics of the individual lakes are summarized in Table II. The level and distribution of phosphorus forms for each sample are indicated in Table III. DOP represented 35–94% of the soluble phosphorus. Total phosphorus data were available for the Moses Lake samples only. The relationship between DOP and the total phosphorus and total soluble phosphorus are in agreement with Rigler's (1964) observations.

Processing of Samples. In view of the highly dynamic nature of the DOP pool, a procedure was devised which would allow concentration of the DOP while assuring minimum chemical and biological alteration of the sample. For the culture systems, gentle separation of the major portion of solids preceded 0.45- μ membrane filtration, the solubility criterion. This pretreatment consisted of centrifugation at 1000 rpm followed by rough filtration through Fiberglas prefilters (Millipore Corp.). The filtrate was quick-frozen in bulk in a Dry Ice-acetone bath and stored until direct lyophilization could be carried out with a Virtis Model 10-200 Freeze Drier and Precision Scientific Model 75 vacuum pump. The isolated dissolved solids could then be stored under vacuum at -10°C until concentrated solutions were obtained by resolution in aqueous systems. Direct extraction of the solids with distilled water or aqueous bases afforded concentration factors of up to 100 and absolute concentrations of 50 mg/l. of DOP phosphorus.

A similar procedure was used for the natural water samples

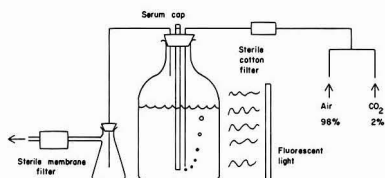


Figure 2. Schematic of the batch algal culture growth apparatus for large volume cultures

Table II. Selected Chemical Characteristics of the Lakes Sampled

	Moses Lake (Sylvester and Oglesby, 1964), mg/l.	Pine Lake (Welch et al., 1970), mg/l.	Lake Washington (Edmonson, 1970), mg/l.
K ⁺	14		1.1
Na ⁺	39–63	3.2–4.5	4.6
Ca ²⁺	20–33	2.8–3.2	8.8
Mg ²⁺	13–24	1.2–1.7	3.3
Cl ⁻	12–14	1.7–3.3	3.8
SO ₄ ²⁻	24–26	5.0–8.0	8.2
HCO ₃ ⁻	140–196	8.0–10.8	40

with slight modification. For on-site processing and for large volumes of water, centrifugation proved impractical and was omitted. An additional ion exchange step was inserted after 0.45- μ filtration to convert free calcium and magnesium ions to sodium ions since these ions would likely interfere with resolution of DOP compounds in concentrated solution.

For the Moses Lake solids, it was found that direct extraction of the solids with distilled water would remove most of the orthophosphate but only 40% of the extractable DOP. Subsequent extraction with 0.1N NaOH would recover the remaining DOP, now representing 85–100% of the phosphorus in the solution. Concentration factors for DOP up to 100 \times were obtained for Moses Lake samples, 140 \times for the Lake Washington sample, and 240 \times for the Pine Lake sample. Absolute concentrations greater than 4–5 mg P/l. DOP did not seem to be available even with increased solids-to-volume ratios. Overall recoveries of total phosphorus on all lake samples ranged from 60 to 90% of calculated quantities. Values for successive extractions were combined.

Analyses. Orthophosphate was determined by the single-solution method of Murphy and Riley (1962). Organic phosphorus was converted to orthophosphate by potassium persulfate oxidation in an autoclave based on procedures of Menzel and Corwin (1965). Readings were made either on a Beckman D.U. or a Hitachi, Perkin-Elmer 139 spectrophotometer at 885 nm. Light paths were 1 or 10 cm, depending on concentration range.

Chlorophyll *a* and total pigment were determined by the fluorescence method of Strickland and Parsons (1968). Readings were made on a Turner 110 fluorimeter.

DNA analyses were made directly on high-molecular-weight isolates using the method of Kissane and Robbins (1958) with reagent proportions given by Strickland and Parsons (1968) but without the extraction sequence. Readings were made on a Baird Atomic SF-1 Fluoriscpec Fluorescence Spectrophotometer. Excitation was at 420 nm and fluorescence measured at 520 nm.

Molecular weight distribution of the extractable DOP compounds was investigated using gel filtration on Sephadex G-75 columns. Upward flow techniques were employed, using a Sephadex K 50/100 column and a gel height of 80 cm (Determann, 1969). Fractions were collected with a Warner-Chilcott Model 1250 automatic fraction collector. The void volume was determined with Blue Dextran 2000. Elution position from the column is expressed as a reduced parameter, *R*, which is the elution volume divided by the void volume. For the G-75 gel, *R* can be related to the molecular weight by

$$\log_{10} \text{mol wt} = 5.729 - 1.030 R_{75}$$

Table III. Phosphorus Forms and Levels for the Lake Samples at Time of Sampling

Lake and date	Soluble P, $\mu\text{g/l.}$			% Organic ^a	Total P, $\mu\text{g/l.}$	% DOP ^b
	Total	Ortho	Organic			
Moses Lake 1 (7-30-69)	80	30	50	62	188	27
Moses Lake 2 (8-29-69)	161	85	76	47	186	41
Moses Lake 3 (10-15-69)	107	70	37	35	187	20
Moses Lake 4 (12-18-69)	93	43	50	54	118	42
Pine Lake (5-9-70)	9.1	1.2	7.9	87
Lake Washington (5-24-70)	14.1	0.9	13.2	94

^a % of the soluble phosphorus which is organic.

^b % of the total water phosphorus which is present as soluble organic phosphorus.

where this relationship holds strictly only for dextrans (Pecsok and Saunders, 1966; Anderson and Stoddart, 1966; Determann, 1969). For the data presented in this paper, the above relationship has been applied to assign approximate molecular weights and should be viewed as only that.

Results and Discussion

For the pure culture systems, when orthophosphate was present in considerable excess, DOP levels up to 500 $\mu\text{g P/l.}$ were obtained after 15 days growth. Cultures 1 and 2 in Table IV behaved in this fashion. After 15 days, the DOP level remained fairly constant in the 350–500 $\mu\text{g/l.}$ range over the 81-day period. Although high DOP levels are desirable, particularly when the organic phosphorus can be separated from the orthophosphate, when both forms are present, if orthophosphate concentrations are extremely high the precision of organic phosphorus results will be poor. Therefore, increased DOP-orthophosphate ratio was sought. The data of Table IV show that reduction of the initial orthophosphate concentration would increase the ratio at the expense of the absolute DOP levels, illustrated by cultures 3 and 4. Increasing the initial orthophosphate to a level sufficient to provide a small but definite residual above complete uptake of orthophosphate seemed to accomplish the desired effect. Under the condition of a slight residual of orthophosphate, it is logical that less turnover from the DOP pool would be required to meet the system's phosphorus needs and the steady-state DOP would increase. This is illustrated by cultures 5–7 which represent a compromise between absolute DOP levels and a high DOP-orthophosphate ratio.

Molecular Weight Distribution. Elution profiles for the algal culture, extractable DOP on Sephadex G-75 were all similar. A representative profile is given in Figure 3 and nearly identical results were obtained when distilled water and 0.1N NaOH were used as the extracting solvent. Essentially two peaks resulted at or near the extremes of the G-75 gel with relatively small quantities of organic phosphorus appearing between these peaks. Thus most of the DOP had an apparent mol wt of 2500 or less and of that material remaining, the greater portion had a mol wt of 50,000 or greater.

Further fractionation of one isolated low-molecular-weight fraction ($R_{75} \geq 2.3-2.9$), Figure 4, indicates that a range of

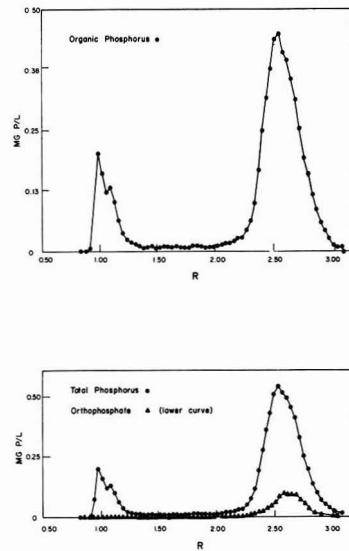


Figure 3. Elution profiles on Sephadex G-75 for phosphorus forms extractable from isolated *Chlamydomonas reinhardtii* soluble solids with 0.1N NaOH (origin, Cr 5)

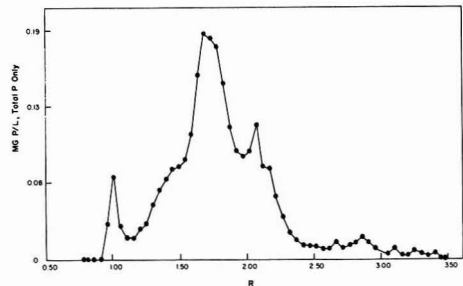


Figure 4. Elution profile of Sephadex G-75 low-molecular-weight phosphorus rechromatographed on Sephadex G-25

Table IV. Soluble Phosphorus Distribution and Level in Various Unialgal *Chlamydomonas reinhardtii* Cultures

Culture no.	Initial P concn, mg/l.	Soluble phosphorus concn, mg/l.				Days cultured
		Total P	Ortho P	Organic P	% Organic P	
Cr 1	6.2	2.3	1.8	0.5	21.8	15
Cr 2	6.2	4.84	4.37	0.47	9.7	81
Cr 3	3.0	0.085	0.004	0.081	95.0	27
Cr 4	2.3	0.077	0.005	0.072	93.5	13
Cr 5	4.6	0.206	0.037	0.169	82.0	12
Cr 6	4.5	0.193	0.026	0.167	86.5	14
Cr 7	4.5	0.177	0.010	0.167	94.4	9

different molecular weights is present for the lower-molecular-weight DOP components. Passage of one isolated G-75 high-molecular-weight peak through the G-100 gel indicated that most of the high-molecular-weight phosphorus was excluded from this gel.

The extractable DOP from the lake samples exhibited behavior similar to that of the algal culture DOP on the Sephadex G-75 gel. Representative results of the Moses Lake distilled water extract and 0.1N NaOH extract samples are given in Figure 5. Figure 6 contains the profiles for the Pine Lake and Lake Washington NH₄OH-extractable DOP. Two peaks occurred, one at each extreme of the gel for most of the samples, similar to those of the algal culture DOP. In all cases, high-molecular-weight phosphorus was present in the sample. The distilled water extracts of Moses Lake samples and the NH₄OH extracts of the other two lakes contained a sizable amount of intermediate-molecular-weight material (assigning the excluded peak as high molecular weight in a relative sense).

The Moses Lake 0.1N NaOH extracts, which were preceded by the distilled water extracts, contained little intermediate molecular-weight DOP. The base extractions were carried out at room temperature for a minimum of 1 to 2 hr as opposed to 30 min contact time at 1° to 2°C for the distilled water extractions. Thus the intermediate-molecular-weight compounds could have been degraded by base hydrolysis or they may simply have been readily water soluble.

Data for various elution profiles of algal culture and lake water DOP on Sephadex G-75 are summarized in Table V.

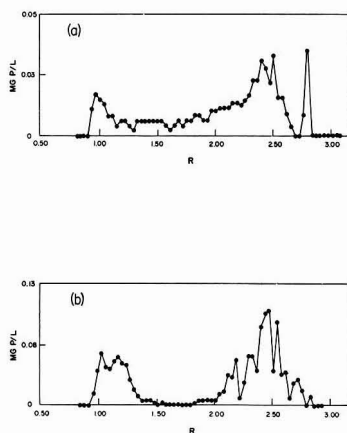


Figure 5. Elution profiles of Moses Lake #2 DOP on Sephadex G-75
(a) Distilled water-extractable DOP; (b) 0.1 NaOH-extractable DOP following distilled water extraction

The data are expressed as the cumulative percent of the total eluted DOP which has been eluted to the point indicated. The lake base extracts were essentially all DOP when applied to the column. But extensive hydrolysis to orthophosphate occurred in most of these samples on passage through the column, thus a more meaningful representation is obtained by tabulating percent of the total phosphorus eluted from the column for these samples. The molecular weight values assigned to each grouping were determined from the relationship presented earlier for dextrans.

The first column, $R \leq 1.2$, actually corresponds to the range expected for a peak centered at $R = 1.0$, material completely excluded from the column. For the algal culture DOP, 15 to 20% of the extractable DOP was in this category. Only slightly more material is included in the range of $R \leq 1.4$, which, generally, entirely included the high-molecular-weight peak.

For the lake samples, 7-20% of the extractable DOP was excluded from the G-75 gel and again somewhat higher values were obtained for $R \leq 1.4$. These ranged from 10-20% generally, but a few samples were around 30%.

The last column, $R \leq 2.4$, represents the point where orthophosphate will normally just begin to elute from the column. For most of the samples, 30-70% of the DOP had eluted from the column, prior to the elution of orthophosphate, indicating this material was generally of apparent mol wt greater than 1000.

Since the total extracted phosphorus and the extracted DOP were always less than 100% of theoretical, extrapolation back to original solution conditions allows only computation

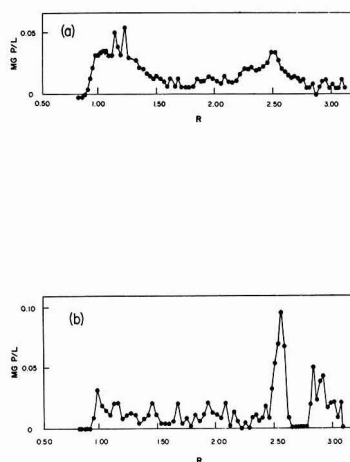


Figure 6. Elution profiles of direct NH₄OH-extractable DOP on Sephadex G-75 for (a) Pine Lake and (b) Lake Washington solids

Table V. Summary of the Percent Distribution of DOP in Various Molecular Weight Groupings for the Extractable DOP Compounds of Pure Algal Cultures and Natural Lake Samples on Sephadex G-75

(Cr = algal culture systems; ML = Moses Lake samples)

Sample	R, 1.2 (MW, 31,000)		R, 1.4 (MW, 20,000)		R, 1.0 (MW, 4,600)		R, 2.4 (MW, 2,400)	
	% Total P	% DOP	% Total P	% DOP	% Total P	% DOP	% Total P	% DOP
Cr 2, H ₂ O		14.7		15.0		15.3		17.0
Cr 4, NH ₄ OH		20.1		22.5		28.0		43.1
Cr 5, NH ₄ OH		15.4		16.5		19.5		32.2
ML-1 base only		23.8		28.2		46.1		59.2
ML-1 base only		22.5		23.4		25.6		29.6
ML-1 base only		19.3		20.9		24.5		31.0
ML H ₂ O		10.0		13.6		25.6		38.0
ML-2a H ₂ O		11.4		14.7		23.1		43.4
ML-2a base	14.5		15.7		19.9		69.3	
ML-2b H ₂ O		21.8		24.5		38.5		68.2
ML-2b base	13.2		15.6		40.1		76.2	
ML-0.1 μ H ₂ O		14.7		20.1		37.1		65.1
ML-0.1 μ base	10.3		13.8		15.8		39.8	
ML-3 H ₂ O		17.8		22.9		43.5		79.4
ML-3 base	6.9		7.6		12.8		62.1	
ML-4 H ₂ O		19.3		29.0		54.8		76.5
ML-4 base ₁	10.4		13.0		22.6		30.7	
ML-4 base ₂	8.0		9.1		13.5		48.0	
ML-4 base ₃	6.6		7.4		7.6		22.6	
Pine Lake (NH ₄ OH)	19.9		31.7		47.2		62.9	
Lake Washington (NH ₄ OH)	8.3		11.0		20.5		25.8	

of minimum values. The actual values could be somewhat higher. Now, on this basis, at least 7-13% of the DOP in the original culture solutions was of apparent mol wt $\geq 30,000$. Similar calculations for the lake samples indicated that at least 5-14% of the natural lake water DOP was of this molecular weight.

DNA Analyses. The high-molecular-weight peaks were isolated and analyzed for DNA content. To allow back calculation to original sample solutions, data were recorded for the volume of sample freeze-dried, the resulting solids, weight of solids extracted, volume extracted, volume applied to the column, and the concentration of DOP in the extracted sample. Since recoveries were less than 100% and the possibility of differential extraction efficiencies for different compounds exists, calculations then must again be considered as the minimum possible values. The actual values may, in fact, be considerably higher. Data for estimated original solution concentrations of DNA are given in Table VI for algal culture and lake samples. For the algal cultures analyzed, minimum values of 34-38 μg DNA/l. present as dissolved material were obtained for the short-term cultures. For the one long-term (81 days) culture, the value was 280 μg/l., nearly an order of magnitude greater. For the lake samples, results from the distilled water and base extracts were composited when appropriate. The results indicate that minimum concentrations of soluble DNA, or its fragments, ranged from 4 to 30 μg/l. for all of the lake samples. The lower values were obtained for Pine Lake and Lake Washington which had lower soluble phosphorus concentrations and lower chlorophyll values.

For the culture samples, 20 to 45% of the high-molecular-weight phosphorus could be accounted for by DNA, assuming DNA to be 8 wt % phosphorus. For the lake samples, 40-60%

Table VI. Percent of High-Molecular-Weight Phosphorus Attributed to DNA and Minimum DNA Concentrations Estimated in Original Culture and Lake Samples

Sample	High mol wt present as DNA, %	Minimum concn of DNA in original solution, μg/l.
Culture no.		
Cr 2	44.9	281
Cr 2	45.4	277
Cr 4	35.4	39
Cr 5	20.6	34
Cr 8 ^a	10.8	13
Lake		
ML-1		30
ML-2a H ₂ O	30.0	
ML-2a base	57.1	
ML-2b base	39.3	20-30
ML-2(0.1 μ) H ₂ O	22.4	
ML-2(0.1 μ) base	39.9	
ML-3 (H ₂ O)	24.6	
ML-3 (base)	57.8	10-15
ML-4 (H ₂ O)	19.6	
ML-4 base ₁ ^b	39.0	
ML-4 base ₂ ^b	42.3	15-17
ML-4 base ₃ ^b	60.0	
Pine Lake	37.8	
Pine Lake (G-100)	44.5	7-10
Lake Washington	48.6	4-9

^a Represents material collected on sterile side of membrane culture system.

^b Sequential base extracts of the same sample.

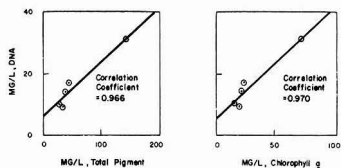


Figure 7. Data points and lines of regression obtained by regressing estimated DNA concentrations on (a) solids total pigment content and (b) solids chlorophyll *a* content, for five of the six lake samples using the UCLA Bio-Med package simple regression program

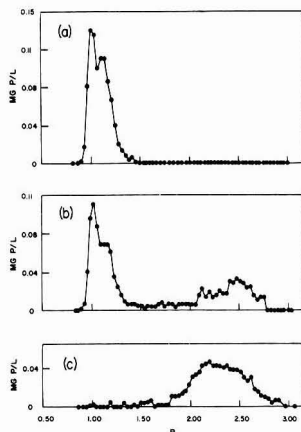


Figure 8. Elution profiles on Sephadex G-75 of (a) control high-molecular-weight culture DOP; (b) DNase-treated high-molecular-weight DOP; (c) DNase-treated commercial DNA (highly polymerized)

of the high-molecular-weight phosphorus was attributable to DNA in the base extracts. In the Moses Lake distilled water extract samples, this was 20–30%.

DNA-Pigment Correlation. Chlorophyll *a* and total pigment concentrations were determined on 3 of 4 Moses Lake samples and the other two lake samples. The estimated minimum DNA concentrations were regressed on both the chlorophyll *a* and total pigment concentrations. Correlation coefficients of 0.970 and 0.966, respectively, were obtained for five data points, both significant at the 99% confidence level. These results are given in Figure 7.

Identification of DNA. Conclusive proof that the high-molecular-weight DOP was in part DNA or its fragments was obtained by subjecting the isolated high-molecular-weight fraction to a DNA specific enzyme, Bovine Pancreas DNase I, in 0.01M pH 7 TRIS Buffer, 0.01M in magnesium ion, for 24 hr at 37°C. Results with the culture DOP are given in Figure 8 for an experiment incorporating a sample and an enzyme control. In the absence of enzyme, no sample breakdown occurred while the pure DNA was completely degraded. The enzyme-treated sample showed 45% degradation. DNA analysis on the same sample indicated that 45% of the phosphorus could be accounted for as DNA phosphorus.

Figure 9 shows similar results obtained for enzyme treatment of a Moses Lake high-molecular-weight fraction. For this particular sample, 44% of the high-molecular-weight DOP was degraded to lower-molecular-weight material. An ultraviolet spectrum of the isolated low-molecular-weight degradation products was that expected for a mixture of oligonucleotides. Hydrolysis of this fraction in 12N HClO₄,

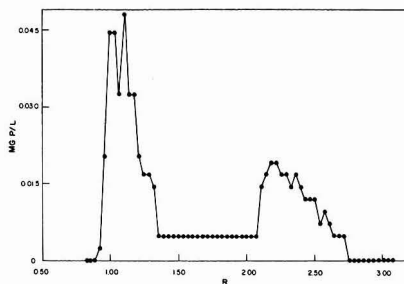


Figure 9. Elution profile on Sephadex G-75 of DNase-treated Moses Lake high-molecular-weight DOP.

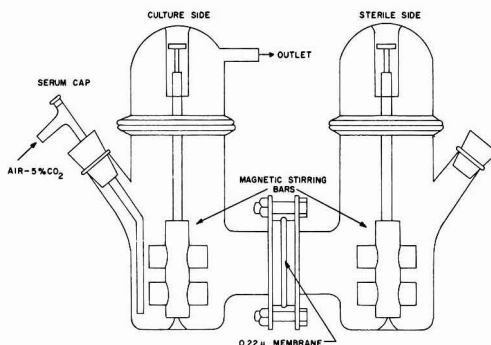


Figure 10. Dual chamber membrane dialysis culture flask used for nonfiltration experiments (Belco Biological Glassware Co.)

led to the identification of the nucleic bases adenine and guanine on two-dimensional thin-layer chromatograms of the hydrolysis products.

Nonfiltration Study. In spite of low-pressure differentials employed during filtration, especially with the later culture samples and the Pine Lake and Lake Washington samples (5–15 cm Hg vacuum), the presence of DNA could indicate cellular rupture during filtration. For this reason, a means of isolating the soluble material without filtration was devised. The device shown in Figure 10 was used to grow the *Chlamydomonas reinhardtii* organisms in one side. The other side remained sterile, separated from the algal culture by a 0.22 μm pore size membrane.

DOP buildup on the sterile side was observed. It contained a high-molecular-weight fraction indicated by the profile in Figure 11, and the general profile behavior on G-75 was similar to other culture samples except the percent of DOP in the high-molecular-weight fraction was somewhat lower. Mass transfer studies with orthophosphate, commercial DNA, and Blue Dextran 2000 indicated equilibrium for orthophosphate required two days. The higher-molecular-weight materials would cross the membrane but at greatly reduced rates. Thus the lower percent high-molecular-weight material is quite likely the result of differential diffusion rates across the membrane.

As with the other culture samples, the nonfiltered high-molecular-weight fraction contained some material which responded as DNA. For the sample shown in Figure 11, the high-molecular-weight DOP fraction was only 11% DNA phosphorus.

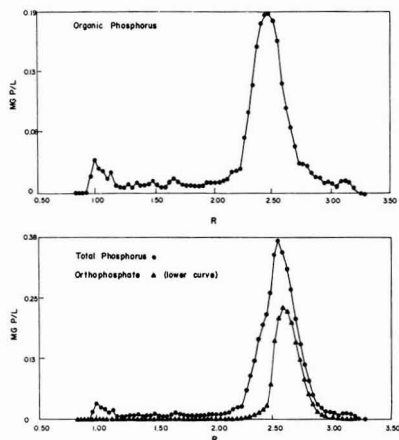


Figure 11. Elution profile on Sephadex G-75 of *Chlamydomonas reinhardtii* culture, 0.1N NH₄OH-soluble DOP isolated from the sterile side of the dual-chamber culture apparatus

Summary

The freeze-drying procedure, which allowed 60–90% recovery of algal culture and natural water DOP, should have kept biological and chemical alteration at a minimum. Even so, in the natural water samples, some hydrolysis of DOP to orthophosphate was experienced. Because of the hydrolysis and less than 100% recoveries, back calculation to the original water samples through weight, volume, and concentration accounting allows only determination of minimum concentrations.

Of the DOP isolated from pure *Chlamydomonas reinhardtii* cultures and natural water samples, a considerable portion is of fairly high molecular weight. Of this high-molecular-weight material, up to 50% is DNA or its fragments. In natural waters, these soluble DNA fragments may be present in concentrations of 30 µg/l. For old algal culture systems, this value can be an order of magnitude higher.

The presence of soluble DNA in the pure algal cultures and the highly significant correlation with chlorophyll *a* and total pigment for the natural water samples suggests this material originates from the phytoplankton. Recent work by Pavoni et al. (1970) suggests that bacteria may also be a source of free polymers, in part DNA, as the result of autolysis in activated sludge systems.

That the DNA and DOP were not the result of cellular rupture during processing was supported by experiments using diffusion across a membrane into a sterile solution. The DNA released at cellular death appears to build up in solution rather than undergoing rapid degradation at cell lysis.

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Quantitative Procedure for Evaluating the Performance of Water and Waste Water Treatment Processes at Naturally Occurring Virus Levels

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■ The insoluble polyelectrolyte technique for concentrating extremely low levels of virus was modified and standardized. This modified procedure was used to evaluate the removal of virus from water and waste water at levels down to 1×10^{-4} plaque-forming units (pfu)/ml. Extrapolation of the results below this level is possible if sufficient quantities of water are available. The efficiency of concentrating the viruses is pH-dependent. At the optimal pH, a constant virus recovery of 25% was achieved for the model coliphage T2 at concentrations of 10^8 to 10^{-4} pfu/ml. The applicability and effectiveness of the procedure is demonstrated using a membrane process of water treatment.

The effectiveness of virus removal by water and waste water unit processes has been under investigation for many years. This type of research has been necessitated by the epidemiological significance of viruses such as the obvious case of the New Delhi hepatitis virus outbreak in 1955–56 (Melnick, 1957), as well as some of the less demonstrable waterborne, virus-caused epidemics enumerated by Weibel et al. (1964).

Almost all the former studies have been conducted at virus titers of 10^4 to 10^8 plaque-forming units (pfu)/ml. These high levels have been required so that any loss of virus within the process could be quantitated by normal counting techniques. Statistically realistic counting levels require minimal titers of 10^2 or 10^3 pfu/ml.

These titers are recognized to be excessive when compared to the concentrations of virus which would normally be found in natural polluted water. In fact, Grinstein et al. (1970) recently demonstrated virus titers in the range of 2×10^{-2} to 2×10^{-1} pfu/ml in the Brays Bayou near Houston, Tex. Some obvious problems encountered with high virus levels are the clumping of virus, the lack of random dispersion in the solute, and protection by organic materials from the medium in which the virus is normally maintained.

These studies were undertaken to develop a method for quantitating the virus-removal capabilities of water and waste water treatment processes at concentrations at which virus can be expected to occur naturally. Many methods have been proposed for the concentration of viruses from large quantities of finished or raw water. These methods include: the gauze pad method (Duff, 1970), hydroextraction (Shuval et al., 1967), ultracentrifugation (Anderson et al., 1967), electrophoresis (Bier et al., 1967), adsorption on inorganic salt complexes (Wallis and Melnick, 1967), ultrafiltration (Gartner, 1967), membrane chromatography (Cliver, 1968), two-phase

polymer separation (Shuval et al., 1967), and adsorption of an insoluble polyelectrolyte (Johnson et al., 1967). All these methods with the exception of the use of insoluble polyelectrolytes encounter logistical difficulties when used to analyze large volumes of samples—i.e., more than a few liters—or when the water contains significant amounts of suspended organic and inorganic solids.

This paper reports the initial results of the use of insoluble polyelectrolyte as applied by Wallis et al. (1969, 1970) to concentrate and quantitatively estimate extremely low virus levels. Bacteriophages rather than enteric viruses were used in this part of the investigation, therefore the results can serve only as a model. The results of studies employing enteric viruses are presently being evaluated; however, the preliminary data are similar to those obtained in the model developed for bacteriophage.

Materials and Methods

Culture Technique. All experiments reported herein were conducted in either phosphate-buffered saline solution (PBS) at pH = 7.2 or natural surface water. Surface water was obtained at Austin, Tex., from Town Lake, which is the last of a series of seven man-made lakes on the Colorado River. This lake receives storm drainage from urban runoff and some rural runoff.

The coliphage T2 was employed throughout this study. Stock cultures were prepared by the plate method using Tryptose-Phosphate Broth (A product of DIFCO Laboratories, Detroit, Mich.) solidified by 1% agar. Plaque assays omitting bottom layer agar were used to titrate the virus (Rizvi and Nova, 1963). Two-tenths of a milliliter of a 24-hr *E. coli* B culture in 7.5 ml of Tryptose-Phosphate Agar were inoculated with samples of phage ranging from 0.1 ml to 0.5 ml. Plaques were counted after 15-hr incubation at 37°C.

Virus Concentration Method. The insoluble polyelectrolyte technique for concentrating virus suspensions employed in these studies was described previously by Wallis et al. (1969, 1970), and Grinstein et al. (1970). The polyelectrolyte PE 60 (A product of the Monsanto Co., St. Louis, Mo.) was used in the water-washed form in all experiments. A concentration of 100 mg/l. of the polyelectrolyte was added to each sample which was then stirred mechanically for 1 hr. The pH was adjusted to the desired level by adding 1N HCl immediately after the addition of the polyelectrolyte.

For 1-liter samples, recovered polyelectrolyte was suspended in 5-ml borate buffer at pH 9 to which 10% calf serum was added. Eight ml of borate buffer-calf serum was used for 5-liter samples. The total available eluate was plated for plaque counting for all low-level studies.

Radioactive Virus. Coliphage T2 labeled with ³H-thymidine was prepared in M9 medium (Eisenstark, 1967). The lysate was clarified by centrifugation at $2500 \times g$ for 15 min at 4°C. The virus was concentrated from the supernatant by high-speed centrifugation at $21,000 \times g$ for 1 hr in the cold. The pellet was allowed to resuspend overnight in $1/10$ the original

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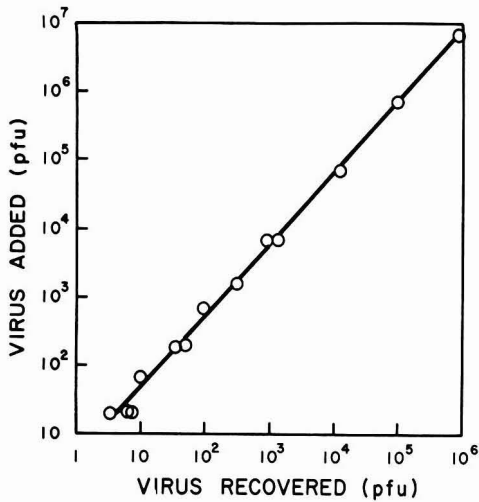


Figure 1. Recovery of T-2 bacteriophage from PBS

volume of phosphate-buffered saline solution. After an additional low-speed centrifugation, 2 ml of virus was layered on a discontinuous sucrose gradient (4 ml each of 37.5%, 33.8%, 30.0%, 26.3%, 22.5%, 18.8%, and 15%w/v) and centrifuged in the cold at $21,000 \times g$ for 45 min. The virus banded at the interface between the 18.8% and 22.5% sucrose layers. It was removed in 4 ml of sucrose with a Pasteur pipette. The plaque titer was 1.5×10^{10} pfu/ml, and the radioactivity was determined by counting in Cabosil with a Nuclear-Chicago Scintillation counter, Model Mark I, to be 2.8×10^4 cpm/ml.

Results

The efficiency of virus recovery as a function of the number of plaque-forming units (pfu) was evaluated. The range studied was from 17 pfu/l. to 6.5×10^6 pfu/l. in 1-liter volumes of PBS. The results obtained are illustrated in Figure 1. The data indicate a relatively constant 25% recovery rate. Significant variability from predicted levels was encountered at extremely low dilutions due to the difficulty of predicting exact numbers of virus added. These data are presented in Figure 2. Virus recovery was not achieved at only two dilutions. In both these cases, total calculated virus count expected in a 5-liter quantity of PBS was 3.3 pfu. The adjusted pH of the PBS when no virus was recovered was greater than 0.5 units above optimum pH. The effectiveness of this technique for recovery of serially diluted low-level virus suspensions at a constant pH of 5.25 can be seen in Figure 3.

Minor differences in pH significantly affected the efficiency of T2 recovery. Consequently, a series of experiments was conducted in which a known amount of virus was added to several 1-liter containers. The pH was adjusted to various levels by 0.25-pH unit increments after 100 mg of PE 60 was added. The data presented in Figure 4 indicate an optimal pH for T2 recovery and that a significant reduction in recovery efficiency results when pH values deviate as little as ± 0.3 pH units. The results of controlled experiments during which no PE 60 was added indicated that no appreciable adsorption of virus to the glassware or inactivation of virus by pH adjustments to pH = 6.5 was detected. These data are contrary to the results of Wallis et al. (1969, 1970), who indicated a much

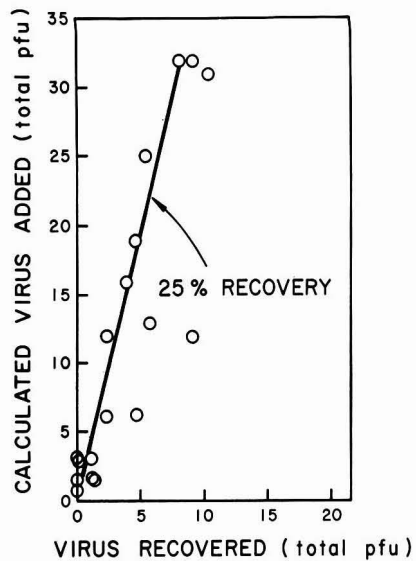


Figure 2. Recovery of T-2 bacteriophage from 5-liter samples of PBS as compared to expected number of virus

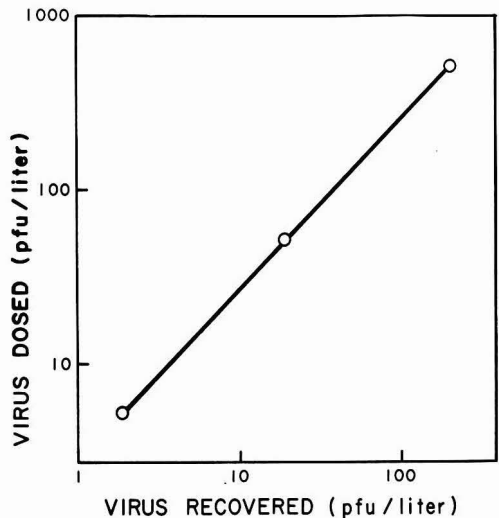


Figure 3. Recovery of serially diluted T-2 bacteriophage from 1-liter volumes by the polyelectrolyte technique

broader range for optimal recovery of polio virus by this method.

The data indicate that a maximum of about 25% of added T2 was recovered from the polyelectrolyte and it was possible that all of the virus might not attach to the polyelectrolyte during the mixing phase of the concentrating technique. Where the filtrate was successively reconcentrated under ideal pH conditions, 22% of the coliphage was recovered on the first polyelectrolyte addition and no additional virus was detected on subsequent concentration attempts. Under less favorable conditions, where pH was 4.75, only 1.2% of the

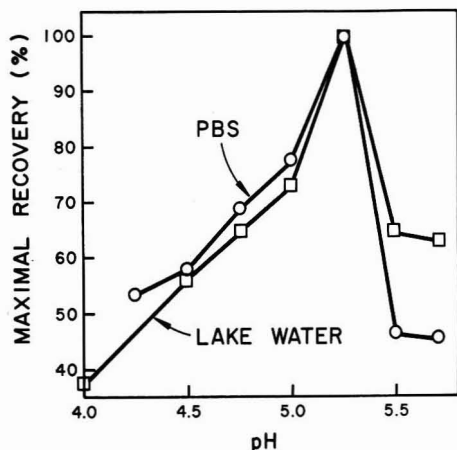


Figure 4. Effect of pH on the recovery of coliphage T-2 by the insoluble polyelectrolyte technique

initial phage titer was recovered on the second concentration attempt, while 15% was recovered during the initial concentration.

The polyelectrolyte was resuspended in borate buffer after initial elution from the polyelectrolyte and plated directly. Less than 10% of the phage initially recovered was detected. This is consistent with expected results since 0.5 ml of the initial 5 ml borate remained with the polyelectrolyte.

Phage labeled with ^3H -thymidine was used to determine the fate of unrecovered virus. This stock was concentrated from the PBS solution as in other experiments. The results of these studies are summarized in Table I. Essentially all of the phage DNA-associated radioactivity was attached to the polyelectrolyte. Twenty-eight percent of the ^3H was recovered in the eluate while 56% remained attached to the polyelectrolyte after borate elution. Infectivity plating indicated that 15% of the initial titer of viable phage was recovered in the eluate and only 1.5% of the viable virus remained associated with the polyelectrolyte after elution.

Numerous attempts to recover indigenous coliphage from samples of water from Town Lake were made. Recoveries from volumes of 5.6 and 18 liters indicated coliphage titers varying 1.5×10^{-3} to 8.5×10^{-3} pfu/ml. The chemical, physical, and biological characteristics of the lake water during some of these experiments are presented in Table II. It is interesting to note that coliform levels decreased drastically between April 19 and 27, but the coliphage titer remained essentially constant. These conditions reflect the fact that the coliphage are propagated in the presence of large numbers of coliform at least to the extent of counteracting their natural inactivation.

Quantities of lake water were filtered through a glass fiber filter to remove suspended solids and 10 coliphage/ml were added. In parallel, containers of unfiltered lake water were dosed with identical amounts of coliphage. These samples were concentrated at pH values ranging from 5.0 to 7.0. Maximal recovery was about 25% of the initial titer in both cases although optimal recovery for the filtered water was observed at pH = 5.5 and at pH = 5.25 for the unfiltered water.

The effectiveness of the methods described were applied to a membrane system of water treatment. The membrane system

Table I. Results of Tracer Studies to Determine the Fate of Unrecovered Virus

State of polyelectrolyte virus complex	Radioactivity		Total viable virus	
	Net counts, cpm	% of Total	Pfu	% of Total
Polyelectrolyte + coliphage	16,000	...	1.5×10^{10a}	100
Eluate (with coliphage)	4,400	28	2.3×10^9	15.3
Polyelectrolyte after elution of coliphage	8,900	56	2.2×10^8	1.5

^a Amount of coliphage added.

Table II. Some Chemical, Physical, and Biological Characteristics of Town Lake Water

Characteristic ^a	Sample 1	Sample 4 ^b	Sample 6
pH, units	8.3	8.2	8.2
Specific conductance, $\mu\text{mhos/cm}$...	570	560
Alkalinity, mg/l. as CaCO_3	...	160	160
Chemical oxygen demand, mg/l.	12	10	...
Filterable solids, mg/l.	8	10	...
Standard plate count at 35°C, organisms/ml	5,000	13,000	...
Coliform, organisms/100 ml	600	3,100	740
Coliphage, pfu/ml	1.5×10^{-3}	8.0×10^{-3}	7.0×10^{-3}
Coliform: Coliphage, ratio	4,000	3,900	1,100

^a All analyses except those outlined in the Methods section were performed according to "Standard Methods for the Examination of Water and Wastewater" (1965).

^b Sample 1 was collected from the lake after several months of essentially no precipitation in the watershed while sample 4 was collected three days following a 1-in. rainfall, the first since sample 1 was collected. Sample 6 was collected 8 days later.

included a bench-scale apparatus similar to that described by Hindin et al. (1968). Cellulose acetate (Membrane HT-00, a product of Eastman Chemical Products, Inc., Kingsport, Tenn.) membranes were used. This system was selected since Hindin et al. (1968) indicated that no virus passed this type membrane at a pressure of 100 atm, a temperature of 25°C, and a flux range of 15.0–19.2 gal/ft²/day. The bacteriophages T7 and $\phi\text{X-175}$ were used and they are considerably smaller than the coliphage T2 used in the study.

A virus level of 4.0×10^{-3} pfu/ml was found to pass the membrane in this study, employing a membrane which was heat-treated to a lesser degree so that the flux was in the range of 100–150 gal/ft²/day at a pressure of 41 atm. Since the volume of product collected during this run was in excess of 3 liters, the probability of normal virus recovery techniques detecting this virus level is extremely remote.

Conclusions

The data presented indicate the effectiveness of insoluble polyelectrolytes for concentrating extremely low levels of

viruses from artificial and natural waters. T2 coliphage recoveries are reliable and reproducible at about 25% of added virus at optimal pH. The ability of the PE 60 to adsorb essentially 100% of the virus in the suspension at the dose and mixing time employed was also demonstrated. Control of the pH is critical for reproducible results using the coliphage.

The major purpose of this study was the standardization of a method for quantitating the effectiveness of water and waste water treatment methods for the removal of viruses at naturally occurring concentrations. The technique described satisfies that need and provides a relatively simple method of virus concentration which is highly reproducible over a broad range of virus levels. However, standardization of the poly-electrolyte for the virus used in a study is essential.

The largest sample of water handled in this investigation was 18 liters. Experimental data indicate that the results can be applied to any manageable volume of water. Additional investigations are in progress at this time with the purpose of simplifying the mechanical problems associated with handling several hundred liters of water, although volumes of 5 and 10 liters would seem to be large enough for most bench and pilot scale studies.

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Evaluation of Filter Materials and Impaction Surfaces for Nondestructive Neutron Activation Analysis of Aerosols

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■ Ten filter materials were tested for suitability for atmospheric particulate sampling and elemental analysis by nondestructive neutron activation using Ge(Li) γ -ray spectroscopy. Trace element contents in most materials are high and are often the principal limitation in analytical sensitivity. Of the commercially available filters tested, Whatman 41 cellulose has the lowest analytical blanks but may clog during prolonged sampling. For some elements, Millipore membrane filters have low blanks but tend to disintegrate during neutron irradiation. Special polystyrene fiber filters may have low blanks and excellent particle retentivity but are fragile. Of commercially available filters, Whatman 41 is optimum from the standpoints of low blanks, particle retentivity, and ease of handling.

The determination of trace element composition of aerosols is an ideal application for nondestructive neutron activation analysis. High sensitivity is needed because of the low atmospheric abundance of total aerosol ($\text{mg}\cdot\text{m}^{-3}$ to $\mu\text{g}\cdot\text{m}^{-3}$) and the even lower elemental levels (10^3 – 10^{-3} $\text{ng}\cdot\text{m}^{-3}$). The multielemental nature and specificity of activation analysis aid in the determination of the chemically complex and highly variable composition of the aerosol. Furthermore, the speed of nondestructive analysis can be used to advantage, for the general difficulty of controlled sampling in the real

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atmosphere is that many analyses are required before valid conclusions may be drawn.

A procedure for the nondestructive neutron activation analysis of aerosols has been developed in our laboratory and applied to a variety of atmospheric samples (Dams et al., 1970). These aerosol samples, which may be taken on highly pure filters or impaction surfaces, are irradiated twice in a nuclear reactor and are counted four times using a lithium-drifted germanium [Ge(Li)] γ -ray detector, after decaying for periods of 3 min to 20 days. Some 30–33 elements may be detected in a given sample, with half-lives ranging from min-

utes to years. Analysis for short-lived isotopes is rapid—more than 10 elements may be determined within an hour of the time of receipt of the sample.

Table I lists the elements determined, their detection limits in typical urban 24-hr filter samples, and representative concentrations in a rural area (Niles, Mich.) and an urban site (East Chicago, Ind.). In samples where the collected aerosol is large relative to filter impurities, the elemental detection limits are predominantly determined by interferences from other elements in the sample, the situation for most elements in the above urban samples. When sample durations become 1–2 hr or less (volumes of a few cubic meters of air), filter impurity levels become more important and indeed may become the limiting factor in determining the detection limits. Such short sampling times, however, are vital for diurnal variations studies, and have been shown to be feasible even for a rural area (Rahn et al., 1971) where samples of 1.5 hr in duration were used to follow the variations of 15 trace elements during a 36-hr period. For this type of study, or for sampling in remote areas where elemental concentrations may be many times lower than in urban areas, impurity levels become a major consideration in the selection of a filter material.

Parkinson and Grant (1963) evaluated impurity levels in three filter materials and found Whatman No. 42 to be the lowest in activatable elements, though they do not report individual concentrations. Keane and Fisher (1968) have used nondestructive neutron activation analysis of NaI(Tl) γ -ray spectroscopy to determine seven inorganic impurity levels in a number of the commoner filter types. Spurny and Fiser (1970) quote impurity levels for seven elements in three filter papers, and Tuttle et al. (1971) found Millipore filters to have satisfactory blank levels for detection of 11 elements in urban air particulate matter using activation analysis.

Physical Properties of Filters

The important physical properties of the commonly used filter materials are well-known and have been thoroughly summarized elsewhere (Lockhart and Patterson, 1964). The principal ones include collection efficiency as a function of both particle size and flow rate, flow rate as a function of pressure drop across the filter (called resistivity below), and flow rate decrease during sampling due to the dust loading on the filter. Of secondary importance are tensile strength, thickness, weight, and hygroscopicity.

Most filters fall into one of two groups—the fibrous type, which is composed of cellulose or synthetic organic fibers, and the membrane type, which features pores of a reproducible diameter.

Experimental

Using the review of Lockhart and Patterson (1964) as a guide, we selected for chemical analysis a number of filters whose physical properties seemed suitable to our sampling purposes and which were expected to contain only low concentrations of interfering inorganic materials. Representatives of both the fibrous type and the membrane type were included (Table II). These were analyzed by our nondestructive procedure discussed above, with the results shown in Table III. Elements which are generally measurable in aerosols but which do not appear in this table have concentrations in the filters which are below the detection limit, and in practice are considered negligible (for Whatman No. 41, the cleanest filter tested, these include V, Cu, Zn, Mg, In,

Table I. Nondestructive Activation Analysis of Aerosols

Element ^a	Detection limit, ng	Concn, ng/m ³ air	
		Niles, Mich. ^b	East Chicago, Ind. ^c
Group I			
Al	40	800	1,000
V	1	3	10
Cu	100	30	900
Ti	200	100	100
S	25,000	...	10,000
Ca	1,000	900	4,000
Group II			
Mg	3,000	800	1,000
Br	20	70	50
Cl	500
Mn	3	30	100
Na	200	200	300
In	0.2	0.02	0.05
Group III			
K	75	400	1,000
Zn	200	50	3,000
Br	25	50	70
As	40	0.05	10
Ga	10	...	1
La	2	1	6
Sm	0.05	0.1	0.4
Eu	0.1	0.04	0.1
Sb	30	1	30
W	5	...	6
Au	1	0.1	...
Group IV			
Sc	0.3	0.5	3
Cr	20	10	100
Co	2	0.3	3
Fe	1,500	600	10,000
Ni	1,500
Zn	100	60	2,000
Se	2
Ag	10	...	3
Sb	8	2	30
Ce	20	2	10
Hg	10	...	4
Th	3	0.4	1

^a Elements were determined under the following conditions:

Group I, $t_{\text{irrad}} = 5$ min, $t_{\text{cool}} = 3$ min, $t_{\text{count}} = 400$ sec
 Group II = 5 min, = 15 min, = 1,000 sec
 Group III = 5 hr, = 20–30 hr, = 2,000 sec
 Group IV = 5 hr, = 20–25 days, = 4,000 sec

^b Av concn over 36 hr, August 21–22, 1969, 1.5 meters aboveground, wind variable <1 m/sec at rural location 5 km from Niles, Mich.

^c Av concn over 24 hr, June 11, 1969, 3 meters aboveground, wind south 5–10 m/sec, in industrial area ~1 km from Lake Michigan.

Table II. Filter Material Investigated

Filter material	Manufacturer's name	Key	Manufacturer	Remarks
Polystyrene	Microsorban	PS	Delbag Luftfilter (Germany)	No longer available
Polystyrene	Microsorban	DMS	Delbag Luftfilter (Germany)	Presently available
Cellulose-organic binder	Whatman No. 41	W41	W. & R. Balston Ltd. (England)	Tightly woven
Cellulose	...	C	C. H. Dexter & Sons (USA)	Loosely woven
Membrane cellulose esters	MF-Millipore	HAWP025	Millipore Filter Corp. (USA)	Pore size, 0.45 μm; diam, 25 mm
	MF-Millipore	HAWP047	Millipore Filter Corp. (USA)	Pore size, 0.45 μm; diam, 47 mm
	MF-Millipore	AAWP025	Millipore Filter Corp. (USA)	Pore size, 0.8 μm; diam, 25 mm
	MF-Millipore	AAWP047	Millipore Filter Corp. (USA)	Pore size, 0.8 μm; diam, 47 mm
Membrane cellulose acetate	Cellotate	EHWP047	Millipore Filter Corp. (USA)	Pore size, 0.5 μm; diam, 47 mm
Membrane cellulose triacetate	Metricel	GA-6	Gelman Instrument Co. (USA)	Pore size, 0.45 μm; diam, 47 mm

Table III. Filter Impurity Levels (ng/cm²)

	PS	DMS	W41	C	HAWP025	HAWP047	AAWP025	AAWP047	EHWP047	GA-6
Cl	3,000	27,000	100	300	1,000	1,000	1,700	1,000	1,800	600
Br	25	1,000	5	20	4	3	<5	<2	6	4
S	— ^a	±30,000	—	6,000	—	—	4,800	—	—	—
Na	80	90	150	700	600	330	520	400	1,800	2,200
K	20	8	15	200	130	100	120	100	—	—
Mg	<200	<1,500	<80	2,400	<300	<200	400	200	—	—
Ca	300	300	140	3,800	670	250	500	370	570	1,250
Ba	7,000	<500	<100	<100	<100	<100	<100	<100	—	—
Al	20	20	12	200	20	10	15	10	60	740
Sc	0.04	<0.01	<0.05	0.2	<0.05	<0.01	<0.01	<0.05	—	—
Ce	<0.4	<1	<0.5	<0.3	<0.5	<1	<0.5	<0.3	—	—
La	<0.2	<0.1	<0.2	<0.3	<0.1	<0.2	<0.5	<0.2	—	—
Ti	10	70	10	50	15	5	10	<10	—	—
Fe	100	85	40	300	40	<300	80	40	—	—
Mn	1	2	0.5	80	7	2	2.5	2	6	2
Co	0.2	0.2	0.1	0.8	0.2	<1	0.4	0.1	—	—
Ni	25	<25	<10	60	<8	<50	14	<20	—	—
Ag	<2	<2	2	3	<4	—	<3	<1	—	—
Cu	10	320	<4	90	20	40	85	60	25	30
Zn	60	515	<25	30	25	20	10	7	—	—
Sb	2.5	1	0.15	0.5	0.5	3	0.4	1	—	—
Cr	5	2	3	12	15	14	20	15	—	—
Hg	3	1	0.5	3	<0.4	<1	<1	0.5	—	—
V	0.06	<0.6	<0.03	0.5	<0.06	0.09	<0.2	<0.05	<0.05	<0.05

^a Not determined.

As, Ca, La, Sm, Eu, W, Au, Sc, Se, Ce, and Th). Because of the relatively high impurity levels in membrane filters EHWP047 and GA-6, analysis was restricted to those elements with short-lived isotopes.

Flow rates were measured in the 20 × 25-cm format (where filters of this size were available) using a General Metal Works high-volume pump, Model GMWL 2000. For the 25- and 47-mm sizes, flow rates were measured with a Gelman Twin Cylinder pump, having a free air capacity of 68 l·min⁻¹ and a maxi-

mum vacuum of 66 cm Hg. Table IV shows the results as flow rates over the exposed or effective surface of the filter.

In addition, the effect of dust loading on flow rate was investigated with W41, C, and HAWP in Ann Arbor, Mich., air, with the results listed in Table IV.

Because some elements are found to be primarily associated with the smaller aerosol particle sizes, it is of interest to determine the degree of penetration, element by element, of actual aerosols through a filter. A 24-hr sampling experiment

Table IV. Selected Physical Properties of Filters^a

Filter material	PS	DMS	W41	C	HAWP025	HAWP047	AAWP025	AAWP047	EHWP047	GA-6
Flow rate (l·min ⁻¹ ·cm ⁻²) 20 × 25 cm (effective surface 400 cm ²)	4.5	4.5	4.5	6
Flow rate (l·min ⁻¹ ·cm ⁻²) 47-mm diam (effective surface 9.62 cm ²)	6.5	6.5	6.5	7	...	2.6	...	4.8	2.6	2.6
Flow rate (l·min ⁻¹ ·cm ⁻²) 25-mm diam (effective surface 3.68 cm ²)	12	13	13	17	4.3	...	7.3
Retention (%) of 0.3 μm DOP aerosol (25-mm diam)	99.96	99.95	99.7	...	>99.98	...	99.97
Retention (%) of 0.3 μm DOP aerosol (20 × 25 cm)	99.8	99.7	91	80 ^b
Volume filtered before 10% reduction in flow (m ³ air/cm ² filter)	48	35	2.0 2.8 ^c	>50 ^c	4.1 ^c	4.1 ^c	6.3	6.3
Tensile strength (kg·cm ⁻¹)	0.15	0.15	1.41	0.29	0.29

^a Flow rates were measured by the authors as described in the text. Except as noted, other data are from Lockhart and Patterson (1964); they also report thickness of W41 = 0.25 mm.

^b Determined by Brar et al. (1969) for total particulate matter by weight in Chicago.

^c Determined by authors in Ann Arbor, Mich.

was performed with two 20 × 25-cm polystyrene filters placed on top of each other, a primary (upper) and a backup (lower) filter. A maximum of 5% of Zn, 2.5% of Br, 5% of La, and 1% of Al were found on the backup filter, with all the other elements essentially completely collected by the primary filter. It appeared, however, that sheets of this polystyrene were not very homogeneous, and the observed thickness difference of a factor of two may account for some of the penetration listed above.

Discussion

Inspection of the filter impurity levels of Table III immediately shows DMS to have extremely high values of Cl, Br, Cu, and Zn, precluding sensitive determination of these elements

in samples taken on this filter material. In addition, irradiation of the filter alone induces high enough activities (mostly from Cl and Br) not only to raise the detection limits of at least 15 other elements by an order of magnitude (column 4, Table VI does not include this additional interference) but also to saturate the counter. This filter is thus eliminated from further consideration for activation analysis purposes.

The impurity levels of two of the membranes, EHWP047 and GA-6, though not prohibitively high, are generally much higher than for the remainder of the filters. Unless very long samples are considered, the impurities here effectively restrict the application of these two materials to sampling in heavily polluted areas. The membrane filters HA and AA have lower concentrations of most elements, but Na, Cr, and Cu could pose problems. Most elements are very low in the polystyrene ps, but Ba and Cl are high enough to prohibit determination of them in samples. Fortunately, neither has a high enough neutron cross section to interfere significantly with the other elements. All the impurity levels of W41 compare favorably with ps, especially the Cl (30 times lower) and Ba.

Table IV displays the sharp contrast in physical properties between the fibrous and membrane types. The latter generally show high flow resistance, raising minimum sampling times by as much as a factor of three. They have extremely high retentivities at all flow rates, even for small particles, and though the effect of dust loading on flow rates is considerable it is not enough to be a problem. Since retentivities are so nearly equal between the two pore sizes investigated, the 75% greater flow rate of the 0.8 μm type represents a real sampling advantage over the 0.45 μm size.

Of the fibrous filter group, the polystyrenes combine high flow rates, high retentivities, and a very small tendency to become clogged. Even at lower air velocities such as sometimes encountered in high-volume sampling, the elements associated with the smaller particles are retained with greater than 95% efficiency.

The cellulose filter (C) allows a very high flow rate but has a poor filtering performance because of the very low retentivity of small particles. Its profitable use seems to be restricted

Table V. Sample/Blank Ratios for 25-Mm Diameter W41 Filters, using Niles, Mich., Concentrations

Element	Concn, ng/m ³	(Sample blank) ^a		
		1-Hr sample	4-Hr sample	24-Hr sample
Cl ^b	100	0.6	2.3	12
Br	70	8	33	160
Na	200	0.8	3	16
K	400	16	62	310
Ca	900	4	15	75
Al	800	40	160	800
Ti	100	6	23	120
Fe	600	9	35	180
Mn	30	35	140	700
Co	0.3	1.8	7.0	35
Sb	2	8	31	160
Cr	10	2	8	40
V	3	>60	>230	>1,200
Cu	30	>4	>17	>80
Zn	60	>1.4	>5.6	>28

^a For 47-mm diam, multiply by 0.37; for 20 × 25 cm, multiply by 0.46.

^b Data from cascade impactor sample taken during same period.

Table VI. Sampling Times to Equal Blank Values or Detection Limits

Element	Sampling time at Niles, hr, on 25-mm filter disc to equal						
	Detection limit	PS blank	DMS blank	W41 blank	C blank	HAWP025 blank	AAWP025 blank
Cl	2	60	500	1.7	4	50	50
Br	0.15	0.8	29	0.15	0.4	0.35	— ^a
Na	0.5	1	0.9	1.5	5	18	9
K	0.1	0.1	0.04	0.085	0.8	2.2	1
Mg	1.5	—	—	—	4	—	1.5
Ca	0.5	0.7	0.6	0.25	5.5	3.8	1.7
Al	0.02	0.05	0.04	0.025	0.3	0.15	0.06
Ti	0.6	0.2	1	0.1	0.5	0.7	0.35
Fe	1	0.3	0.25	0.1	0.6	0.35	0.4
Mn	0.05	0.08	0.15	0.035	4	1.5	0.3
Co	2.8	1.5	1	0.6	3.3	3.5	4
Cu	2	1	25	—	5	5	12
Zn	0.7	2.5	18	—	0.75	2.5	0.6
Sb	2	3.5	1.5	0.2	0.5	2	1
Cr	0.8	1	0.35	0.5	1.5	7.8	6

^a If for the blank value only a higher limit was found or if it was not determined.

to less critical applications in those heavily polluted areas where its virtual freedom from clogging can be employed to greatest advantage.

Whatman No. 41 also allows high flow rates but has a somewhat lower retentivity than the polystyrenes or membranes. This difference is insignificant at high linear velocities (such as obtained through a 25-mm filter) but may become troublesome under other conditions. The effect of dust loading on flow rate is greater for W41 than for any of the other filters tested. The practical consequences of these properties will be treated in more detail below.

For a given filter type, Table IV also illustrates the effect of varying pump-filter combinations on flow rates per unit area. The pumps used here are representative of the common types currently in use. One type, the modified vacuum cleaner variety used with 20 × 25-cm high-volume filter holders, provides very high total flow rates but must be used with low resistivity filters because of its small vacuum. The other type, such as is used with 25- and 47-mm diam filter holders and some inertial impactors, provides a higher vacuum, but its smaller free air capacity means lower absolute flow rates. These pumps are used most effectively when purity of sample, or high sample/blank ratio, is desired rather than large total samples. For highly sensitive analytical methods such as neutron activation, this purity of signal may be of greater importance than the larger but less pure signal from high-volume pumps, especially for the shorter-lived isotopes whose detection limits are well below atmospheric concentrations and where absolute sample size is not so important. Indeed, Table IV reveals a threefold difference in flow rate per surface area between 25 mm and 20 × 25-cm sizes, making collection on the former preferable for the shorter sampling periods. Because they do not depend on airflow for their cooling, the high-vacuum pumps can also be equipped with high-resistivity filters for special applications.

One drawback to the small filters is that their effective surface area is considerably less than their total area. For example, using Gelman holders, the unexposed edge zone is 25% of the total for a 25-mm filter and 45% for the 47-mm size. In contrast, the 20 × 25-cm size is large enough that

samples for analysis can be cut wholly from the exposed interior.

Selection of a particular pump-filter combination is often dictated by the specific goal of the sampling, with the stringency of the filter impurity requirements increasing as the sample time decreases. For example, Table V shows that for 24-hr samples on Whatman No. 41 paper there is little practical difference between a 20 × 25-cm sample and a 25-mm filter, for in each case the sample/blank ratios are well over 10 for most elements. Under these conditions a considerably less pure filter could satisfactorily be used. But when the sampling time is decreased to roughly 1 hr, the differences in impurities and flow rates become much more critical.

The selection factors of flow rate, clogging, and impurity levels can be quantitatively combined into a figure of merit, the sampling time needed to collect an amount of a given element equal to the amount present as impurity within the filter. Table VI gives these numbers for various filters and the atmospheric concentrations of the Niles, Mich., sample of Table I. Though corresponding numbers for remote or polluted urban locales may vary from these by a factor of 10 in either direction, the filter/filter ratios remain valid. Comparison of column 2 with the others illustrates that the ultimate sensitivity of determination of several elements in very short period samples is often limited by the filter impurity levels rather than by interferences from other elements in the sample, examples being Cl, Br, Na, Cu, Al, Mn, Zn, and Sb.

In general, W41 shows the lowest values of the figure of merit for most elements, with PS slightly higher (its Cl is much higher), and DMS, HAWP025, and AAWP025 considerably higher for most elements. For the two membranes, HAWP025 and AAWP025, these high values are due in part to their high resistivity and consequent low flow rates, while the high DMS values reflect actual impurity levels. From the standpoint of activation analysis, the membranes have another disadvantage, for under irradiation they become increasingly brittle and highly susceptible to electrostatic charge induction. After a few hours' irradiation they are nearly impossible to handle, requiring dissolution in water or acid solution and nullifying the nondestructive aspect of the analysis. Because their es-

Table VII. Polystyrene-Cellulose Efficiency Comparison

Element	Atmospheric concn, ng/m ³ ^a		Concn ratio Whatman No. 41/ polystyrene
	Polystyrene	Whatman No. 41	
Cl	4,400 (500) ^b	7,500 (500)	1.7 ^c
Br	350 (90)	500 (50)	1.4
S	15 (15)	43 (25)	~3 ^c
Na	900 (150)	1,300 (200)	1.4
K	4,000 (400)	4,200 (200)	1.0
Mg	730 (400)	760 (150)	1.0
Ca	4,100 (800)	3,900 (500)	1.0
Al	2,300 (400)	2,800 (200)	1.2
Ga	4.5 (1.0)	4.6 (1.5)	1.0
Sc	4.9 (0.6)	3.4 (0.5)	0.7
Ce	17 (3)	12 (2)	0.7
La	4.6 (0.5)	4.6 (0.5)	1.0
Sm	0.67 (0.10)	0.67 (0.10)	1.0
Eu	0.18 (0.04)	0.13 (0.03)	0.7
Ti	170 (50)	280 (80)	1.6
Fe	22,000 (4,000)	15,000 (3,000)	0.7
Mn	240 (40)	280 (30)	1.1
Co	3.9 (0.5)	2.9 (0.4)	0.7
Ni	55 (55)	70 (60)	~1 ^c
W	1.5 (0.7)	<2	... ^c
Ag	3 (3)	2.5 (2.0)	~1 ^c
Cu	130 (20)	160 (20)	1.2
Zn	4,400 (200)	4,300 (200)	1.0
As	29 (7)	35 (8)	1.2
Sb	21 (5)	21 (5)	1.0
Cr	90 (15)	70 (15)	0.8
Hg	1.7 (1.1)	<1.6	... ^c
V	58 (5)	66 (5)	1.1
Se	16 (3)	14 (3)	0.9
Th	1.0 (0.2)	0.8 (0.2)	0.8
Mean			1.02 ± 0.05

^a Concentrations and standard deviations from East Chicago, Ind., 24-hr samples on 47-mm diam filters.

^b Large filter impurity correction lends added uncertainty.

^c Excluded from mean.

essentially absolute collection efficiency down to at least a particle diameter of 0.3 μm does not seem to represent a significant sampling advantage over most of the other filters, we have abandoned the use of membrane filters.

Cellulose or Polystyrene?

The general requirements of activation analysis of our special interest in short-period samples narrow down the original list of possible filters to two types, the tightly bound cellulose (W41) and the polystyrene (ps). Though the highly pure ps is apparently no longer available on a routine basis, there is no reason in principle why it cannot be made, and so will be considered further below.

Subsequent testing of another cellulose filter, TFA 810 (The Staplex Co., New York, N.Y.), has shown it to be very similar to W41 in physical and chemical properties. It thus may serve as an effective substitute when the somewhat cleaner W41 is not available. In the following discussion W41 will be considered the representative of the tightly bound cellulose filters, which as a class will be referred to simply as cellulose.

Though the figure-of-merit listings suggest W41 as the best filter choice, other physical properties seem to recommend polystyrene. In particular, the comparative dop efficiencies of Lockhart and Patterson (1964) show W41 to drop to as low as 61% collection efficiency (at 0.3-μm diam) at 7.3 cm-sec⁻¹ face velocity (where Microsorban is still 99.87% efficient), while rising to 99.98% at 283 cm-sec⁻¹. This evidence may not be as clear-cut as it seems, though, for three other studies of W41 efficiencies exist, with somewhat conflicting results (Smith and Surprenant, 1953; Fitzgerald and Detwiler, 1954; Lindeken et al., 1963). The lowest efficiency was found by Smith and Surprenant, 23% for 0.3 μm dop at 10 cm-sec⁻¹. Fitzgerald and Detwiler used 0.35 μm duraluminum at this same velocity, obtaining an efficiency of 91%. The most detailed measurements, those of Lindeken et al., were obtained with solid polystyrene latex aerosols over a wide range of diameters and flow rates, with all efficiencies found to be greater than 74%. This solid aerosol was chosen to better simulate the natural aerosol than could liquid dop and may account for the higher efficiencies found. Lockhart and Patterson and Lindeken et al. agree on the rapid increase of efficiency with flow rate, and at typical actual sampling velocities of greater than 35 cm-sec⁻¹ (and usually greater than 70 cm-sec⁻¹) they both give values in excess of 90%.

Informative as they are, we feel that these findings are somewhat unrealistic, however, because they are based on numbers obtained using clean filters rather than the dust-loaded filters of an actual sample. Another measurement of Lindeken et al. showed a very rapid increase in the collection efficiency of W41 with time, presumably because of plugging of air passages by the collected particles. Under their laboratory conditions, which seem nearly comparable to atmospheric sample accumulation rates, initial efficiencies of 75% rose to greater than 95% in approximately 30 min, suggesting that in practice, the results obtained with cellulose and polystyrene filters should be nearly indistinguishable.

To check this we collected simultaneous 24-hr 47-mm ps and W41 filter samples in one of the most industrialized areas of East Chicago, Ind., results of which are shown in Table VII. Of 30 elements listed, 25 agreed to within 1 std dev, and in the case of Cl, the discrepancy may be due to its high impurity levels in the ps. For 24 elements (Cl, S, Ni, W, Ag, and Hg not included) the W41/ps atmospheric concentration ratios averaged 1.02 ± 0.05, lending weight to the idea that little or no efficiency differences can be seen in actual sampling. In the case of shorter-period samples where the dust loading may not increase the W41 efficiencies to such an extent, we prefer to use a 25-mm filter size. Collection velocities here are usually much larger than with the 47-mm size, bringing even the initial efficiencies into the 95%-or-greater range.

Another potential problem of cellulose is its well-known hygroscopicity. For applications involving weighing, these filters must be equilibrated at constant relative humidity before weighing. That this can be successfully implemented on a routine basis is demonstrated by the experience of the Bay Area Pollution Control District of San Francisco, Calif., which uses W41 for all its total particulate sampling.

The thinness of cellulose as compared to polystyrene or glass fiber makes small-sized thickness inhomogeneities more important, and definite variations in light transmittance through a clean filter can be seen. These, however, are of a size scale very small relative to irradiation aliquots, and our experience has not shown them to be a problem. For 24-hr high-volume filters, the smallest piece needed for irradiation is approximately 1 cm² (for the short irradiation), and re-

Table VIII. Impurity Levels in Durethene Polyethylene, No. 12010

Element	Concn, ng-cm ⁻²
Cl	8 (2)
Br	1.0 (0.5)
Na	2.5 (0.4)
K	1.2 (0.3)
Mg	8 (6)
Al	6.8 (1.0)
Sc	<0.006
Ce	<0.009
La	<0.04
Ti	11 (6)
Fe	<11
Mn	0.10 (0.02)
Co	0.02 (0.01)
Ni	<1.3
Ag	<0.3
Cu	1.0 (0.5)
Zn	2 (1)
Sb	0.04 (0.01)
Cr	<0.3
Hg	<0.1
V	0.010 (0.003)

producibilities here are usually 10–20% or better.

On the positive side, the thinness of cellulose offers some distinct advantages over polystyrene. Since physical size of the irradiation aliquot is limited by flux gradients in the reactor core and the need to simultaneously irradiate several samples and a standard, the five- to sixfold increase in packaging efficiency offered by cellulose over polystyrene represents a real gain for the long-lived isotopes, where activities are lowest and sample size is the limiting factor in many elemental sensitivities.

Another advantage of the cellulose filters is their high tensile strength. Not only is routine rough handling during sampling possible, but much of this tensile strength remains after irradiation. The polystyrenes, on the other hand, are quite fragile and require delicate handling, a property somewhat inconsistent with any proposed wide-scale use by local air pollution control agencies. In particular, the polystyrenes cannot be used for total particulate determinations because of the loss of some edge material on removal from the filter holder after sampling. This property alone eliminates them from consideration for general use.

Summary

Need for a Standard Filter. According to our experience, reasonable criteria for the selection of a single filter for use in all situations are: minimum impurities, maximum flow rate, and ease of handling both before and after irradiation. Of the filters presently available, Whatman No. 41 (or TFA 810) seems to best meet these requirements. Though it is not an ideal filter, particularly in its hygroscopic and dust loading properties, compensations for these features can satisfactorily be made. Practical tests, both by our laboratory and others, have shown the utility of this filter under all types of sampling conditions.

Now that the means for high-precision trace element analysis of atmospheric particulate matter are commensurate with the increasing interest in this field, we feel it to be imperative

that local air pollution control agencies begin regular sampling on inorganically pure filters, to establish a national stockpile for future analysis. Such a stockpile now exists, but the vast majority of these samples are on glass fiber filters, all varieties of which introduce high blanks into the nondestructive analytical procedure rendering the samples useless. We feel that a national stockpile should be accumulated on a standard filter type, and that the need to begin the stockpile supersedes the lack of an ideal filter. Cellulose should be adopted temporarily until the development of a clearly superior type, and sampling at the local level could then be divided between cellulose and glass fiber filters. Unfortunately, since local sampling is normally used only for total particulate determination, and cellulose is more difficult to use and no better for this purpose, the work of local agencies would be complicated with the promise of little or no immediate gain for them. But in the long run, the creation of a national reservoir of potential trace element data would seem to be worth such inconveniences and might spur the development of a new filter type.

Impactation Surfaces. A growing number of atmospheric samples are being taken with inertial impactors, for size distribution both of total particulate matter and individual elements. A major part of our trace element work has been done with Andersen Samplers, seven-stage cascade devices where the aerosol particles impact onto circular plates some 9.6 cm in diam. For nondestructive purposes we have found it convenient to cover the plates with a thin polyethylene sheet, which then becomes the actual impactation surface. The polyethylene circle with its impacted aerosol is then analyzed by the same procedure described above for the filters.

Since air does not pass through these circles, physical properties such as collection efficiency, flow rate, and clogging do not need to be considered, the only important property being durability of the material under prolonged irradiation. On the other hand, elemental impurity levels become even more important because of the relatively low flow rates for impactors (e.g., 28 lpm for the Andersen Sampler); the partitioning of the sample among several stages; and the large collection area per stage.

Of the common organic materials which might be used for collection surfaces, we found Mylar and Teflon to be unsatisfactory. The Teflon becomes quite brittle under long irradiations, and the Mylar has large Mn and Sb impurity levels.

The best material we have found is polyethylene. Impurities here seem to be associated with the bulk of the material rather than the surface, making the thinnest sheeting the best. After analysis of different lots from different manufacturers we have settled on Durethene 12010 (Sinclair-Koppers Co., Chicago, Ill.), thickness 0.001 in. Impurity levels for this material are listed in Table VIII. As was the case for the filters, long-period samples have detection limits determined primarily by mutual elemental interferences, while for shorter samples the impurity levels for a few elements may become limiting. The low flow rates and sample division mentioned above serve to lengthen the sampling times needed to achieve the same precision as with filters. Another difference from the filters is that the elemental interferences vary greatly from stage to stage because of the variation of size distribution patterns for the elements.

This polyethylene withstands irradiations of 3×10^{17} n-cm⁻², and though it is more brittle after irradiation it can still be easily handled. Impurity levels are low enough to allow sampling times of less than a day, though other considerations have led us to sample for as long as 2–3 weeks.

Another feature of thin sheets such as these is their easy implementation to total particulate measurements. Since the mass of material per stage will be very small, a collection surface which is to be weighed before and after sampling should itself have as little mass as possible. The glass or stainless steel surfaces included in impactors are heavy enough to cause large errors when determining the difference between two large numbers, but use of polyethylene greatly eases this situation. In addition, polyethylene has no hygroscopicity problems.

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Observations on Bactericidal Properties of Digested Sewage Sludge

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■ Liquid digested sewage sludge sampled directly from the digester exhibited a thermostable bacteriotoxin. The liquid phase of digested sludge rather than the solid phase contained the toxic agent. Of a variety of possible sources of toxicity, proteins, parasitic relationships, competition for nutrition, and antibiotics, were ruled out. *Escherichia coli* from stock culture had a higher mortality rate after addition to sludge than *E. coli* isolated from sludge. Sludge-isolated *E. coli* lost their tolerance after several transfers in lactose broth.

A major stumbling block to disposal of liquid digested sewage sludge over extended areas of agricultural land is the public health consideration. There is concern that this material, partially composed of raw settled sludge, might spread pathogens and diseases. Yet, sewage treatment plant employees do not have above average instances of enteric diseases. Irrigation of soil with liquid digested sludge is an officially accepted practice in Great Britain, Germany, and France. It is also widely done in the United States (Evans, 1970).

The fate of pathogens during the process of anaerobic digestion is uncertain. Some organisms such as *Salmonella*

typhosa, *Escherichia coli*, and the amoebic dysentery organism *Endamoeba histolytica* do not proliferate in the digester, on the contrary they are rapidly eradicated from the sludge (Kabler, 1959; Lohmeyer, 1959). In spite of this toxicity, if the initial undesirable microbial population is high, the digested sludge at the end of the fermentative period will harbor some enteric microbes. Such is the case with fecal coliforms.

Fuller and Litsky (1950) and Langley et al. (1959) failed to prove the existence of antibiotics or bacteriophages in digested sludge with *E. coli* and *Salmonella typhosa* as test organisms. Fuller and Litsky (1950) have shown eradication of *S. typhosa* and coliforms in raw sludge cakes to be pH-dependent; Langley et al. (1959) indicated that the die-off of *S. typhosa* in digested sludge could be reversed by addition of tryptophan. Evidence for the presence in digested sludge of a fecal coliform population resistant to the bactericidal agent is given below.

Experimental

Escherichia coli ATCC 11775 was grown aerobically at 27°C in lactose broth (Difco). Unless otherwise specified, counts were made by the membrane filter-high temperature method, hereafter referred to as MFC (Geldreich et al., 1965).

Organic carbon contents of digested sludge samples were measured with the wet dichromate oxidation procedure of Mebius (1960). Dried sludge solids and dried residues of sludge liquor separated by centrifugation were analyzed.

Metals were determined by atomic absorption spectrophotometry by directly aspirating centrifuged sludge liquor. A Beckman Model 979 instrument was used.

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Table I. Comparison Between the Membrane Filter-High Temperature (MFC) and the MPN-EC Medium Techniques for Counting Fecal Coliforms

Source of digested sludge	Fecal coliform, cells/ml	
	MPN-EC medium 95% confidence limit	MFC
Chicago, Calumet Plant	4.9×10^3 - 4.2×10^2	1.6×10^3
Urbana-Champaign	1.5×10^3 - 1.2×10^4	1.6×10^5
Urbana-Champaign	3.4×10^5 - 3.7×10^2	8.0×10^3

Results and Discussion

Fecal coliforms were present in digested sludge, but their density in sludge samples aged in contact with air gradually decreased. A reduction from 4×10^4 to 7×10^3 and 3×10^2 fecal coliforms per ml was observed after 19 and 32 days, respectively. Agreement in fecal coliform counts was obtained with the MFC and MPN-EC (most probably number-EC medium, American Public Health Association, 1965) methods (Table I). In contrast to this slow die-off, *Escherichia coli* ATCC 11775 grown anaerobically in lactose broth disappeared within 24 hr when added to nontreated or autoclaved digested sludge incubated at 27°C in 50-ml Erlenmeyer flasks on a rotary shaker (Table II). As high a die-off rate as that above was reported by Langley et al. (1959) for a laboratory-grown strain of *S. typhosa* added to digested sludge manufactured in the laboratory.

The bacteriolytic effect on the *E. coli* of stock culture may have been a function of the bacterial strain. However, the phenomenon assumed a higher significance when it was discovered that digested sludge-adapted fecal coliforms could be transformed into susceptible strains. Specifically eight distinctive fecal coliform strains, isolated from digested sludge, were maintained in lactose broth. Following one transfer in the broth, six strains survived reintroduction into autoclaved digested sludge, but two were killed. After several transfers covering a two-month period, all isolates no longer adapted to the digested sludge environment behaved like *E. coli* ATCC 11775. The above results prompted further study of the bactericidal properties.

Since toxicity was not eliminated by heat sterilization, the bacteriolytic effect could not be attributed to a protein, parasitic relationship, or nutritional competition with other organisms. The bactericidal properties were localized in the liquid phase of digested sludge (Table III) thus eliminating several of their possible sources. Most components of digested sludge occur in the solid phase. The liquid phase, for example, contains less than 0.05 ppm sulfide, less than 10 ppm organic carbon exclusive of methane and carbon dioxide, and only traces of heavy metals. Although all digested sludge samples were collected at the same treatment plant (Calumet, Chicago), about half of the batches were not toxic. This ephemeral characteristic of the toxicity also noticeable in the data of Langley et al. (1959) with *S. typhosa* further reduces probable causes. Hence, methane and CO saturation of the liquid phase, presence of bicarbonate and ammonium ions (up to 500 ppm-N) at pH values 7.0 to 8.6, low redox potential, and lack of oxygen, properties common to all sludge samples, could not be considered as the principal bacteriotoxic factor.

Langley et al. (1959) upheld the view that elimination of *S. typhosa* is not caused by toxic compounds, but rather results from a nutritional deficiency which can be satisfied by

Table II. Bactericidal Properties of Digested Sludge Toward Laboratory-Grown *Escherichia coli* as Determined by the Membrane Filter-High Temperature Method

Incubation, hr	Fecal coliform, cells/ml		
	Digested sludge	Digested sludge supplemented with <i>E. coli</i>	Autoclaved digested sludge plus <i>E. coli</i>
0	25×10^2	25×10^6	26×10^6
24	20×10^2	41×10^2	<10

Table III. Localization of Bactericidal Properties in Digested Sludge Liquid Phase^a

Medium	<i>Escherichia coli</i> after 24 hr incubation, cells/ml
Saline solution, 1.0% NaCl	3×10^7
Digested sludge, autoclaved	10^5
Liquid phase, autoclaved	10^5
Liquid phase, nonautoclaved	10^5
Precipitate, resuspended with liquid phase, autoclaved	10^5
Precipitate, resuspended with distilled water, autoclaved	11×10^7

^a Liquid phase obtained by two successive centrifugations; the first one at 5000 g for 20 min; the second one done at 30,000 g for 60 min on the supernatant liquor from the first centrifugation. Both precipitates were resuspended to original volume with either distilled water or supernatant liquor.

additions of tryptophan. We found that with *E. coli*, reversal of the toxicity could be achieved by addition of 5 g/l. tryptone (Difco) to the digested sludge. This amount was in excess of the usual nutritional needs. At 2.5 g/l., tryptone did not prevent die-off of *E. coli*. The energy and growth factors brought with tryptone could not be replaced by lactose and/or yeast extract (Difco). Deficiencies in oxidizable organic material and an essential nutrient do not create a toxic medium. For example, the same fecal coliform population which rapidly died off in digested sludge liquor remained stationary in physiological saline solution.

Heat-sterilized sludge and its liquid phase were assayed for antibiotics by the diffusion technique in nutrient agar (Difco). Incubation was carried out aerobically at 27°C. Under these conditions, no antibiotic activity was detectable. Volatile fatty acids have been held responsible for the exclusion of *E. coli* and salmonellas in the rumen of bovines (Hollowell and Wolin, 1965). However, their range of bacteriostatic and bacteriolytic action is limited to pH values below 7.0 and to concentrations above 60 μmoles/ml; conditions which are not prevalent in digested sludge.

Differences in die-off rates of *E. coli* in digested sludge as measured by the pour plate and MFC procedures coupled with the characteristics of the toxicity previously discussed suggested that heavy metals should be investigated as a source of bacteriolytic behavior. The pour plate technique gave higher fecal coliform counts and a lower rate of die-off than the MFC method (Figure 1). Shipe and Fields (1954) had similar results with *E. coli* cells which had been suspended in zinc or copper sulfate solutions. They assumed that either toxic metals were concentrated on the membrane surface or that some cells weakened by the metals could no longer form colonies on the membrane. Nearly all of the heavy metals present in digested

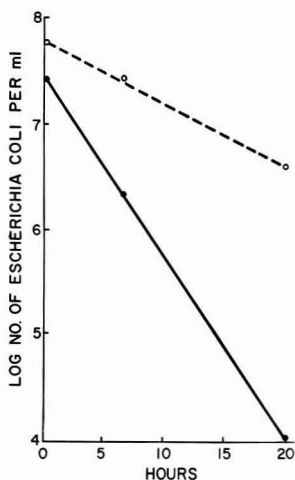


Figure 1. Die-off of *Escherichia coli* in autoclaved digested sludge

Determination done by the membrane filter-high temperature method (solid line) and by the pour plate technique with nutrient agar (broken line)

sludge occur in the solid phase. Analyses of centrifuged sludge liquor showed 0.057 to 0.10 ppm Cu, nondetectable to 0.10 ppm Ni, and 0.075 to 0.15 ppm Zn. These concentrations were lower than those which were shown to cause a reduction of 5% or less in digester efficiency (Public Health Service, 1965). Cd and Cr were not detected in the liquid phase although they were present in the solids. Even at low concentrations, metals can be toxic to *E. coli*. For example, as little as 0.3 ppm Cu or 0.5 ppm Cd affects the metabolism of *E. coli* (Weed and Longfellow, 1954; Malaney et al., 1959). Moreover, sublethal concentrations of several metals can accumulate to toxic levels (Winslow and Dolloff, 1928).

An objection to assigning the observed toxicity to heavy metals could be raised because of precipitation of metals by carbonate, hydroxide, and phosphate anions in the liquid phase of sludge. To check the effect, 2×10^4 cells/ml of *E. coli* ATCC 11775, as determined by the pour plate technique with nutrient agar, were suspended in buffered and unbuffered Cu solution. The buffered solution was composed of $10^{-2}M$ $CuSO_4 \cdot 5H_2O$ and 0.1M phosphate at pH 7.0. Based on the solubility product of copper phosphate ($10^{-26.7}$), the theoretical solubility of copper in the buffered solution was $10^{-11.6}M$. The concentration of copper in the unbuffered solution was $10^{-6}M$ (0.83 ppm). As expected, within 12 hr the *E. coli* cells were killed in unbuffered solution, but survived in buffered solution. One mechanism for metals to enter solution in digested sludge is through chelation with naturally occurring organic compounds. In this form they might retain toxic properties. To test this possibility, a model system was developed with Cu and protocatechuic acid as a complexing agent (Table IV). When the Cu salt and protocatechuic acid were present in equimolar quantities, the die-off rate was approxi-

Table IV. Toxicity of Chelated Copper Toward *Escherichia coli*

Incubation, hr	<i>Escherichia coli</i> , cells/ml ^a			
	CuSO ₄ ·5H ₂ O, protocatechuic acid molar ratio ^b			
	10 ^{-3c} /10 ⁻³	10 ^{-6c} /10 ⁻⁴	10 ⁻³ /0	0/10 ⁻³
0	53 × 10 ²	54 × 10 ²	77 × 10 ²	62 × 10 ²
4	32 × 10 ²	42 × 10 ²	119 × 10 ²	56 × 10 ²
11	0	35 × 10 ²	79 × 10 ²	55 × 10 ²
48	0	20	137 × 10 ²	31 × 10 ²

^a Counts made by the pour plate technique with nutrient agar.
^b Solutions made in 0.1M phosphate buffer pH 7.0, heat-sterilized.
^c Protocatechuic acid added only after copper solution in phosphate buffer had stood at room temperature for 12 hr.

mately proportional to the copper concentration. Neither the buffer-Cu nor the buffer-chelate solution was toxic. Complexation of Cu and protocatechuic acid apparently took place increasing the Cu toxicity. Chelation of metals is possible in digested sludge (Ardakani, 1970). The digestion process depends on a large population of viable microorganisms. If heavy metals in solution caused toxicity as was observed with *E. coli*, digestion itself would probably have been severely inhibited unless the microbial population in the digester had acquired a high level of tolerance toward chelated metals. An observation of such a tolerance was reported by Malaney et al. (1959). Within six days or less of addition of as much as 50 ppm Zn, 20 ppm Cu, or 16 ppm Ni, a microbial population from sewage recovered 35-50% of its original activity. They described the toxicity as inhibitory, not lethal.

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Residues of DDT in Lake Trout as a Function of Age

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■ In lake trout of accurately known age, residues of *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT increased progressively with age from about 1 ppm at 1 year to concentrations of about 14 ppm or higher at 12 years. The correlation between total residues (*p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT) in fish and their age was highly significant.

Reports of DDT residues in fish and other aquatic species are numerous. In a comprehensive study (Burdick et al., 1964), it was shown that loss of viability in eggs of lake trout occurred when the DDT concentration in the eggs reached levels of 2.9 ppm or above. Owing to their importance as game fish in New York State, much attention has been given to the possible adverse effects of DDT on lake trout. In this work a study was made of the concentrations of *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT in lake trout (*Salvelinus namaycush*) as a function of the age of the fish.

Experimental

Lake trout are annually stocked as marked yearlings in Cayuga Lake as a part of a long-term study on population dynamics and therefore provide a population with known age members (conducted by Department of Natural Resources, Cornell University in cooperation with the New York State Department of Environmental Conservation). The 1968, 1969, and 1970 gill net samples, representing as many age groups as possible, were taken for analysis. The unviscerated fish were mechanically chopped and thoroughly mixed. The fish were analyzed by electron affinity gas chromatography as previously described (Gutenmann and Lisk, 1963) except that the gas chromatographic column was different. It consisted of a U-shaped borosilicate glass tube, 7-mm i.d. and 6 ft long. The column packing was prepared by mixing equal weights of 10% DC-200 on 100–200-mesh Gas Chrom Q and 15% QF-1 on Gas Chrom Q. The column was operated at 200°C. Fat determinations were performed by the published method (Horwitz et al., 1970) employing a 16-hr extraction in a Goldfish fat extractor with a 2 to 1 (v/v) solvent mixture of chloroform to methanol.

Results and Discussion

Table I (deposited with the ACS Microfilm Depository Service) lists the results of analysis of fish for *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT with *p,p'*-DDE constituting the major metabolite. The age, sex, length, weight, and % fat in the fish are indicated. As age progressed (up to 12 years) length, weight, and residues of *p,p'*-DDT and its metabolites increased concomitantly. The % fat increased significantly ($r = 0.59$, $n = 26$) with age and could therefore serve as an increasing reservoir for fat-soluble DDT residues (Anderson and Fenderson, 1970). The relationship between total residues (the sum of *p,p'*-DDE, *p,p'*-DDD,

and *p,p'*-DDT) and age is illustrated in Figure 1. This bar graph was prepared by using the average value of total residues for each set of fish of given age sampled in a given year.

Table II lists the relationship by year between total residues (*p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT) and age of the trout. The correlation between age and residues was highly significant. Total residues (*p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT) also correlated well with fish weight ($r = 0.89$). The relationship between total residues (TR) and weight was $TR = 0.534 + 0.927(wt)$. Correlation between total residues and fat content was not significant. The relationship of sex to total residues in fish in given age groups could only be tested for trout 5–8 years old and sampled in 1969 where a sufficient number of both sexes of fish were represented. Female trout had higher residues and this difference was highly significant ($F = 13.53$, d.f. = 1, 28).

Within a given fish species, Reinert (1970) found DDT and dieldrin levels to increase with an increase in size. Anderson and Fenderson (1970) found DDE and DDD to increase with age and fat content in landlocked salmon. They found DDT significantly higher in high-fat fish between 3 and 5 years old. Interestingly, they found after age 5, DDT decreased with age when fat was high and remained constant when low. They did not specify the ages of the fish over 5 years old.

Linn and Stanley (1969) reported a significant decline in TDE residues in fish in Clear Lake in California over the period 1958–65 after aquatic applications of TDE for gnat control were terminated. Decline but long persistence of DDT in crayfish has also been reported (Dimond et al., 1968). The results obtained with lake trout in this study indicated a slight decline in residues from 1968–70. Although the use of DDT near Cayuga Lake has diminished (for instance, the use of DDT in Ithaca at the southern tip of Cayuga Lake for control of elm tree bark beetles was discontinued in 1966), the extent of DDT pollution of the lake by agricultural runoff, drift, and other sources were unknown and the total period of fish sampling (two years) was too short to verify a definite decline in DDT content with time.

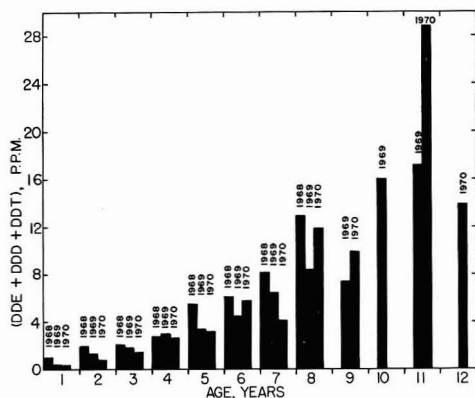


Figure 1. Total residues (*p,p'*-DDE, *p,p'*-DDD plus *p,p'*-DDT) in lake trout as a function of age

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Table II. Relationship Between Total Residues (*p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT) and Age for Lake Trout

Year	Regression	Coefficient of correlation, <i>r</i>
1968	fish DDT = 0.383 age fish DDT = 0.690 <i>e</i>	0.93
1969	fish DDT = 0.333 age fish DDT = 0.583 <i>e</i>	0.94
1970	fish DDT = 0.332 age fish DDT = 0.481 <i>e</i>	0.92

The kinetics of accumulation and the toxic effect of chlorinated insecticides in fish are complex and influenced by many factors in addition to age, size, and fat content. It has been reported that absorption of dieldrin (Fromm and Hunter, 1969) and endrin (Ferguson and Goodyear, 1967) by fish from water is mainly through the gills. Owing to the comparatively high concentrations of chlorinated insecticides in the food chain, ingested food material is considered the major source of DDT for fish in natural waters (Macek and Korn, 1970). (Analysis of smelt and alewives, two major sources of food for trout, taken from Cayuga Lake in 1968 showed residues of *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT, respectively, of about 0.5, 0.1–0.2, and 0.2–0.4 ppm.)

COMMUNICATIONS

Device for Field Determination of Selected Heavy Metals in Natural Waters

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■ A relatively simple and inexpensive self-contained portable device, designed as a three-electrode polarograph, for in situ determination of lead, cadmium, zinc, and iron in natural waters has been developed and tested. The analyses for these four metals may be completed in less than an hour, with results accurate to within ± 0.1 ppm. Capability for application of the instrument to the determination of other metals is built-in.

The analysis of natural waters in situ—i.e., in or near the natural environment—for certain heavy metals has long been difficult, owing to the lack of suitable portable devices for such measurements (Stickley, 1967). The instrument herein described was developed and tested in response to this need. The metallic elements of prime concern were those most likely to be toxic to fish (van Duijn, 1967; Hawksley, 1967), inasmuch as the metallic ion content of sport-fishing waters is one of the important areas of interest in field analysis.

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Received for review July 12, 1971. Accepted December 15, 1971. Supported in part by grant from the New York State Conservation Council. Table I will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, DC 20036. Refer to the following code number: ES&T-72-451. Remit by check or money order \$3.00 for photocopy of \$2.00 for microfiche.

At the outset, it was obvious that electrochemical methods are particularly well-suited to the type of measurement under consideration (Mancy and Nolan, 1967). A simple polarographic device (Coleman and Van Atta, 1967) was a logical choice for adaptation to field use. The principal problems to be resolved were: nature of fundamental circuitry, nature of electrolyte-electrode systems, and sufficient sensitivity to measure the required metallic ion concentrations.

Apparatus

Fundamental Circuitry. A number of prerequisite characteristics must be considered in the design of such an instrument, including: appropriate compromises between instrument sensitivity and field reliability, adaptability of the circuitry to the electrode-electrolyte system, relative simplicity and convenience of field operation, and maintenance.

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The approach adopted involved the application of operational amplifiers employing a three-electrode system. Dropping mercury-indicating, platinum-counter, and saturated-calomel reference electrodes were selected. The design consisted of six individual circuits, each designed and interconnected to produce an operational whole compatible with the previously enumerated characteristics. These individual circuits include: a controller operational amplifier circuit whose basic function is to apply and control the potential of the electrode system in the polarographic cell, as supplied from the ramp supply circuit which permits the proper predetermined voltages (based on the nature of the working electrode, electrolyte, and electroactive species) to be selected by an appropriate control; the current-to-voltage converter circuit; the current compensation circuit designed so that the polarographic residual currents may be compensated for, thus permitting the simple measurement of the waves via a two-point measurement technique; the read-out circuit; and the battery test circuit. A detailed description, schematic diagrams, and operating instructions are available from the authors on request.

Polarographic Test Cell. A polarographic test cell was designed which would be suitable for use in a portable instrument. The cell consists of a 1-in. o.d. glass vessel 1 $\frac{1}{4}$ in. tall, fitted snugly with a machined nylon cover containing access holes, reference electrode, the dropping mercury capillary, counter electrode, and a gas bubbler tube for oxygen purging. The mercury reservoir was constructed from a Cole-Parmer polyethylene gas sampling tube (125-cc capacity), modified by cutting the chamber length to 1 $\frac{1}{4}$ in., rotating the stopcock 180° from its original orientation, and resealing the stopcock onto the cut end with epoxy cement. The stopcocks are mercury tight, so that they may be closed for storage and travel, but are easily opened for operation.

Oxygen-Purging Apparatus. Owing to the well-known polarographic reduction waves for dissolved oxygen, some technique was necessary for removal of the gas prior to measurement of metallic ions. Although nitrogen is normally used for this purpose in the laboratory, Freon-12 was selected, since it is readily available in inexpensive disposable 15-oz containers. These cans, along with a convenient and necessary dispensing valve suitable for repeated use with any size can of the gas, are available from most automotive supply stores.

Sample Preconcentration Apparatus. Due to the low concentration levels of metallic ions in sport-fishing water samples, a preconcentration step is recommended (Ullman et al., 1962; Crose, 1970). A simple and convenient field preconcentration apparatus consisting of a graduated 250-ml beaker and holder for a Lenk LP Laboratory Burner with a Meker-type flame adapter (Dynalab Corp., Rochester, N.Y.) was used.

Experimental

Electrolyte. Preliminary studies of electrolyte systems containing various metal ions resulted in the selection of trisodium citrate as the most suitable medium for use with the instrument and electrode systems selected. This electrolyte permits measurement of Pb(II), Cd(II), Zn(II), and Fe(III) ions. Cu(II) is masked by the electrolyte anodic wave, Ni(II) is not reducible in citrate media, and Cr(III) does not interfere at concentrations up to about 0.2 ppm—a concentration considerably larger than generally found in natural waters. The advantages of the citrate medium are: each of the four measurable ions gives a reasonably well-

Table I. Standard Water Composition: Test Solution Preparation

Component	Std concn, ppm	Test soln concn, ^a ppm
Pb(II)	300.0	30.0 + x
Cd(II)	150.0	15.0 + x
Zn(II)	50.0	5.0 + x
Fe(III)	50.0	5.0 + x
Na ₃ citrate	0.20M	0.02M

^a Test solutions are prepared by mixing 1.0 ml of standard water with 8–9 ml of preconcentrated sample, followed by dilution to 10 ml with distilled water and oxygen-purging with Freon-12 prior to measurement; x = concentration of metal ion from unknown samples.

defined wave, so that the two-point polarographic measurement technique is feasible; the citrate complexes Fe(III) so that its wave does not interfere with Zn(II) and serves to maintain the pH required to prevent hydrogen discharge interference, and no polarographic maxima are observed for metal ion concentrations up to 50 ppm.

Polarographic Analytical Measurements. Based on the location and nature of the polarographic waves for the four cations in the citrate medium [$E_{1/2}$ values vs. SCE: –0.43 for Pb(II), –0.57 for Cd(II), –1.03 for Zn(II), and –1.36 for Fe(III)], potentials selected for two-point measurement of wave heights (vs. SCE) were: Baseline, –0.35; Pb(II) wave, –0.50; Cd(II) wave, –0.70; Zn(II) wave, –1.20; and Fe(III) wave, –1.43. Initially, the direct wave height comparison measurement technique was attempted—i.e., the height of a wave was determined by the difference in polarographic current measurement at two successive reduction potentials, and concentrations of the measured ions were then determined by reference to appropriate calibration curves. However, for the low concentrations commonly encountered in water samples, these measurements were all too frequently of the same general magnitude as the observed experimental error. Consequently, the standard addition technique was selected for quantitative measurements. This also led to minimization of sample matrix effects.

Analytical Procedure

Sampling. The precise method of sampling, based on the location and nature of the sample and the specific application of results, must be determined by the analyst.

Preconcentration. Transfer the desired volume of sample to the concentration beaker. Add 2 or 3 drops of 1:1 nitric acid and evaporate to well under 10 ml but not to dryness. If noticeable buildup of solid material appears on the inside wall of the beaker during evaporation, repeat the addition of nitric acid. Cool for at least 5 min, adjust the pH to within 5 to 7 by dropwise addition of 1:1 ammonia, testing with EM-Reagents Non-Bleeding pH Indicator Sticks.

Test Solution Preparation. Transfer 1.0 ml of the standard water (Table I) to a 10-ml graduate, and add the preconcentrated sample from the beaker. Dilute to 10 ml with distilled water, and mix thoroughly. Rinse the cell vessel and electrodes with about 3 ml of the test solution and half-fill it with the test solution. After appropriate adjustment of the electrode assembly, purge the solution with Freon-12 for 5 min before completing the measurement.

Test Solution Measurement.—The standard addition procedure requires that one test solution containing only the standard be measured, followed by a second measurement for the standard plus sample. Measurements on the standard

Table II. Analysis of Synthetic Water Samples
(Samples preconcentrated 100 to 10 except as indicated)

Sample	Content, ion	Taken, ppm	Found, ppm	Error, ppm
A	Pb(II)	0.25	0.26	+0.01
	Cd(II)	0.12	0.12	0.00
	Zn(II)	0.05	0.06	+0.01
	Fe(III)	0.04	0.03	-0.01
A ^a	Pb(II)	0.25	0.30	+0.05
	Cd(II)	0.12	0.17	+0.05
	Zn(II)	0.05	0.12	+0.07
	Fe(III)	0.04	0.05	+0.01
B	Pb(II)	4.00	4.10	+0.10
	Cd(II)	0.50	0.52	+0.02
	Zn(II)	1.00	0.95	-0.05
	Fe(III)	1.00	0.90	-0.10
C	Pb(II)	0.50	0.48	-0.02
	Cd(II)	2.00	2.02	+0.02
	Zn(II)	0.50	0.45	-0.05
	Fe(III)	0.20	0.25	+0.05
D	Pb(II)	1.00	1.05	+0.05
	Cd(II)	1.00	1.01	+0.01
	Zn(II)	0.20	0.18	-0.02
	Fe(III)	1.50	1.40	-0.10
E ^a	Pb(II)	1.50	1.55	+0.05
	Cd(II)	0.75	0.70	-0.05
	Zn(II)	0.25	0.36	+0.11
	Fe(III)	0.25	0.35	+0.10

^a Without preconcentration; sample mixed directly with standard water.

should be made daily, as for the test solution, except that distilled water is added during the test solution preparation in place of the preconcentrated sample solution.

Results and Discussion

Analysis of Synthetic Samples. A number of synthetic water samples containing various concentrations of Pb(II), Cd(II), Zn(II), and Fe(III) were prepared and analyzed with the instrument by the procedures presented. The results of these analyses are given in Table II. Probably the most significant trends shown by these results are: low concentrations of zinc and/or iron are quite likely to yield high results, and lead and cadmium results are likely to be considerably more accurate than those for zinc and iron, (expected on consideration of the nature of the polarographic waves—the sharp, well-defined nature of lead and cadmium waves compared with less distinct zinc and iron waves). High results for iron may be expected, since the wave is very close to the hydrogen discharge wave in the citrate medium. The pH of the system dramatically affects the location of this discharge wave, necessitating rough pH adjustment to the 5–7 range after preconcentration.

Analysis of Natural Waters. In this study, the Esmarch APHA-type Water Sampling Apparatus was used in sampling natural waters such as lakes, rivers, streams, and pools. This apparatus permits one to collect a 200-ml sample at any convenient depth. A depth of 3 ft was arbitrarily selected for this study.

A selection of various natural waters, collected from various locations, was analyzed, using the same method and procedure described for synthetic samples. These results are given in Table III. Although these results do not necessarily reflect accuracy, they do show the relative reproducibility of analyses for concentrated vs. unconcentrated samples. The concen

Table III. Analysis of Selected Natural Water Samples

No. ^a	Source of sample ^b	pH ^c	Pb(II), ppm	Cd(II), ppm	Zn(II), ppm	Fe(III), ppm
1(a)	Sport-fishing stream	6.0	N ^d	N	0.02	1.22
1(b)			N	N	N	1.48
2(a)	Artificial impoundment	7.5	0.01	N	0.02	0.04
2(b)			N	N	N	0.06
3(a)	Surface runoff	6.5	0.01	0.02	N	0.30
3(b)			N	0.02	N	0.06
4(a)	Polluted creek	5.5	0.02	N	0.15	1.35
4(b)			N	N	0.09	1.70
5(a)	Great lake	7.5	N	N	0.24	0.08
5(b)			N	N	0.32	0.11
6(a)	Large river	6.5	0.03	N	0.11	0.62
6(b)			0.02	N	0.15	0.70
7(a)	Farm well	7.0	N	0.02	0.28	0.18
7(b)			N	0.01	0.20	0.26
8(a)	Strip-mine pit	3.5	0.05	0.01	0.75	2.44
8(b)			0.07	0.01	0.60	2.86
9(a)	Industrial effluent	6.5	0.78	0.42	0.45	0.56
9(b)			0.80	0.38	0.54	0.70
10(a)	Mine drainage slough	5.0	1.40	0.32	3.42	0.25
10(b)			1.44	0.30	3.65	0.20

^a Samples designated (a) analyzed after 200 to 10 preconcentration; those designated (b) analyzed without preconcentration.

^b Samples collected at average depth of 3 ft under surface of water with Esmarch APHA-type Water Sampling Apparatus.

^c pH of original sample, estimated to nearest 0.5 pH with EM-Reagents Non-Bleeding Indicator Sticks (0–6 pH).

^d N indicates that the metal was not measurable with the apparatus and technique used.

trated sample results are likely to be the more accurate because at least some of the organic matter present in a natural sample, which could complex a metal ion and affect analysis adversely, is destroyed by nitric acid during preconcentration.

Comparison of instrument reliability estimates with toxic limits for fish and permissible concentrations for water supplies indicates that the analyzer is applicable for measurements of critical values for these ions in most waters. The level of biological and/or organic pollution expected in so-called sporting waters—the type of waters for which the analyzer was designed—may be much less than in waters closer to civilization.

Advantages of the Analyzer. Among the advantages of the instrument described are: the device is readily portable, weighing about 15 lb; it is capable of yielding analytical results, in the field, for some metal ions which are relatively difficult to determine by other techniques under similar conditions; it is relatively easy to operate, suitable for use by nontechnical personnel; the chemical operations required are extremely simple; it is designed for relatively simple maintenance, requiring only occasional replacement of propane (each 6-oz can may concentrate 6–10 samples), Freon-12 (each 15-oz can is sufficient for 20–30 analyses), and batteries (lifetime is widely variable); the cost of the total instrument

(under \$400) is quite minimal in comparison with other currently available equipment; and a variable potential mode incorporated in the analyzer permits the exploration, with the instrument, of the possibilities for adapting the device to the use of other electrolyte systems and/or other metallic ions.

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Design of System for Removing Water-Soluble Materials from IPC-1478 Filter Paper

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■ A system has been designed for substantially reducing the water-soluble materials contained in IPC-1478 filter paper. Preliminary flow rate and collection efficiency experiments have shown that the procedure does not affect these characteristics. The present limitation is the time involved.

Recent interest in bulk particulate sampling in the atmosphere has brought about a search for a suitable filter medium (U.S. Department of Commerce, 1971; Gross and Beadle, 1970). The desirable qualities include high flow rate, ease of making or acquiring the filter material, high collection efficiency at typical face velocities and over a broad particle size range, lack of contamination, and low pressure drop across the filter. A survey of the available material (Lockhart et al., 1964) shows that a cellulose type of filter would be applicable. Three of the common types of cellulose paper, TFA-41 distributed by the Staplex Co., Whatman No. 41 manufactured by W. & R. Balston, Ltd., England, and IPC-1478 designed by the Institute of Paper Chemistry, were selected for consideration.

The Whatman No. 41 and the TFA-41 filter materials consist of a tightly packed, high-resistance material, whereas the IPC-

1478 is a loosely woven, low-resistance paper made from second-cut cotton linters with a cotton scrim backing material for added strength. The IPC-1478 paper shows a plateau of relatively constant penetration with increasing filtration velocity for a 0.3- μ test aerosol where the others show a decrease in penetration with increasing face velocity (Lockhart et al., 1970). At 170 meters/min, IPC-1478 has a penetration of 80%, where TFA-41 and Whatman No. 41 are 0.03 and 0.02%, respectively. For these reasons IPC-1478 was chosen as a suitable medium even though it is heavily contaminated with water-soluble components.

To combat the contamination problem, it seemed desirable to develop a process for removing, or at least substantially reducing, the water-extractable contaminants. A system is herein described that does this without affecting the desirable characteristics of the paper.

Operation

The cleansing process involves four procedures: loading, washing, drying, and unloading of the filter paper. Figure 1 is a diagram of the loaded "washing machine." The filters are loaded into holders with stainless steel screen on both sides of the filter. These holders are placed in the washing machine with spacers that position them about 10 mm apart. One nipple from each of the two air distribution manifolds directs drying air into this space during the drying cycle. When all the filters are loaded and the lid is fastened, the washing cycle can commence.

The washing procedure consists of a series of extractions

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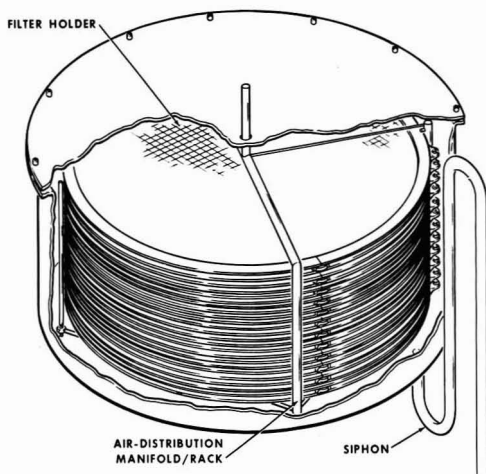


Figure 1. Diagram of washing module

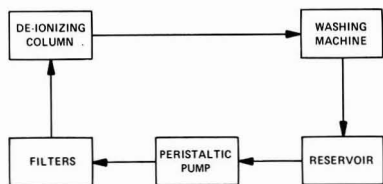


Figure 2. Block diagram of washing cycle

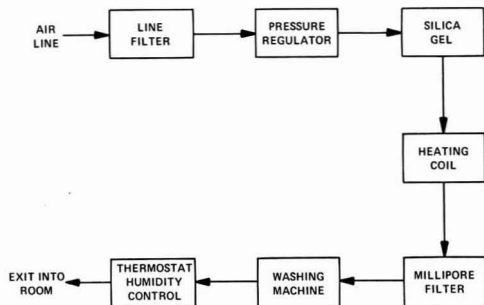


Figure 3. Block diagram of drying cycle

with filtered and deionized water saturated with Kronisol (di-butoxyethyl phthalate from the FMC Corp.). During their manufacture the filters are impregnated with Kronisol to improve their collection efficiency. The wash water is saturated with Kronisol (0.03%) so that as little Kronisol as possible will be removed from the filters during the washing procedure.

A block diagram of the washing procedure is shown in Figure 2. The Kronisol solution is pumped from a reservoir, by a peristaltic pump (Manostat Corp. No. 72-895) at a rate of about 700 ml/min; through a filter, which removed all particles larger than 1 μ ; through a deionizing column; and finally into the bottom of the washing machine. The tank slowly fills until all the filters are immersed, and then the tank is drained by an automatic siphon. The siphon returns the solution to the reservoir for reuse.

Figure 3 is a block diagram representing the drying cycle. Drying is achieved by passing warm purified air around the filter paper. In-house air is passed through a filter (Mine Safety Appliance Co. No. 10-81857) which removes particulate matter down to 0.3 μ . The air, at 60 psi, passes through a column of silica gel (39 mm in diam \times 196 cm long) and into a heating coil of copper tubing. The heating coil is encapsulated by two 600-ml heating mantles, which are controlled by a variable autotransformer. When the air emerges from the heating coil, it is filtered through a 142 cm diam, 0.45- μ Millipore filter and is distributed uniformly between the filters by means of the distribution manifolds. As the air leaves the tank, it passes over a thermostat and a humidity control (Honeywell No. H 46 D). The thermostat controls the current to the heating mantles and prevents overheating of the filters. Humidity control is set at 10%. When the exiting air reaches 10% relative humidity, a light alerts the operator.

Results

Chemical analysis of the water-soluble extract of both the washed and unwashed paper are given in Table I. It is apparent that the washing procedure substantially reduces the water-soluble contaminants in the filter with the exception of ammonium ion and total nitrogen, both of which are at low levels initially.

As a check to see if the flow characteristics of the *IPC-1478* paper had been changed by the washing procedure, washed and unwashed paper were flown in the NCAR Saberliner. The Saberliner is equipped with a sampling foil in which the air volume can be measured with a pitot tube. Both the washed and unwashed paper gave pressure drops of 6.0 in. of water which corresponds to 38 m³/min of airflow at 35,000 ft.

A check of the particle collection efficiency of the washed vs. the unwashed was performed by comparing the amount of sulfate collected on both during an *RB-57F* aircraft flight. For this test, washed and unwashed filters were alternated in the U-1 sampling foil of the aircraft. Three samples and two flight blanks were collected for both the washed and unwashed paper. After compensation for the sulfate in the blank, the average amount of sulfate on the unwashed filters was 337 μ g as compared to 349 μ g in the washed filters. This slight difference is well within experimental variation.

Discussion

It is evident that the washed filters are superior to the unwashed filters in terms of water-soluble contaminants. The preliminary data indicate that the flow rates and efficiency were not altered by the washing process.

The major drawback is the time involved in the cleaning process. Loading, washing, drying, and unloading 12 filters presently takes 24 hr. This reduces the availability of the filters unless a stockpile of cleaned filters is maintained. Experimentation with the placement of filters is now being carried out in an attempt to substantially reduce the time required for the cleaning process.

It is apparent that the washed paper should be of value for any sampling program that requires a filter which is not contaminated with water-soluble materials. It must also be remembered that *IPC-1478* paper has a high (>90%) collection efficiency only with face velocities in excess of 600 m/min at ground level but at 60,000 ft a face velocity of 300 m/min will give a collection efficiency about 95% for 0.3- μ particles (General Mills Inc., 1959). This is also true of the washed *IPC* paper. The washed *IPC-1478* paper has been used effectively for atmospheric sampling of aerosols aboard the *RB-57F* aircraft and

Table I. Contaminant/Filter,^a μg

Contaminant	Unwashed filter	Washed filter	Reduction, %
SO ₄ ²⁻	1340	76	94.3
Cl ⁻	410	30	92.7
Na ⁺	745	75	89.9
K ⁺	45	0	100.0
Mg ²⁺	110	23	79.1
Ca ²⁺	750	113	84.9
NH ₄ ⁺	7	7	0
N ^b	19	19	0

^a Av of fine 42-cm diam filters.
^b Total inorganic fixed nitrogen.

from a balloon sampling module. Plans are being made for extensive use of the washed paper in the future for both aircraft and balloon sampling.

Stafford and Ettinger (1971) have shown that IPC-1478 paper that is impregnated with Kronisol is above 90% efficient at face velocities greater than 600 m/min at atmospheric pressure. The efficiency increases particularly for particles under 0.3 μ , with increasing face velocity. Because of this, ground-level sampling is feasible provided a sufficient face velocity is main-

tained. Preliminary work using a 37-mm diam washed paper on the inlet side of a Spencer Tubo-compressor have demonstrated face velocities from 1000-1500 m/min. Further work with this is planned.

The washed IPC-1478 paper is also being used for sampling in conjunction with sulfur isotope work. By reducing the large sulfate content of the filter, the need for an isotope correction for the filter is negligible. This makes the isotope work much easier and more reliable than was previously possible.

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Mercury Uptake by Selected Agricultural Products and By-products

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■ Sorption of mercury compounds from water by various agricultural products was surveyed by specific atomic absorption spectroscopy. The best adsorbents found are polyphenolic materials—e.g., tannins—as in walnut expeller meal and peanut skins, and proteins, as in wool and feathers. At low pH, sorption of mercuric salts by wool roughly follows a Freundlich isotherm in the concentration range 0.001–20 g of Hg/l. Namely, $\log_{10} x \cong 0.33 \log_{10} C + 1.9$, in which x mg of Hg are bound per gram of wool from a solution with the residual concentration C , g of Hg/l. Sorption from methylmercuric chloride at pH 6 is about $1/7$ as much in the range 0.001–0.2 g of Hg/l. Reducing and alkylating wool with vinylpyridine (for instance) increased sorption 1.7 times. These data indicate the possible use of agricultural products to remove and recover mercury from contaminated materials.

Mercury pollution causes justifiable public concern. Although the danger of mercury to health has long been known, the problem is brought into focus by instances of poisoning by contaminated foods and the demonstration that various water sources and seafoods have mercury contents with an apparently low, uncertain margin of safety. Consequently, mercury adsorption by various agricultural products—including by-products and derivatives—is being evaluated here to discover useful scavengers. This report calls attention to the relative

mercury binding efficiencies of various agricultural products and to the feasibility of increasing binding by chemical modification.

Clean, undyed wool was chosen for initial study (Friedman et al., 1971) because of its relatively high content of actual and potential binding sites for mercurials (Speakman and Coke, 1939; Leach, 1960; Webb, 1966) and because its chemical nature, insolubility, and physical form as crimped and resilient fibers suggest that it may make an efficient and acceptable adsorbent filter for purifying drinking water and other beverages. Wool was also reduced and alkylated as described by Friedman and Noma (1970). In various experiments, adsorption from aqueous mercuric acetate, mercuric chloride, and methylmercuric chloride was measured by specific atomic absorption spectroscopy. Uptakes from representative agricultural products were compared. Among these, materials with high tannin contents and chemically modified wools seem especially promising.

Tables I-III show these comparisons. Table I suggests that mercury uptake by the various materials is roughly proportional to protein content. The keratins wool and feathers are particularly effective. Binding by wool was about doubled by reduction. Table II shows that polyphenolic materials, tannins, such as walnut expeller meal and peanut skins, may be even more effective. Materials that are mainly carbohydrate (cellulose, starch, rice straw, bagasse) took up very little mercury.

Under test conditions, mercuric chloride was taken up in substantial amounts at all pH's from 2 to 10, but best near or below 2 and near 9. Less methylmercuric chloride was ad-

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Table I. Mercury Sorption by Protein-Containing Materials^a

	Sorption from HgCl ₂ at pH 2		Sorption from CH ₃ HgCl at pH 10	
	Mercury adsorbed, mg/g	Residual concn, mg of Hg/l.	Mercury adsorbed, mg/g	Residual concn, mg of Hg/l.
Wool				
intact	35.6	280	17.8	380
reduced	65.6	10	56.9	28
Albumin				
bovine serum	33.3	300		
Blood meal	20.6	415	22.2	340
Chicken feathers				
whole	24.4	380	16.7	390
ball-milled	33.3	300	15.6	400
Soy flour	11.1	500		
Silk	8.9	520	13.3	420
Gelatin	8.9	520		
Wheat gluten	8.9	520	15.6	400
Wheat flour				
whole	4.4	560	5	495
bran	3.3	570		
None (control)		600		540

^a In these tests, 1.5-gram samples were shaken at 21 °C for 30 min in 150 ml of solution containing 600 or 540 mg of mercury/l. Binding is calculated assuming all materials to have 11% moisture as found for wool. Essentially no mercury was taken up by cotton, starch, rice hulls, or rice straw under the conditions of these tests.

sorbed than mercuric chloride by the more effective proteins, and its pH dependence differed; it showed binding maxima near pH 10 and 6.

When our results (Friedman et al., 1971) and published sorption results for wool (Barr and Speakman, 1944; Hojo, 1958; Leach, 1960; Speakman and Coke, 1939) are graphed logarithmically, they turn out to be roughly represented by isotherms according to Freundlich. For the inorganic salts in the pH range 2-4,

$$\log_{10} x \cong 0.33 \log_{10} C + 1.9_4 \quad (1)$$

This gives the mercury sorption, x (mg of Hg bound/g of wool) for a given residual concentration, C (g of Hg/l.), usually within a factor of two within the range of C from 0.001 to 40. We confirm that wool can bind more than half of its weight of mercury from concentrated mercuric acetate or mercuric chloride.

For methylmercuric chloride at pH 6, the corresponding Freundlich relationship is:

$$\log_{10} x \cong 0.4 \log_{10} C + 1.3_0 \quad (2)$$

This holds with about the same precision as above in the range of C from 0.001 to 0.2 g of Hg/l. In this range, the binding varies from $1/7$ to $1/5$ that from HgCl₂.

Table III indicates that introducing additional binding sites, such as imidazole, pyrrolidone, and pyridine groups, increases the mercury-binding capacity of wool. This increase may result in part from increased accessibility of the wool to the mercury (Leach, 1960). Alkylated derivatives have the advantage over reduced wool of being stable toward oxidation.

As much as 90% of the mercury bound by wool from concentrated solutions can be recovered by extraction with so-

Table II. Mercury Sorption by Agricultural By-Products^a

Material	Sorption from mercuric acetate	
	Mercury adsorbed, mg/g	Residual concn, of Hg/l.
Walnut expeller meal	880	11
Peanut skins	820	12
Wool	580	14
Rice straw	280	17
Plum pit shells	240	18
Peanut hulls	220	18
Rice hulls	180	18
Sugar cane bagasse	180	18

^a In these tests, half-gram air-dried samples were shaken with 50 ml of 0.1M aqueous mercuric acetate (20 g Hg/l.) at pH 3.4-3.7 for one day at room temperature. The supernatant liquid was filtered through glass wool and analyzed.

Table III. Mercury Uptake by Wool Fibers and Chemically Modified Wool Fibers^a

Sample	Modifying agent	Mercury adsorbed, mg Hg/g wool
Control	None (untreated wool)	500
1	<i>N</i> -vinylimidazole	650
2	<i>N</i> -vinylpyrrolidone	750
3	2-vinylpyridine	850

^a One g of material was treated with 100 ml of 0.2M aqueous mercuric chloride solution for 24 hr at room temperature. The keratin material was then removed from the solution, washed thoroughly, and analyzed for mercury by atomic absorption spectroscopy. Chemical modifications of wool were carried out as described by Friedman and Noma (1970).

dium citrate, sodium ethylenediaminetetraacetate, sodium thiocyanate, or even sodium chloride solutions. The rest that is more firmly bound appears related to the content of sulfhydryl groups. Thus, adsorbed mercury is less completely recovered from reduced wool, in which disulfide bonds have been converted to sulfhydryl groups.

Finally, the Freundlich relationships, extrapolated, can be used to make a preliminary guess of the amount of wool needed to remove mercury from water under given conditions. On this basis, an industrial waste with 138 mg of Hg/l. would need to be treated batchwise with about 0.1 kg of wool/l. at low pH to bring it to the mandatory maximum level permitted in a public water supply, 5 mcg/l. (5 ppb). Countercurrent processing would decrease the amount needed to about 3 g/l. treated. We are continuing to explore theoretical and practical aspects of this problem.

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industry trends

Babcock and Wilcox has sold its first industrial vortex incinerator to Hyon Waste Management Services, Inc., a Chicago-based waste disposal company. The \$400,000 contract marks Babcock and Wilcox's entry into the industrial incinerator field.

Warner Co. (Philadelphia, Pa.) has created Waste Tech, Inc., by a merger of Warner's wholly owned solid waste subsidiaries with ChemTech Industries, Dallas, Tex.

Waste Management, Inc. (Chicago, Ill.) has acquired three solid waste handling firms—Southwest Towns Refuse Disposal Service, Inc. (Chicago Ridge, Ill.); Banner Disposal Service, Inc. (Joliet, Ill.); and Elgin Disposal, Inc. (Elgin, Ill.)

IKOR Inc. (Burlington, Mass.) has entered the noise control field by acquiring an equity interest in Cambridge Collaborative, Inc.

J. F. Pritchard and Co. (Kansas City, Mo.) has begun building a Stretford unit near Herscher, Ill., for National Gas Pipeline Co. of America (Chicago, Ill.). The unit will remove hydrogen sulfide from gas at the rate of one long ton/day.

Honeywell's Industrial Division has been awarded a \$417,000 contract to automate secondary sewage facilities for the city of Portland's (Ore.) Columbia Blvd. plant.

Combustion Engineering has formed Thermal Energy System Co., Inc. (THESCO) in a joint venture with M. DeMatteo Construction Co. to build a \$26 million incinerator which will raise steam to sell to industry.

Bechtel Corp. (San Francisco, Calif.) has formed four new environmental divisions within its scientific development organization—Ecology and Water Group, Air Quality Group, Process Technology Group, and Regional Planning and Economics Group.

Interindustry Emission Control Program (IEEC) an industry-sponsored cooperative venture, has been extended for a sixth year, through 1972. IEEC members

include American Oil Co., Atlantic Richfield Co., Fiat S.p.A., Marathon Oil Co., Mitsubishi Motors Corp., Nissan Motor Co., and Toyo Kogyo Co., Ltd.

Permutit will supply the largest reverse osmosis water treatment plant ever ordered to Cavanagh Communities Corp., Miami, Fla. The 500,000-gal/day plant will cost about \$300,000.

International Pulp and Paper Co. will spend \$7.8 million on air and water improvement projects on its Gardiner, Ore., mill by 1974.

Beckman Instruments has installed seven end-of-assembly line emission measurement systems in Ford Motor Co.'s Pico Rivera, Calif., plant.

Dow Chemical has signed a licensing agreement with Bio-Rad Laboratories (Richmond, Calif.) to market Dow's line of hollow fiber devices for water treatment in the U.S.

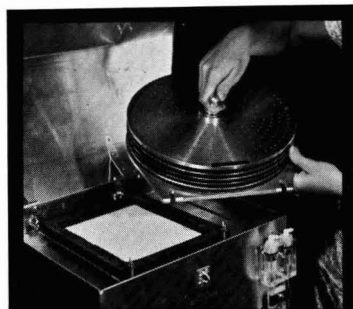
Du Pont has established a worldwide marketing organization for its Permapermeator reverse osmosis unit with designation of six new distributors in Europe and the Far East.

Westinghouse will build a second 930,000-kW nuclear plant for Spain's largest electric utility, Iberduero S.A.

Owens-Illinois says that more than 138 million lb of old bottles and jars were purchased from the public at a cost of about \$1.3 million last year for recycling at the company's 18 domestic glass container plants.

Peabody Welles, Inc. (Roscoe, Ill.) has acquired rights for the Simcar turbine aerator, developed by Simon-Hartly, Ltd., Stoke-on-Trent, England.

International Water Resources Association (IWRA) has been recently formed as a not-for-profit, nongovernmental scientific association for interdisciplinary discussion of water resources and technology. Membership information is available from IWRA, E320 Science Complex Bldg., University of Milwaukee, Milwaukee, WI 53201.



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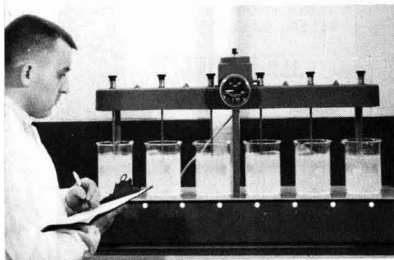
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Silica monitors

Models 651B and 1234B are updated versions of earlier analyzers for monitoring the silica content of water. 651B is used for phosphate-free samples while 1234B minimizes phosphate interference. Range is from 5 ppb to 5 ppm. Hach Chemical Co. **61**



Stirrer

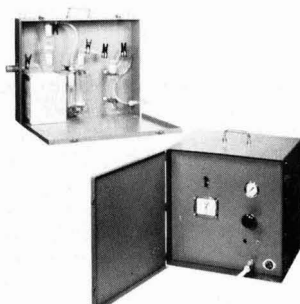
Six-place paddle stirrer is designed for flocculation laboratory comparison tests. Phipps and Bird, Inc. **62**

CO monitor

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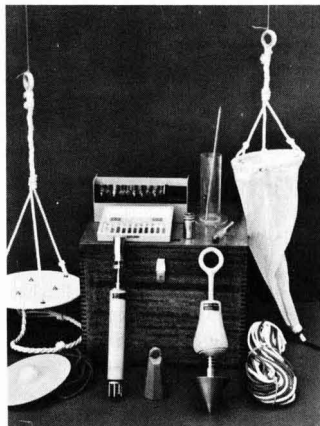
Centrifuge

Model No. 913 Clarifuge is exceptionally compact machine which occupies far less floor space than conventional continuous discharge centrifuges. Handles neutral or corrosive liquids at flow rates from 5-15 gpm. Leon Barrett Co. **64**



SO₂ train

AP-2000 series source sampling train is used for determining amounts of SO₂ and SO₃ in stack gases. Sampling method meets EPA requirements. Scientific Glass Blowing Co., Inc. **65**

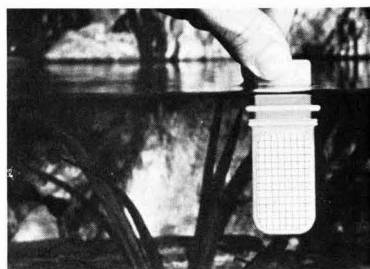


Oceanography kit

Kit provides equipment for analyzing marine, estuarine, and fresh water for pH, DO, CO₂, salinity, calcium, magnesium, total hardness, and transmitted light. InterOcean Systems, Inc. **66**

Flow meter

Model 61R provides permanent chart record of effluent flow in open channels. Has variable chart speed and digital totalizer which eliminates need to calculate total volume. Leupold and Stevens, Inc. **67**



Coliform test

Simple dip test for detecting coliforms is a presterilized disposable device using standard Millipore filter to isolate and concentrate bacteria. Subsequent incubation reveals countable colonies on plates. Range is 1-80 colonies/ml. Dilution expands range. Millipore Corp. **68**

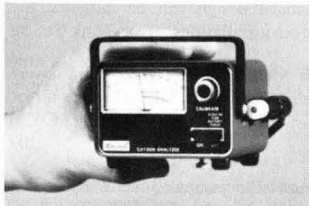
Two-stage scrubber

Adjustable wet scrubber provides two-stage cleaning of dust-laden gas streams of particles down to submicron size. Preassembled standard units handle volumes as high as 33,800 cfm. Air Purification Methods, Inc. **69**

Compactor

Trash compactor holds 15 gal. of compacted refuse and has a slide-out dolly for easy unloading. Operates on any standard 15-A outlet. Compaktion Engineering **70**

Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into the back of this issue and mail in the card. No stamp is necessary.



Oxygen analyzer

Analyzer instantly indicates amount of oxygen in any enclosure to help employers meet OSHA job safety requirements. Performs continuous or intermittent monitoring, has high- and low-limit alarm warnings. Edmont-Wilson 71

Programmer

Low-cost programmer can be used to automate almost all manual plant operations with up to 10 sequential processes. Precipitair Pollution Control 72

Adsorber

Gasketless charcoal adsorber is high-efficiency, leakproof unit originally developed for nuclear containment, but suitable wherever hard-to-handle or toxic materials are being used. Barneby-Cheny 73

Exhaust purifier

Diesel downtime is reduced by new exhaust purifier with replaceable catalytic cartridge. Eliminates cost of stocking spare mufflers. Granlin Corp. 74

Flowmeter probe

Series Pt-200 turbine flowmeter probe accurately measures stream velocities in larger pipeline sizes. Probe is corrosion resistant, simple to install, and easy to maintain. Mead Instruments 75

Separator

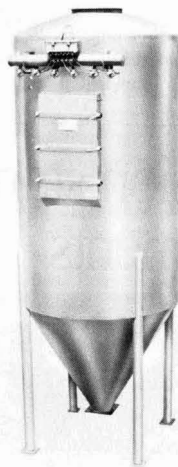
Prepackaged Hydro-Gard oil/water separator operates at moderate flow rates. Oil may be reclaimed and water recycled if desired. Cylindrical access risers permit below-grade installation with easy access for maintenance and cleaning. Inland Environmental 76

Particle counter

HIAC PC-305 SSTA automatic particle counter counts and sizes particles in gas or liquids on line or from sample bottles. Features automatic base line correction. High Accuracy Products Corp. 77

Sampler

Liquid sampler employs fluidic logic control circuit of new design to control sampling frequency and duration. Sample lift is adjustable from 2 in. to 280 ft. Brandywine Valley Sales Co. 78



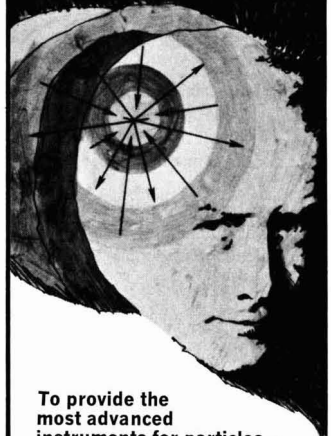
Dust Collectors

Sanitary dust collectors are designed for applications involving the collection and recovery of products for human consumption such as powdered milk, sugars, salt, dextrin, grains, cocoa, and the like. Stainless steel surfaces are of 28 or higher finish, with special finishes available. Flex-Kleen Corp. 79

Process control

Automatic process control for water treatment plants is designed to be used in conjunction with company's coagulant control center. Unit varies coagulant dosage according to effluent quality and corrects for fluctuations. Neptune Microfloc 80

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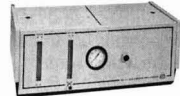
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new literature

Sewage conditioning. Bulletin describes use of Dynamic Sewage Conditioner to chop and shred difficult materials in closed system. Franklin Miller, Inc. 91

Recycled paper. Brochure printed on reclaimed fiber paper tells of advantages of Clearstream bond. Samples available. Gilbert Paper Co. 92

Precipitators. Pamphlet describes costs and operating characteristics of Precipitair modular electrostatic clean air systems. Precipitair Pollution Control 93

Water quality equipment. Brochure briefly describes monitoring equipment in company's automated environmental instrumentation line and analytical laboratory services available. Raytheon Co. 94

Corrosion aids. Booklet explores pollution control methods and devices and gives information on use of mechanical fasteners in environments involved. IRT Harper, Inc. 95

Data sheet. Pamphlet provides data on low-cost air-supported reservoir and tank covers associated with water treatment and distribution. Industrial Covers 96

Oil booms. Brochure describes latest advances in oil slick cleanup by boom methods. Slickbar, Inc. 97

Film. Reprint from Filmmakers Newsletter tells of making documentary on effects of stripmining in W.Va. and reaction of local residents. Film is also available. McGraw-Hill 98

Package plants. Brochure lists line of package waste water treatment plants. Standard design can be modified for custom installations. Texas Tank Co. 99

Test Meters. Four-page bulletin covers line of flow meters for testing dry air or gases. Specs are given. The Singer Co. 100

Nonmetallic pumps. Bulletin lists glass fiber-reinforced nonmetallic pumps in various sizes for a variety of applications. Sethco Pump Co. 101

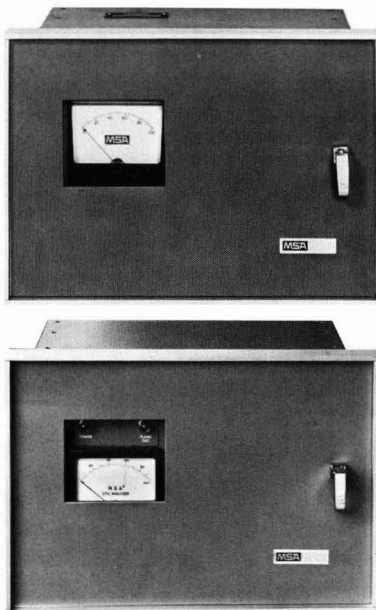
Catalog. 1972 catalog offers a line of 2500 chemicals for reagent use. Apache Chemicals 102

Systems. Wallet-sized folder describes company's services, systems, and products to help control pollution in the environment. Johns Manville 103

Check auto emission standards with MSA instruments. EPA does.

The government chose our hydrocarbon and carbon monoxide analyzers to prove your compliance with the federal emissions standards. You'll find the same instruments monitoring the air you breathe, stack emissions and in-plant pollution.

Involve an MSA man in your emission problems. He knows exactly what you're up against. Write Mine Safety Appliances Co., Pittsburgh, Pa. 15208.



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Ion exchange report. Bulletin entitled "Economic and Technical Considerations in Selection of Ion Exchange Equipment" is designed to serve as a guide for engineers involved in purchase of ion exchange equipment. Graver Water Conditioning Co. **104**

Turnkey service. Bulletin describes company's capabilities in turnkey approach to environmental problem-solving. Nalews-Weston **105**

Data sheet. Sheet details specs of new battery-powered, hand-held conductivity meter for measuring pollution in industrial or commercial water systems. Myron L Company **106**

Surveillance equipment. Bulletin features environmental surveillance equipment for evaluating and protecting against noise. Mine Safety Appliances Co. **107**

Filter specs. Data sheets describe cfm capacity, media area, face velocity, media velocity, pressure drop, efficiency, and physical size of soc filters. Thermo-Kinetics, Inc **108**

Analysis service. Technical bulletin details capabilities of laboratory in detection, sampling, analysis, and measurement of water contaminants. Alpha Analytical Laboratory **109**

Catalog. Catalog entitled "Viewpoints" is issued bimonthly and features products and apparatus for ecology markets. Horizon Ecology Co. **110**

Bark-burning boilers. 8-page brochure describes line of steam-raising, bark-burning incinerators with boiler capacities ranging to 1 million lb/hr steam. Combustion Engineering, Inc. **111**

Filtration unit. Bulletin describes Osmotik Pilot Processor, adaptable to either reverse osmosis or ultrafiltration operation by use of interchangeable membrane types at different pressures. Calgon Corp. **112**

Library index. Recently updated edition of index on vibration/shock/noise control lists technical articles exploring either theoretical or practical aspects of energy control design and application. Lord Manufacturing Co. **113**

Capabilities brochure. Publication tells of expertise of company specializing in air pollution studies. Environmental Resources, Inc. **114**

Meter selection. Reprint is offered on selection of meters for gas measurement which recently appeared in serialized form in trade journal. Singer **115**

Applications notes. Two brief notes deal with measurement of mercurials and difficult-to-measure plating constituents such as tin, copper, and zinc. Texts cover methodology, sample preparation, and use of company's atomic absorption equipment. Spectrametrics **116**

Beta irradiators. Data sheet describes characteristics of ⁹⁰Sr high-energy beta emission sources and applications in environmental surveillance. International Chemical and Nuclear Corp. **117**

Paper products. Booklet for consumer tells of ecological consequences of use of disposable paper items. American Paper Institute **118**

Waste water survey. Pollution control surveys are explained in new bulletin which describes company's capabilities in environmental services. Dearborn Chemical Corp. **119**

Health service. Third bulletin in series from company describes hearing conservation services tailored to assist industry and government in developing hearing conservation programs as integral part of occupational safety activities. Dow Chemical Co. **120**

Auto pollution. Booklet entitled "The Environment" was prepared to give technical community an overview of company's environmental activities. General Motors Corp., Detroit, MI 48202 (Write direct)

Patent reproduction. Free reproduction of first patent for boiler water treatment printed on heavy weight antique parchment, suitable for framing. Drew Process Chemicals, 701 Jefferson Road, Parsippany NJ, 07054 (Write direct)

Seminar schedule. Brochure lists seminar schedule of company on sound and vibration topics. B&K Instruments, Inc., 5111 West 164th Street, Cleveland, OH 44142 (Write direct)

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Noise Pollution: The Unquiet Crisis. Clifford R. Bragdon. xv + 280 pages. University of Pennsylvania Press, 3933 Walnut St., Philadelphia, PA 19104. 1971. \$15, hard cover.

Gives facts and figures, precise scientific measurements, and accurate data on what noise is, what it does, and how to combat it. The author pinpoints noise levels of automobiles, buses, subways, airplanes, household appliances, and children's toys in charts and tables and relates these data to the measurable social, physical, and psychological damage they do to human beings. Intended for the interested citizen, urban planners, architects, hospital administrators, public health officials, transportation executives, lawyers, realtors, sound engineers, manufacturers, and community leaders. ■

Advances in Environmental Science and Technology, Vol. 2. James N. Pitts, Jr., Robert L. Metcalf, Eds. vii + 354 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1971. \$17.95, hard cover.

Features topics ranging from broad considerations of air pollution and specific measurement techniques to environmental pollution by mercury and toxicity and carcinogenicity of aflatoxins. This series aims to delineate and solve the multitude of environmental problems man's technology has created. ■

Chemical Reactions in Urban Atmospheres. Charles S. Tuesday, Ed. xiv + 287 pages. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, NY 10017. 1971. \$14.50, hard cover.

Topics considered include thermal and photochemical reactions of oxides of nitrogens with hydrocarbons, atmospheric role of singlet molecular oxygen, photooxidation of alkyl nitrites and of formaldehyde, and the chemical forma-

tion of atmospheric aerosols. Of special interest to those in atmospheric chemistry field, but also of interest to chemists, ecologists, research workers, and engineers concerned with air pollution. ■

Environment and Development. M. O. de Almeida, W. Beckerman, I. Sachs, and G. Corea. 84 pages. Carnegie Endowment for International Peace, United Nations Plaza at 46th St., New York, NY 10017. 1972. \$1.00, paper.

Deals with issues concerning developing countries and the environment. Why should developing countries be concerned with environmental issues at early stages in their development? What greater pollution is there than poverty, starvation, sanitation, and deteriorating housing? Environmental standards may affect products from developing countries. ■

Energy and Power: A Scientific American Book. viii + 144 pages. W. H. Freeman & Co., 660 Market St., San Francisco, CA 94104. 1971. \$3.25, paper.

Articles taken from *Scientific American* giving a detailed discussion of energy and power and placing this subject in its scientific context. Recommended for students and professionals in many areas of the physical and social sciences. ■

Environmental Law, Vol. 1. Arnold W. Reitze, Jr., North American International, P.O. Box 28278, Central Station, Washington, DC 20005. 1971. \$13.95, hard cover.

First of two volumes containing extensive and authoritative commentaries on the full range of environmental legal matters, from underlying philosophies to radioactivity and solid waste. Volume 1 stresses pollution control and is intended for general reading by lawyers, reference, and supervised study in either a one-semester law school class or the first half of a two-semester course. ■

Environmental Quality: Now or Never. Charles L. San Clemente, Ed. xv + 320 pages. Michigan State University, East Lansing, MI 48823. 1972. \$4.00, paper.

Contains some 34 articles covering environmental visions, ecology, problems-answers, water treatment innovations, multiple complexities, and positive responses. Aim of the authors is to present recent man-made changes in the environment and possible ways of correcting these changes. ■

Water and Water Pollution Handbook, Vol. 3. Leonard L. Ciaccio, Ed. xi + 512 pages. Marcel Dekker, Inc., 95 Madison Ave., New York, NY 10016. 1972. \$27.50, hard cover.

Third of a four-volume treatise on water and water systems. This volume is concerned with the physical-chemical characteristics of water environments and the design of measurement systems. Also includes water standards and analyses for selective parameters. Written for personnel waste treatment and water purification plants; transportation industry; service industries; government enforcement agencies; government, industrial, and university research laboratories; and sanitary, civil, and consulting engineers. ■

Man's Impact on Climate. William H. Matthews, William W. Kellogg, G. D. Robinson, Eds. xvii + 594 pages. MRR Press, 28 Carleton St., Cambridge, MA 02142. 1971. \$19.50, hard cover.

This report reproduces, complements, and supplements material in the Study of Critical Environmental Problems (SCEP) report. Provides an overview of the present state of knowledge about the climate and the atmospheric processes that produce climate and climate change and the interaction of pollutants with these processes. Discusses monitoring and modeling tools and actions that might be taken to improve problems that are understood. ■

Principles of Water Quality Control. T. H. Y. Tebbutt. ix + 179 pages. Pergamon Press, Inc., Maxwell House, Fairview Park, Elmsford, NY 10523. 1971. \$5.50, paper.

Designed as a text for undergraduate civil engineering courses and as preliminary reading for postgraduate courses in public health engineering and water resources technology. The text is based on lectures by the author to undergraduate civil engineers augmented by material prepared for extramural short courses. ■

Air Pollution and the Social Sciences: Formulating and Implementing Control Programs. Paul B. Downing, Ed. xv + 270 pages. Praeger Publishers, 111 Fourth Ave., New York, NY 10003. 1971. \$16.50, hard cover.

Assessment of sociological, psychological, political, legal, and economic aspects of the air pollution problem. Focuses on reassessing air quality standards, cost-effectiveness analysis of alternative control devices, legislative implementation, need for policy studies, and winning public acceptance for control programs. From the University of California Project Clean Air Program. ■

Dimensions of the Environmental Crisis. John A. Day, Frederic F. Fost, Peter Rose. viii + 212 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1971. \$5.95, hard cover.

"The principle purpose of this book," say the authors, "is to emphasize the many interrelated dimensions of the environmental crisis, and hence to demonstrate that a permanent solution can come only through an interdisciplinary approach in which knowledge of the humanities is integrated with that of science and technology." Text is suitable for college students, professional people, and others concerned in finding realistic solutions to environmental problems. ■

Renovated Waste Water. James F. Johnson. ix + 155 pages. University of Chicago, Dept. of Geography, 5828 S. University Ave., Chicago, IL 60637. 1971. \$4.50, paper.

Results of a study made under a fellowship granted by Resources of the Future, Inc. Covers the municipal water problem: an alternative, municipal water supply from sewage effluent, comparative cost analysis at three sites, consumer attitudes toward renovated waste water, and the prospect for renovation. ■

Urban Water Resources Management. 132 pages. American Society of Civil Engineers, 345 E. 47 St., New York, NY 10017. 1971. \$8.00.

Collection of papers delivered at the Engineering Foundation Research Conference held in 1970. Covers the many facets, dimensions, problems of urban water resources management, and approaches and methods for stimulating and accelerating adoption of improved management practices. ■

Anaerobic Biological Treatment Processes. Robert F. Gould, Ed. x + 196 pages. American Chemical Society, 1155 Sixteenth St., N.W., Washington, DC 20036. 1971. \$9.00, hard cover.

Papers chosen from a symposium sponsored by the Division of Water, Air, and Waste Chemistry of the American Chemical Society. Anaerobic decomposition as a waste treatment technique is jeopardized by continuing reports of failing and stuck digesters. The papers were chosen for the biological and engineering expertise they contain regarding the state-of-the-art of this field. Covers methane fermentation, process control, energetics and kinetics of anaerobic treatment, phase separation by dialysis, and applying process kinetics to anaerobic processes design. ■

Environmental Engineering Teaching Reference Community. John M. Bell, David L. Brenchley. Environmental Engineering, School of Civil Engineering, Purdue University, Lafayette, IN 47901. 1971. \$5.00, paper.

Dawson, Fairfax County is a hypothetical community developed by the authors as a teaching aid for undergraduate and graduate courses in environmental engineering. The environmental problems encountered involve social, political, economic, and technical aspects. Students will find this classroom material relevant and in need of immediate application. ■

Biochemical Ecology of Water Pollution. Patrick R. Dugan ix + 159 pages. Plenum Publishing Corp., 227 W. 17 St., New York, NY 10011. 1972. \$14.50, hard cover.

Examines water pollution by interrelating gross examinations with biological reactions occurring at the cellular and molecular levels. Includes: degradation of organic pollutants; organic, mineral, and heat pollution; pollution by recalcitrant molecules; anaerobic decomposition and methane fermentation; solutions, suspensions, colloids, and biological implications of bound water. ■

Environmental Education in the Community College. Arden L. Pratt. 140 pages. Publications Office, American Association of Junior Colleges, One Dupont Circle, Washington, DC 20036. 1971. \$4.50, paper.

Discusses the extent of present programming in two-year colleges and the possible demands for tomorrow since community junior colleges figure to play a primary role in producing technicians and skilled personnel needed for environmental positions. Community colleges can be a major resource for meeting such needs, but there is a dearth of information about areas of need which hinders educational planning. ■

May 18-20

American Society for Hospital Engineers

Institute on Hospital Solid Waste Management
Chicago, Ill.

All facets of hospital solid waste management will be discussed including legal considerations, community health hazards, and choosing appropriate disposal systems to fit individual health care institutions. Write: Edward J. Bertz, Secretary, AMHE, 840 N. Lake Shore Dr., Chicago, IL 60611

May 21-24

American Society of Chemical Engineers

72nd National Meeting
St. Louis, Mo.

Sessions cover air and water pollution, solid waste, and radiation. Contact: G. L. Esterson, Dept. of Chem. Eng., School of Eng. and Applied Sciences, Washington Univ., St. Louis, MO 63160

May 24-25

Process Equipment Manufacturers' Association

PEMA Spring Meeting
Chicago, Ill.

Includes forum on waste water equipment. Contact: Art Parchen, Executive Director, P.O. Box 8745, Kansas City, MO 64114

May 27-June 4

EPA, SAE, DOT, and others

TRANSPO '72 and International Conference on Transportation and the Environment

Washington, D.C.

Addresses a wide range of environmental issues, including air and noise pollution, congestion, and land use policies. Write: SAE Meetings Dept., 2 Pennsylvania Plaza, New York, NY 10001

June 1-2

Mass. Dept. of Community Affairs and University of Mass.

Regionalized Solid Waste Management Conference

Newton, Mass.

Barriers and advantages to regional disposal will be evaluated. Covers site selection, legislative provisions, regulations, and assistance. Contact: Ruth Kreplick, Technical Guidance Center for Environmental Quality, Marshall Hall, University of Mass., Amherst, MA 01002

June 1-2

Vanderbilt Univ. and Tenn. Dept. of Public Health

Eleventh Annual Environmental and Water Resources Engineering Conference
Nashville, Tenn.

Will emphasize interrelationships among water resources engineering, water quality control, water supply, municipal and industrial waste treatment, and solid waste management. Write: Edward L. Thackson, Vanderbilt Univ., Box 133-Station B, Nashville, TN 37203

June 2-4

American Water Works Assoc. and Water and Wastewater Equipment Manufacturers' Assoc., Inc.

92nd Annual AWWA Conference and WWEMA Exhibit
Chicago, Ill.

Contact: AWWA, 2 Park Ave., New York, NY 10016

June 4-7

American Society of Mechanical Engineers

1972 Fifth National ASME Incinerator Conference
New York, N.Y.

"Waste Processing—Its Ecological Impact" theme. Program will stress improvements and trends in incinerator design and operation in the U.S. and abroad. Contact: Maurice Jones, ASME, 345 E. 47th St., New York, NY 10017

June 5-7

American Gas Assoc. and Institute of Gas Technology

Second Conference on Natural Gas Research and Technology
Atlanta, Ga.

Includes an all-day session on safety and pollution research. Contact: AGA, Inc., 1515 Wilson Blvd., Arlington, VA 22209, or IGT, 3424 S. State St., Chicago, IL 60616

June 5-7

AIME and AICE

North American Rapid Excavation and Tunneling Conference
Chicago, Ill.

Includes environmental implications, geological hazards, and transportation systems. Contact: Alexander Scott, AIME, 345 E. 47th St., New York, NY 10017

June 6-7

Walter C. McCrone Associates

Stack Sampling Seminar
Chicago, Ill.

Includes compliance regulations, sampling methods, errors, cost estimates, automated monitors, particle sizing, and size selective sampling devices. Contact: Mrs. Nancy Nazareus, Walter C. McCrone Assoc., 493 E. 31 St., Chicago, IL 60616

June 7-9

University of Rochester

Fifth International Conference on Environmental Toxicity
Rochester, N.Y.

Contact: Public Relations—0121, Medical Center, University of Rochester, 260 Crittenden Blvd., Rochester, NY 14620

June 11-14

American Society of Mechanical Engineers

Summer Annual Meeting
Washington, D.C.

Write: ASME, 345 E. 47th St., New York, NY 10017

June 13-14

American Society for Metals

3rd All-Industry Workshop on Pollution Control
Cleveland, Ohio

Geared for managers and engineers with how-to responsibilities for pollution control at the plant level. Write: H. E. Chandler, Managing Editor, Metal Progress, American Society for Metals, Metals Park, OH 44073

June 13-15

University of Missouri

6th Annual Conference on Trace Substances in Environmental Health
Columbia, Mo.

Write: Delbert D. Hemphill, Univ. of Mo., Columbia, MO 65201

June 13-16

AIChE, IEEE, ISA, and others

1972 Summer Simulation Conference
San Diego, Calif.

Will summarize advances in mathematical modeling; includes environmental technology modeling. Write: L. E. Randolph, A3-250-AAB1, McDonnell-Douglas Astronautics Co./West, 5301 Bolsa Ave., Huntington Beach, CA 92647

June 14-16

Pollution Control Association of Ontario

Pollution Control Show
Toronto, Ontario

Devoted to all aspects of pollution and environmental control and will be held annually. Open to Canadian and U.S. companies and to government agencies active in pollution control. Contact: R. J. Frewin, Petlock, Ruder & Finn Ltd., Suite 500, 101 Bloor St. W., Toronto 181, ONT

June 18-22

American Nuclear Society

1972 National Meeting
Las Vegas, Nev.

Contact: ANS, 244 E. Ogden Ave., Hinsdale, IL 60521

June 19-21**American Water Resources Assoc. and Colorado State University**

Watersheds in Transition National Symposium
Fort Collins, Colo.

Covers the management of watersheds and their water resources in view of changing environments, priorities, and methods. Contact: American Water Resources Assoc., P.O. Box 434, Urbana, IL 61801

June 19-22**Air Pollution Control Association**

65th Annual Meeting and Exposition
Miami Beach, Fla.

Open to all individuals in industry, government, science, and education concerned with air pollution control. Includes equipment exhibition plus 150 technical papers. Write: Public Relations Dept., Air Pollution Control Association, 4400 Fifth Ave., Pittsburgh, PA 15213

June 21-24**National Solid Waste Management Association**

8th Annual International Refuse Equipment Show & Congress
Denver, Colo.

Topics include land disposal, stationary compaction/container systems, management of collection operations, manpower development & incentives, new developments in resource recovery, and trends in the solid waste industry. Contact: NSWMA, #214, 1145 Nineteenth St., N.W., Washington, DC 20036

June 26-28**American Society of Civil Engineers**

Specialty Conference
Rochester, N.Y.

Titled "Nutrient Removal—How to Do It." Contact: ASCE, 345 E. 47th St., New York, NY 10017

Courses**May 19 deadline****Adelphi University**

Marine and Environmental Science Workshops
Garden City, L.I., N.Y.

Eight summer courses and workshops for credit in marine sciences. Also, eight credit courses in environmental geology, and others. Bachelor's degree is major requirement. Write: Leonard S. Stein, Dean, Summer Sessions, Adelphi Univ., Garden City, L.I., N.Y. 11530

May 19**Technomic Publishing Co.**

Design and Operation of Domestic Sewage and Industrial Waste Water Treatment Systems Seminar
Norwalk, Conn.

Will cover principles and methods of physical, chemical, and biological treatment of domestic sewage and industrial waste water. Fee: \$90. Write: Program Div., Technomic Publishing Co., Inc., 265 W. State St., Westport, CT 06880

May 22-26**Cambridge Collaborative**

Acoustics and Noise Control in Buildings Seminar
Cambridge, Mass.

Will include sources of noise in buildings, acoustical performance of walls and floors, noise control devices, and transmission of sound in open spaces within buildings. Fee: \$390. Contact: Jerome E. Manning, Cambridge Collaborative, 40 Ames St., Cambridge, MA 02142

May 22-26**University of Missouri—Rolla**

Water Pollution Control/Waste Treatment and Disposal Short Course
Rolla, Mo.

Will present the fundamental concepts and discuss physical, chemical, and biological treatment of waste water. Fee: \$250. Write: Ju-Chang Huang, Dept. of Civil Engineering and Environmental Research Center, Univ. of Missouri—Rolla, Rolla, MO 65401

May 22-26 and May 30—June 2**Manhattan College**

17th Summer Institute in Water Pollution Control
Bronx, N.Y.

Stream and Estuarine Analysis or Biological Waste Treatment offered the first week, and Advanced Topics in Mathematical Modeling of Natural Water Systems the second week. Total fee: \$425. Limited number of grants available. Write: Donald J. O'Conner, Environmental Engineering & Science Program, Manhattan College, Bronx, NY 10471

May 22—June 16**American University**

Environmental Systems Analysis
Washington, D.C.

Survey course of multidisciplinary integrated ecological analysis of three environmental systems of earth—air, land, and water. Contact: Martha Sager, Environmental Systems Institute, American University, Washington, DC 20016

meeting guide

May 31—June 1**George Washington University**

Air Pollution Control Short Course
Washington, D.C.

Will provide state-of-the-art information on air pollution control for engineers and technical personnel working in this field. Fee: \$140. Contact: Continuing Engineering Education Program, George Washington Univ., Washington, DC 20006

June 5-9**George Washington University**

Noise Control in Industry and Transportation Short Course
Washington, D.C.

Designed for engineers and scientists in industry and transportation who are concerned with noise control methods. Fee: \$315. Write: Continuing Engineering Education Program, George Washington University, Washington, DC 20006

June 5-9**University of Tulsa**

Designing to Meet Effluent Guidelines in Refineries Short Course
Tulsa, Okla.

Covers influences of state and federal guidelines, effects on biological treatment systems, incineration, and other topics. Fee: \$200. Write: Chemical Engineering Dept., University of Tulsa, 600 S. College Ave., Tulsa, OK 74104

June 5-10**University of Wisconsin-Extension**

Urban Transportation Short Course
Milwaukee, Wis.

Contact: Lowell Jackson, Univ. of Wis.-Extension, Dept. of Engineering, 600 W. Kilbourn Ave., Milwaukee, WI 53202

June 7-9**Cyrus Wm. Rice Div.—NUS Corp.**

18th Annual Water Seminar
Pittsburgh, Pa.

Presents to management, engineering, and operating personnel a series of lectures on modern practices in industrial water management and water technology. Fee: \$300. Write: Cyrus Wm. Rice Div., NUS Corp., 1910 Cochran Rd., Pittsburgh, PA 15220

June 11-16**Instrument Society of America**

Process and Environmental Analytical Instrumentation Short Course
Pittsburgh, Pa.

Designed for scientist or engineer who can benefit from a survey of fundamentals and applications of process and/or environmental instrumentation. Fee: \$300. Write: Instrument Society of America, Short Courses, 400 Stanwix St., Pittsburgh, PA 15222

(Continued on p 468)

June 12-23

George Washington University

Modeling Hydrologic and Water Resources Problems Short Course
Washington, D.C.

Will cover modern concepts applied to watershed models, streamflow synthesis, water quality, irrigation scheduling, urbanization, data collection, and regionalization. Fee: \$490. Contact: J. E. Manfield, Director, Continuing Engineering Education Program, George Washington Univ., Washington, DC 20006

June 12-23

George Washington University

Traffic Flow and Transportation Systems Short Course
Washington, D.C.

Fee: \$490. Write: Continuing Engineering Education, Schools of Engineering and Applied Science, George Washington Univ., Washington, DC 20006

Illinois Institute of Technology

Environmental Control Graduate Training
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University of Colorado

Water Resources Graduate Training
Boulder, Colo.

Interdepartmental program provides in-depth training in water quality control and management and broad-based studies in water management and engineering. For students with backgrounds in engineering, chemistry, biology, or related sciences. Write: J. Ernest Flack, Dir., Water Resources Training Program, Engineering Center, OT 4-34, University of Colorado, Boulder, CO 80302

International

May 24-26

Norwegian Society of Professional Engineers

International Symposium: The Fluorine Problem in the Primary Aluminum Smelting Industry
Trondheim, Norway

Designed for engineers in the aluminum smelting industry. Includes types of emission-reducing equipment, formation of pollutants, effects on the environment, and reducing effects. Contact: Tore Fagerhus, The Norwegian Society of Professional Engineers, Kronprinsensgt. 17, Oslo 2, Norway

June 5-16

United Nations

United Nations Conference on the Human Environment
Stockholm, Sweden

Attendance officially limited to government delegations. Extra seats on a first come, first served basis. Write: Whitman Bassow, Senior Public Affairs Officer, United Nations Conference on the Human Environment, Rm. 1061J, United Nations, New York, NY 10017

June 12-17

Society of Engineering Science, EPA, NOAA, and Washington University

International Meeting of the Society of Engineering Science
Tel Aviv, Israel

Theme: "Pollution: Engineering and Scientific Solutions." Focuses on environmental quality, international legal questions, government programs, and education for environmental awareness. Contact: Organizing Committee, Society of Engineering Science, P.O.B. 16271, Tel Aviv, Israel

June 18-24

International Association on Water Pollution Research

6th Annual International Conference on Water Pollution Research
Jerusalem, Israel

For information: Israel Host Committee, P.O.B. 16271, Tel-Aviv, Israel

July 11-14

Institute of Water Engineers

Symposium on Advanced Techniques in River Basin Management: the Trent Model Research Program
Birmingham, England

Contact: Paul Banbury, Institute of Water Engineers, 6-8 Sackville St., Piccadilly, London W1X 1DD, England

September 5-9

Swiss Electroplating Society

8th Congress of International Union for Electrodeposition and Surface Finishing
Basle, Switzerland

A special symposium will deal with problems of waste water from electroplating. Write: Organizing Committee, Interfinish, P.O. Box CH-4021, Basle, Switzerland

October 2-6

Commission of the European Communities and U.S. EPA

International Symposium on Environmental Health Aspects of Lead
Amsterdam, The Netherlands

Program will cover uptake and metabolism, subclinical effects, epidemiological studies, sources, and monitoring. Write: J. Smeets, Secretary, Health Protection Directorate, Commission of the European Communities, 29 Rue Aldringen, Luxembourg

October 10-14

Society of Chemical Engineers (Japan) and AIChE

First Pacific Chemical Engineering Congress
Kyoto, Japan

Includes sessions on air pollution control and water pollution control. Write: American Institute of Chemical Engineers, Japan Meeting, 345 E. 47 St., New York, NY 10017

October 26, 1972—September 7, 1973

UNESCO

International Course in Environmental Science and Technology
Delft, The Netherlands

Post-graduate course is related to inter-governmental research program on "Man and the Biosphere" focusing on causes, implications, and solutions of environmental problems. Contact: Netherlands Universities Foundation for International Cooperation, 27 Molenstraat, The Hague, The Netherlands

November 3-9

Sewage Engineering Association of the German Federal Republic and others

International Sewage and Refuse Engineering Exhibition and European Sewage and Refuse Symposium
Munich, Germany

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December 4-8

Ministry of Water Resources (Mexico) and International Association of Hydrological Sciences

International Symposium on the Planning of Water Resources
Mexico City, Mexico

International experts will compile methodologies and experiences of many countries toward enhancement of international cooperation. Contact: Ing. Gerardo Cruickshank G., Subsecretario de Planeación, Secretaría de Recursos Hídricos, Reforma No. 69-11° Piso, Mexico, D.F.

July 1973

AAAS and National Council of Science and Technology of Mexico

1973 Inter-American Scientific Meeting
Mexico City, Mexico

Includes air and water pollution discussions. Contact: American Association for the Advancement of Science, 1515 Massachusetts Ave., N.W., Washington, DC 20005

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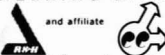
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INDEX TO ADVERTISERS IN THIS ISSUE

Accu-Labs Research, Inc.	470	Nupro Company	390
Alpha Metals, Inc.	471	Falls Advertising Company	
Steven Wyna Communications			
Anderson 2000 Inc.	459	Oakite Products, Inc.	391, 471
Aquaterra Biochemicals, Inc.	472	Marsteller Inc.	
Arkon Scientific Labs	472	O'Brien & Gere Engineers, Inc.	469
Sobel Advertising		Oilwell Research, Inc.	471
		Olympus Corporation of America- Precision Instrument Div.	411
The Bendix Corporation, Process Instru- ments Div.	392	Gallanos Advertising Agency, Inc.	
D'Arcy-MacManus-Intermarco, Inc.			
Biospherics, Inc.	399	George T. Peckham	469
Pallace Inc.		Philips Electronic Instruments	411
Brandt Associates, Inc.	388	J & M Condon, Inc.	
Calgon Corporation	IBC	Radiation Management Corporation	471
Ketchum, MacLeod & Grove, Inc.		Raytheon Environmental Systems Center	470
Catalytic, Inc.	471	Proviaida, Eastwood & Lombardi Inc.	
Arndt, Preston, Chapin, Lamb & Keen, Inc.		Research Appliance Company	394
Chemec Process Systems Inc.	470	W. F. Minnick & Associates	
Advertising Design Associates		Reynolds, Smith and Hills	471
The Chester Engineers	470	W. R. Hollingsworth & Associates	
W. S. Hill Co.		Ryckman, Edgeley, Tomlinson & As- sociates	471
Control Data Corporation, Research Div.	469	W. B. Saunders Company	399
Crobaugh Laboratories	471	Alycon Advertising Agency	
Dames & Moore	470	Science Associates, Inc.	469
Datametrics	388	Sierra Research Corp.	471
S. Gunnar Myrbeck & Company, Inc.		B. P. Myer Associates, Inc.	
		Southwestern Laboratories	470
ecoLogistics, inc.	469	Boone Advertising, Inc.	
Albert Dib		SpectroChem Laboratories, Inc.	470
Environmental Research Corporation	461	Stewart Laboratories, Inc.	471
Jack Wenger Advertising, Inc.		H. C. Swope and Associates	469
Environmental Research Group, Inc.	469		
		Texas Electronics, Inc.	470
Fabric Research Laboratories, Inc.	469	The Jordan Co.	
Fluidyne Engineering Corporation	471	TRC—The Research Corporation of New England	470
Ernest F. Fullam, Inc.	469		
		Woodward-Evicon, Inc.	471
Galbraith Laboratories, Inc.	470	York Research Corporation	469
Galson Technical Services, Inc.	470	Thomas A. Blanchard Associates	
General Testing Laboratories, Inc.	470		
Hach Chemical Co.	OBC	Advertising management for the American Chemical Society Publications	
Wesley Day and Company, Inc.		CENTCOM, LTD.	
Heil Process Equipment Corporation	471	(formerly Century Communications Corp.)	
Ashby Associates, Inc.		Edward P. Blanchard, President; Thomas N. J. Koevwer, Executive Vice President, 142 East Avenue Norwalk, Connecticut 06851 (Area Code 203) 853-4488	
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Industrial Pollution Testing Labora- tories	469		
Kem-Tech Laboratories, Inc.	469		
Kuljian Corporation	469		
William Jenkins Advertising			
Limnetics, Inc.	471		
The Brady Company			
Metcalf & Eddy Engineers	471		
Millipore Corporation	389		
Czyryca/Design, Inc.			
Mine Safety Appliances Co.	462		
Ketchum, MacLeod & Grove Inc.			
MIT Press	390		
Franklin Spier Incorporated			
The Mogul Corporation	IFC		
Mills Hall Walborn Inc.			
Nalews-Weston	421		
Mead-Ross Associates			
The National Center for Resource Re- covery, Inc.	472	PRODUCTION DIRECTOR Joseph P. Stenza	
New York Testing Laboratories, Inc.	469	PRODUCTION ASSISTANT Peggy Downey	
Samuel Rosaler Advertising			
The C. W. Nofsinger Company	471		

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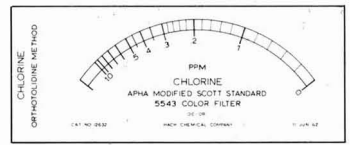
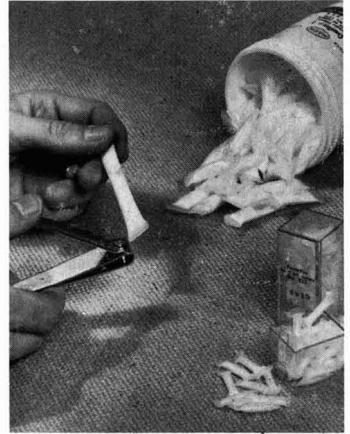
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