ENVIRONMENTAL Science & Technology

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Noise - Fourth form of pollution 720



Dangerous Demons of Pollutermist Captured by Brink® Mist Eliminators



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of particles to trap mists is the Brink Mist Eliminator. It also uses impaction and direct interception. Brownian diffusion becomes significant when particles are under 3 microns in size.

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ENVIRONMENTAL Science & Technology

Volume 4, Number 9, September 1970

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Washington, D.C. 20036 SUBSCRIPTION SERVICE: All communications re-	
tion of CHANGE OF ADDRESS, should be sent to Subscription Service Department, American Chemical Society, 1155 Sisteenth St. N.W., Washington D.C.	
20036. Change of address notification should include beth eld and new addresses, with ZIP numbers, and be accompanied by mailing label from a recent issue	
Allow four weeks for change to become effective. SUBSCRIPTION RATES 1970: Members, domestic and foreign, I year SS.00: nonnembers, domestic and	
foreign, \$7.00. Postage: Canada and Pan American Union, \$3.00: all other countries, \$3.50. Single copies: current issues, \$1.50: rates for back issues or volumes	
are available from Sprcial Issues Sales Dept., 1155 Sixteenth St., N.W., Washington, D.C. 20036, Claims for missing numbers will not be allowed if received	
mere than 60 days from date of mailing plus time normally required for postal delivery of journal and elaim. No claims allowed hereave of failure to notify	
The Subscription Service Department of a change of address, or because copy is "missing from files." Published monthly by the American Chemical Se-	
elety, from 20th and Northampton Sts., Easton, Pa. 18042. Executive Offices. Editorial Headquarters, and Subscription Service Department, 1155 Sisteenth St	
N.W., Washington, D.C. 20036. Advertising Office: 142 East Ave., Norwalk, Cunn. U6851. Second class postage paid at Easton Pa. 18012.	
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Variations in phosphorus uptake by algae

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H. S. Azad and J. A. Borchardt

Phosphorus is an essential ingredient in the conversion of solar energy to biochemical energy by plants. In laboratory studies, two strains of green algae showed different phosphorus uptakes under different environmental and physiological conditions. The cause and effect relationships influencing algal growth are discussed along with the interaction of these factors with existing phosphorus concentrations.

Water-clay interactions in North Carolina's Pamlico Estuary

D. A. Dobbins, P. C. Ragland, and J. D. Johnson

A natural estuarine environment, where fresh and marine waters meet, has been examined to show the chemical relationship between various waters and sediments in a 50-mile profile of the estuary and over a wide salinity range. The change in the ratio of cationic equivalents is controlled by entrapment of saline water after storms. The data are explained by changes in the natural system unrelated to contamination from municipal wastes.

Concentration of trace metals by solvent extraction and their determination by atomic absorption spectrophotometry

S. L. Sachdev and P. W. West

Trace metals in the atmosphere, including the majority of inorganic carcinogenic materials, can now be determined in environmental studies using an improved analytical procedure. The ten metals—AI, Be, Co, Cu, Cd, Fe, Pb, Ni, Ag, and Zn—are determined at the p.p.b. level with the exception of AI. The method avoids interference from 34 other metal ions.

The atmospheric thermal oxidation of nitric oxide in the presence of dienes

W. A. Glasson and C. S. Tuesday

The ultimate fate of two atmospheric air pollutants hydrocarbons and nitric oxide—which are found in automobile emissions, is unknown. It has been suggested that thermal oxidation could explain the conversion of NO to NO₂, the brown component in smog. But thermal oxidation is unimportant at any time, either day or night, in this conversion. The diene promoted photoxidation of NO is 7–25 times faster than the corresponding thermal oxidation.

Potassium formate process for removing SO₂ from stack gas 757

P. M. Yavorsky, N. J. Mazzocco, G. D. Rutledge, and E. Gorin

An all-liquid recycle and recovery system is available for the removal of SO₂ from industrial stack gases. The system does not require reheat of the cleaned stack gas and alleviates all other waste disposal problems, except for the usual fly ash disposal problem. Removal is affected by scrubbing of the gases with concentrated solutions of potassium formate at 200° F. Other advantages include mild conditions for regeneration of the scrubbing solution and sulfur recovery.

Mercury in the marine environment

765

768

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D. H. Klein and E. D. Goldberg

Mercury levels in marine sediment and three marine organisms—crab, whelk, and rock scallop—are 500 times or more greater than those in seawater of the California coastal environment of La Jolla and Palos Verdes. The subject of mass poisoning in aquatic life of recent note, mercury is released to the environment at an estimated rate of 4000–5000 tons annually.

Communications

Recovery of DDT and dieldrin from tissues of Coturnix Japonica stepwise during residue analysis

R. M. Prouty and E. Cromartie

A 5-step procedure for the analysis of bird tissues for chlorinated hydrocarbons pesticides has been evaluated using C-14 labeled DDT and dieldrin. Losses of pesticides are largely due to codistillation occurring during evaporation of eluates. Overall recovery is from 70–94%.

Preparation of glass fiber filters for sulfuric acid aerosol collection

S. C. Barton and H. G. McAdie

Glass fiber filters are frequently used to collect aerosol samples of sulfuric acid. In previous collection of samples on such filters, atmospheric SO_2 was oxidized on the glass surface and would interfere with the analysis. Now this interference can be avoided by treating the filters with hot sulfuric acid followed by thorough rinsing before collecting the sample.

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Gone with what wind?

DEAR SIR:

Parke C. Brinkley, in Viewpoint, ("Pesticides are important as antipollutants," ES&T, May 1970, p. 369), states that the pollen of ragweed and goldenrod brings such suffering to hay fever victims that the pollen count is a figure of great concern during the hay fever season. Like a great many other people, Mr. Brinkley is misinformed by the popular myth that goldenrod is a serious cause of pollen allergies.

It was demonstrated several decades ago that the goldenrods (*solidago spp.*) are insignificant factors in terms of the total amount of potentially allergenic pollen in the air. The pollen from this genus is larger and stickier than that of ragweed. Goldenrod is insect pollinated rather than wind pollinated. With the possible exception of a few species out of the dozens in existence, almost no goldenrod pollen is aerially disseminated. It is said to appear very infrequently on the slides used to determine pollen counts. Goldenrod is guilty only by association, only because it often blooms at about the same time that ragweed pollen is shed into the wind.

Statements such as that which Mr. Brinkley made have served to carry this popular myth on through the years.

David J. Schimpf

416 W. Fairview St. Arlington Heights, Ill. 60005

Pesticide views draw more fire DEAR SIR:

Parke C. Brinkley's May 1970 Viewpoint article in ES&T ("Pesticides are important as antipollutants") expresses a level of ecological naivete which is incredible in a responsible citizen, but fully understandable from the economic viewpoint of the National Agricultural Chemicals Associa-



tion. From the ecological point of view, most of what Brinkley has said is sheer nonsense.

Cockroaches, mice, rats, pest insects, algae, ragweed pollen, and cereal weevils are all classed as pollutants by Brinkley. To pollute means to befoul the natural state of the environment. Each of these "pests" is a member of a natural community. It is complete nonsense to claim that these creatures are pollutants, although they are certainly significant pests. We have had these symbionts with us for as long as man has been on this earth. Using synthetic chemicals to decimate these populations does far more polluting than leaving these to complete their natural, though noxious, life cycle. Furthermore, a host of former, insignificant plant-eating insects has been "promoted" to major pest status by the use of the very chemicals that Brinkley so righteously sells the public.

If one accepts Brinkley's point of view, then any organism which befouls our concept of living (such as the human litterbug) forfeits his right to survive. By the same faulty logic, since pesticides (especially chlorinated hydrocarbon insecticides and certain herbicides) pollute our desired wildlife, crops, and man himself, they should be eradicated. Both viewpoints suffer from the same logical fault of non sequitur. Just as species in the natural communities cannot befoul in ecological terms (although species can "befoul" if we have the appropriate attitude), pesticides do not have to be polluting agents. Chemicals become pollutants when ecologically dangerous chemicals are manufactured, and then misused by a misinformed public. Mr. Brinkley might do better to insist that ecological knowledge be sold along with his chemicals rather than more chemicals.

James P. Ludwig

Center for Environmental Studies Bemidji State College Bemidji, Minn. 56601

DEAR SIR:

Mr. Brinkley's implication that pesticides are the best—or even the easiest—method to control what he calls "pollutants" simply does not hold up even under cursory investigation. Salmonella food poisoning, typhoid, amoebic dysentery, animal hairs, and droppings in food are the results of careless food handling and improper sanitation. Using pesticides in such situations only substitutes one contaminant for another.

The use of herbicides in weed control is complete ecological nonsense. Most weeds are pioneer plants which thrive in disturbed areas such as roadsides, vacant lots, and yards. Applications of herbicide merely set back normal succession to an earlier stage which favors such weeds as ragweed and goldenrod—incidentally creating a further market for more herbicides. Mowing these plants at the proper stage of their growth effectively eliminates the problem of pollen.

Gerald F. Wambach Rt. 3, Box 121

Bemidji, Minn.

DEAR SIR:

We agree with Mr. Brinkley that it is desirable that man keep his "house" in order-that bedbugs make poor bedmates and that a whiff of hydrogen sulfide or putrifying fish makes life a little less enjoyable. Our differences are based on the methodology which we would employ to keep our "house" in order. Mr. Brinkley would spray for bedbugs, lice, and fleas, while we would improve sanitation procedures; he would use chemicals to deter algal blooms, while we would treat our sewage effluent and reduce the amount of excess fertilizer used in agriculture-two major factors involved in premature eutrophication.

Mr. Brinkley would attack nature, while we would first monitor ourselves, and then, if necessary, use extensions of nature's own controls to ensure minimal ecological disruption. Most importantly, Mr. Brinkley would increase the use of chemicals, which are by definition toxic, at a time when our Earth is becoming choked with the products of man's activity, while we would reduce the use of these noxious chemicals.

23 Concerned graduate students and faculty

Department of Zoolooy University of South Florida Tampa, Florida 33620

(This letter was signed by all 23— Ed.)

Environmentalism vs. capitalism DEAR SIR:

The Editorial in the June 1970 issue (page 457), plus the accompanying Viewpoint by Denis Hayes (page 461) confirm my suspicion that the "environmental activists are more anticapitalist than they are antipollution."

First, Hayes summarily decries "the advertising that sells us useless products." Under capitalism, the individual consumer (not Mr. Hayes) determines which products are useful and which are not. In order to know of available products, the consumer must rely on advertising for information. Hayes clearly departs from this system.

Second, he impugns capitalism by demanding that industry put "lives ahead of profits." The implication that a corporation "whose first goal of making profits" is adverse to human life is completely false. Under the specialization of skills and knowledge inherent in capitalism, the making of profits is the only way an industry knows it is producing those things that individuals need for their lives (as determined by each consumer). Third, Hayes' proposal for permanent representation of the "public interest" on corporate boards indicates that the goal of the activists is not the abatement of specific cases of pollution which are known to be harming people's lives. It is the permanent subduing of all private enterprise to the "public interest" as determined by a few self-appointed environmentalists. There is no such thing as the "public interest" apart from the interests of each individual as determined by each.

Finally, a new "constituency" is called for which affirms "the enhancement of life over the culture of death." The private enterprise system to Hayes has clearly resulted in pestilence, famine, poverty, disease, and death. He can mouth this diatribe to the dying peasants of communist Russia and China, socialist India, and tribal Africa and perhaps go unopposed, but not in America.

Kurt Leininger Medical Service Corps. Edgewood Arsenal, Md.

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Crying wolf once too often

Warnings of impending environmental doom are beginning to lose their impact on an increasingly blasé public

o news is good news: so goes the saying. A necessary corollary to this timeworn old saw seems to be that all news is bad news. The news media have had a field day supplying an apparently masochistic public with all manner of ill tidings from the environmental front. The stream of bad news has a mesmerizing effect: last week it was lead particles in the air; this week it's mercury in water supplies; next week, who knows? Maybe tellurium in your favorite toothpaste. Each new hazard is touted as the probable cause of imminent death or disfigurement. One pollutant follows another in the terrible roll call of death dealing substances. And the public—believe it or not—is beginning to yawn at it all.

The point we are trying to make is not that these pollution hazards and others do not exist, it is that constant overblowing of all potential dangers is undermining the credibility of any of them. You cannot tell people every day that they are being choked to death and poisoned without first scaring them out of their wits and then, as they realize they are still alive and in reasonably good health, making them disregard everything else you warn them about.

Washington Post columnist William Raspberry has cogently pointed out that there is a fundamental flaw in the way in which news is reported. Raspberry cites the way in which riots are written up; a small skirmish will rate a few words, a demonstration in which people are arrested merits a column, but a riot in which there is death and injury may take half the front page. The worse the news, the greater the coverage. So it is with news of the environment. If one of our readers cares to predict that sonic booms will cause tidal waves to engulf Atlantic City or San Diego, then the front pages of daily newspapers and a prominent place on evening Tv news programs will surely be his.

Lest you think that the foregoing is exaggerated beyond belief, let's look at an example. Two ideas that have had wide currency in recent years are that carbon dioxide in the atmosphere will cause global temperatures to increase markedly before the year 2000, and that DDT in the oceans is inhibiting phytoplankton photosynthesis and so cutting off the world's oxygen supply. Both ideas have been given coverage in press stories; both were refuted by scientists at a month-long Study of Critical Environmental Problems (SCEP) convened in July under the sponsorship of M.I.T. Conclusions of the study were carried in the press with only brief mentions—if any—of the CO_2 and DDT findings. What was played up was a conclusion that ssT's may increase cloudiness in the stratosphere and a recommendation that no commercial ssT flights be undertaken until research reveals what damage may be caused.

Our purpose here is certainly not to take issue with the findings of SCEP; indeed, the study was conducted with the very highest standards of scientific objectivity. It is to contend that scientific objectivity carries very little weight with the media. When the ACS published its report "Cleaning Our Environment: The Chemical Basis for Action" last year there was widespread disappointment in the general press because the report's contents were not meaty enough. Recommendations to the effect that "We do not know enough, more research is needed" just do not appeal to someone looking for a headline. Yet, the fact that science does not know very much about the effects of pollution on climate and global ecology is infinitely more terrifying than any glib contention that this or that pollutant will bring the world to a shattering end in 1992, especially when the contention stems, as it sometimes does, from a scientist speaking about subjects in which he is not truly expert.

The big danger is that crying wolf once too often will render the public totally insensitive to situations in which death and destruction really are serious and immediate threats.

D. H. Michael bowen



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viewpoint

Edmund S. Muskie U.S. Senator from Maine

Corporate responsibilities include environment

The environmental honeymoon is over. The days of rhetoric are fading, the surge of multipage advertising supplements is ebbing, and the glow of togetherness and cooperation may be on the wane.

We saw an early and welcome spurt of enthusiasm—by students, corporations, and public officials. That enthusiasm created great expectations. Students thought they had at last found an issue that could embrace all Americans in an effort to reclaim and restore the society. Corporations thought that their expressions of concern and announcements of plans for action could remake images tarnished by years of neglect. Public officials thought that the time had finally come when the public would support expensive programs to restore the environment—and, not incidentally, support them for their efforts.

Now students have gone back to the war, industries are turning to other advertising themes, and public officials are filling fewer pages of the *Congressional Record* with environmental statements. And our air, and water, and land? They are still waiting for the kind of attention they deserve. The visibility of the environmental movement may have declined, but the public will not forget the promises that were made during that honeymoon.

To a great extent, the leadership in moving to reclaim our environment must come from government. It is the business of government to regulate industries and to inform the public of health hazards—no matter which companies may be hurt. But it must also be the business of corporations to become involved in the environmental effort and to eliminate the barriers of distrust which exist between corporations and so many Americans.

American corporations can look forward to more and more movements like Campaign GM. Most supporters of Campaign GM—and I supported that effort did not see it as a blind assault on corporate practices, but rather as a direct appeal to corporate consciences. A corporate response of increased advertising and public relations efforts is not an adequate answer to that appeal. Students and other concerned Americans can tell the difference between an advertising budget and a research budget.

The corporate response must change, but all of us know that corporations—like the government—are institutions, and institutions do not talk or think or respond by themselves. They must be made to respond—by people in and out of the corporate structure. Campaign GM was an illustration of how people outside the corporation can apply pressure for change. I supported that effort because I felt that the pressure was appropriately applied. General Motors and the automotive industry had not met their responsibility to control automotive emissions.

The time has come to put an end to the notion that our corporations live lives of their own, surviving on profits made at the expense of our human and natural environments. For those who insist that corporations must do more to protect and enhance the environment, the road will not be easy. E. B. White wrote some years ago:

People are beginning to suspect that the greatest freedom is not achieved by sheer irresponsibility. The earth is common ground and we are its overlords, whether we hold title or not. Gradually the idea is taking form that the land must be held in safe-keeping, that one generation is to some extent responsible for the next, and that it is contrary to the public good to allow an individual to destroy almost beyond repair any part of the soil or the water or even the view.

We are beginning to appreciate that philosophy. It is a philosophy that tells us that survival will not take care of itself. That we owe a future to our children. And that all of us must be guardians of that future. The time must pass when we relax in the notion that some of us—corporations in particular—can evade that responsibility.



Edmund S. Muskie is completing his second term in the Senate. He is a former Governor of Maine (1954–58)

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WASHINGTON

ON CEQ report urges national policies on energy, land use

President Nixon transmitted to Congress August 10 the first annual report of the Council on Environmental Quality (Es&T, July 1970, page 545). The report provides a broadly useful summary of environmental knowledge in a form that is readable by the layman. Chief among the report's recommendations are: • Development of national policies on energy, transportation, and land use; • Establishment of one major river basin as a demonstration area for advanced water quality management techniques. Although CEQ urges passage of the environmental legislation President Nixon has sent to Congress, chairman Russell Train said at a press conference he doubts that there will be "any major legislative developments" stemming from the report in either the present or the next (92nd) Congress.

Justice Department will spare polluters full force of 1899 act



Atty. Gen. John Mitchell

Guidelines issued by the Department of Justice to U.S. attorneys throughout the country will limit enforcement under the 1899 Refuse Act to those discharges that are "either accidental or infrequent, but which are not of a continuing nature resulting from ordinary operations of a manufacturing plant." Justice is leaving enforcement of laws against continuous sources of water pollution to the Federal Water Quality Administration (FwQA) under the assumption that Congress intended FwQA to deal with such offenses. The little-used 1899 act authorizes the federal government to bring action against those who discharge "any refuse matter of any kind or description whatever . . . into any navigable water of the U.S. . . ." without a permit from the Secretary of the Army or the Army Corps of Engineers.

Senate passes solid waste legislation

The Senate has passed the Resource Recovery Act (S. 2005) (ES&T, May 1970, page 390) without, however, including an amendment offered by Sen. Jacob Javits (R.-N.Y.) which would have required all car owners to pay a fee guaranteeing proper final disposal of their autos. The bill as passed will: • Continue the programs authorized by the 1965 Solid Waste Disposal Act for another four years; • Provide \$150.5 million for solid waste demonstration programs; •Authorize \$155 million for resource recovery system demonstrations; • Authorize \$2 million for a National Commission on Materials Policy. The Senate returned S. 2005 to the House, where a slightly different bill was passed in June.

HEW sets up incentive program for clean car development

Health, Education, and Welfare Secretary Elliot Richardson has established a Federal Clean Car Incentive Program to speed development of a "low-pollution" automobile. The program, to be administered by the National Air Pollution Control Administration (NAPCA), will involve three phases: prototype, demonstration, and fleet. Prototype vehicles exhibiting acceptable emissions, road performance, and mass production potential may be considered for the demonstration phase, in which NAPCA will purchase ten vehicles for testing. Cars that successfully complete demonstration will be eligible for the fleet phase. NAPCA will purchase a 300-car fleet for extensive testing under typical driving conditions. Development costs are expected to be reflected in the purchase price the agency will pay, but developers will retain all patent rights.

STATES N.J. takes legal action against nine industrial giants

Richard J. Sullivan, commissioner, State Department of Environmental Protection, has instituted action against Cities Service Oil Co., E. I. du Pont de Nemours and Co., Inc., Mobil Oil Co., General American Transportation Corp., General Aniline and Film Corp., American Cyanamid Co., B. P. Oil Corp., Enjay Chemical Co., and Humble Oil and Refining Co. for objectionable odors. This is the first time that a case involving multiple respondents has been attempted under Chapter VI of the N.J. Air Pollution Control Code. Since it is impossible to ascribe the odors to any one industry in that area, the case is planned to bring all contributors together.

California speeds enforcement of January water quality law

The Porter-Cologne Water Quality Control Act, operative Jan. 1, 1970, has facilitated dealing with violators of that law (ES&T, September 1969, page 793). If Cease & Desist (C&D) orders have not been followed by compliance, the case is turned over to the state attorney general for enforcement. In northern California, a number of municipalities and sanitation districts as well as dairies have been cited. Military reservations, food processing plants, railroads, shipping lines, meat packing industries, private disposal firms, airports, and manufacturers have received C&D orders throughout the remainder of the state.



Pennsylvania strengthens Clean Streams Act

Gov. Raymond Shafer has signed into law the 1970 Amendments to the Pennsylvania Clean Streams Act, giving the Sanitary Water Board increased power in dealing with pollution violators. The Board now regulates • potential pollution sources; • discharge of industrial wastes into municipal systems; • the number of small treatment plants along streams; • mining operations; • radiation pollution; and can assess civil penalties up to \$10,000. The pollution strike force, formed by Shafer, consists of six attorneys general who report to the state attorney general and work with the Health Department. The strike force will represent Pennsylvania at hearings, as well as seek injunctions against and prosecute pollution violators.

Connecticut issues new air pollution regulations

Recently adopted Connecticut regulations include: • control of objectionable odors; • a general prohibition of air pollution; • air quality standards for particulates and sulfur dioxide. F. M. Foote, commissioner of the state's Department of Health, says that the air quality standards coincide with those approved by NAPCA for the section of Connecticut included in the New York City interstate air quality region. These are now the standards for the entire state. The odor and general prohibition regulations are all-inclusive and cover a range of air pollution violations that are not specifically listed in other state regulations.



Pa.'s Governor Shafer

STATES Missouri's water quality standards approved by Interior

Secretary of the Interior Walter J. Hickel has approved, in full, water quality standards for the state of Missouri. The state adopted December 31, 1975, as the target date for establishing secondary treatment (or its equivalent) of sewage entering the Missouri River or its tributaries. Missouri's Water Pollution Board (WPB) had advanced the date from 1982 to 1975 earlier this year. The main point at issue between Interior and the state had been dissolved oxygen levels in the Missouri and Mississippi Rivers, now set at 5.0 mg./liter. The approved standards are understood not to contain language recognizing a large drop in dissolved oxygen concentration occurring during periods of heavy flow, a compromise which state officials had hoped to achieve (see letter from WPB executive secretary Jack K. Smith to Es&T, May 1970, page 363).

INDUSTRY Eight firms charged with mercury pollution

Interior Secretary Walter J. Hickel passed to the Justice Department a list of eight firms who, he said, had been found to be discharging "sufficient quantities of mercury into the nation's waterways to constitute a serious hazard to public health." The firms are: Diamond Shamrock Corp. (Alabama, Delaware), Olin Mathieson Chemical Co. (Georgia, New York), Pennwalt Chemical Co. (Kentucky), Oxford Paper Co. (Maine), International Mining and Chemical Co. (Maine), Allied Chemical Co. (New York), Weyerhauser Co. (Washington), and Georgia-Pacific Corp. (Washington). Georgia-Pacific has since been dropped from the list.

More optimism on markets for air monitors

Another estimate of air pollution instrumentation markets has been published, this time by Creative Strategies, Inc., an investment planning service. The report sees a need for \$100 million in instrumentation in 1970–74, an annual compound growth of 35% from \$6 million in 1969. The estimated annual expenditures of \$36 million in 1974 are just a little more than half those forecast for that year by a recent Esso Research-NAPCA survey (ES&T, August 1970, page 639), but the difference is likely one of parameters and timing. Creative Strategies studied automatic instruments only, and indicates increased demand beyond 1974, while Esso's ten-year forecast indicates at least two market segments may be past peak demand in 1974. Creative Strategies points out that four companies—Beckman, Leeds & Northrup, Litton, and Technicon—serve over 80% of the market for automatic instruments and systems.



OSW San Diego facility

Desalting demonstration grants go to two companies

The Office of Saline Water (osw) in the Department of Interior has awarded two contracts for testing and operation of desalting facilities. The first, for \$200,000, goes to American Hydrotherm Corp. (New York, N.Y.), for one year of operation of a test and development facility at Wrightsville Beach, N.C. Main object of the contract will be to check out design and performance of vertical tube evaporators. The second contract, \$84,687 to Aqua-Chem, Inc. (Milwaukee, Wis.), calls for Aqua-Chem to demonstrate equipment reliability for a two-stage reverse osmosis plant to be built at osw's test facility in San Diego. Both projects will assist osw in preparing accurate estimates of cost involved in continuously desalting water.

TECHNOLOGY

DGY SO₂ plays dual role in sludge conditioning

Sulfur dioxide greatly improves sewage sludge processing and produces as a filtrate a potential animal food supplement, says R. B. Dean of the Federal Water Quality Administration (FwQA). He described the process, developed at Foster D. Snell, Inc., under FwQA contract, in a paper coauthored with R. J. Bouthilet for the 5th International Water Pollution Research Conference. Steam cooking sludge with 0.5% SO₂ increases soluble solids, improves filtration efficiency by a factor of 100, and reduces moisture in the filter cake. The SO₂ also hydrolyzes polysaccharides and proteins in the filtrate, which can be concentrated into organic molasses containing as many as twelve amino acids, including all those essential for nutrition. Rat feeding tests showed the material to be nontoxic and an adequate energy substitute for cane molasses in animal diets. Estimated production costs for the material are 0.015 cent per pound, compared with 2–5 cents for conventional molasses.

Desulfurization promises new lease on life for coal

A process developed at the Southern Research Institute for Jolevil Association (Birmingham, Ala.) removes about half the sulfur in bituminous coals, says Jolevil's president H. Leroy Thompson. The new process, for which a patent application has been filed, involves wet oxidation of the pyritic sulfur in coal with air at 150–200 p.s.i. and temperatures up to 250° F. Although the process doesn't remove organic sulfur (about 50% of the total) Thompson believes it's a reasonable and economic first step toward total sulfur removal. It's too early for accurate cost estimates, Thompson continues, but 50 cents per ton might be reasonable. The process could be a factor in current trends in SO₂ control, which place emphasis on fuel selection in meeting pollution control codes (ES&T, June 1970, page 474).

Air pollution from incinerators will be continuing problem

Arthur D. Little has assessed the air pollution threat from waste incinerators for the National Air Pollution Control Administration and reports that: • Incinerators could become a major aggravating facet in urban air pollution in 15–25 years. • A projected 400% increase in the plastics component of waste could increase hydrogen chloride emissions from halogenated polymers three times by 1980 and five and one-half times by 2000. • Particulate emissions will increase fivefold by 2000, even with the 52% average efficiency of control units installed in the past five years. To stop completely the trend, average efficiency of 90% is necessary. • A sizeable percentage of pollutants, such as small particles and combustible gases, cannot be controlled by existing devices. The report concludes that substantial advances in incinerator technology will have to come from federal and state funded research, because municipalities are too inherently conservative and private industry is cautious about the large capital investments required to enter this market.

Incinerator	furna	ce	emissions
(thous	ands	of	tons)

	1968	2000
Mineral		
particulates	90	708
Combustible		
particulates	38	131
Carbon		
monoxide	280	829
Hydrocarbons	22	64
Sulfur dioxide	32	161
Nitrogen oxides	26	147
Hydrogen		
chloride	8	219
Volatile metals		
(lead)	0.3	0.055
Polynuclear		
hydrocarbons	0.01	0.03
Est. Total	496	2259

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Noise – Fourth form of pollution

Referred to as unwanted sound, sound out of place, sound without value, or vibrational energy out of control, noise in the environment has reached a level of national importance and public concern. Like other forms of pollution, noise is a by-product of twentieth century technology. But unlike other forms of pollution, noise is not persistent, not cumulative, and not transported over great distances by the atmosphere. Noise dies out rapidly once the noise generation process stops.

To be sure, noise pollution has not reached the crisis stage of the other three forms—air pollution, water pollution, and solid waste disposal. The fact that federal noise abatement programs are not to be transferred to the new Environmental Protection Agency (EPA) (ES&T, August 1970, page 627) does not indicate that noise pollution and its abatement are unimportant problems. It is merely that the other forms have been seen as demanding more urgent priorities.

Certainly, the public's noise awareness increases each day. It may be true that the man-in-the-street's concern is directed at aircraft noise at this time. But chances are that if he is an industrial worker, he has heard of in-plant noise reduction programs.

In any event, noise is a growing nuisance. Some scientific evidence indicates that noise is harmful to physical and mental health; hearing loss is only one example. Other noise experts believe that man's tolerance to noise is quite high and that most environmental noise conditions can be adapted to without ill effects.

Essentia'ly, noises can be grouped into three types—transportation noises, occupational noises, and community noises. Noises from a'l these sources have incrensed over the past ten years and will double in the next ten according to most indications.

Transportation noise

Although aircraft noises are more often the source of nuisance complaints from the general public, highway noises run a close second, largely because nearly everyone is exposed to them in daily activities. Tire noises are the main problem. Assuming that a highway vehicle—whether a passenger car, bus, or truck—is in a good state of repair, highway noise is attributed to tires on the vehicle operating in excess of 60 m.p.h. At lower speeds, engine noises tend to predominate.

Occupational noise

Several industries can be singled out for occupational noisiness, including steel, paper-making, textile, petroleum, and wood products, to mention a few. In general, the noise sources in these industries are the machinery, in plants with metal to metal operating parts, or high-speed equipment such as blowers (petroleum cracking plants), looms (textile plants), or high-speed stamping operations (wood products). In some cases, the personnel exposure time is small. For example, it may be necessary to perform a maintenance check on a particular piece of noisy equipment once each day. But the check might only take 15 minutes. In other cases, however, the operator might be exposed to the noise for the full eighthour day.

Community noise

Community noises, both indoor and outdoor, are on the increase. In fact, these noises are beginning to approach in overall severity of those found in mechanized industry. Not only are dishwashers, lawnmowers, air conditioners, and the like recognized noise problems, the simple increase in numbers of such appliances produces a larger noise burden. Community noise exposures can therefore become a problem, if indeed they are not one already.

Regulations

Both federal and state regulations have been enacted to reduce the noise burden. Most are directed at a particular noise source, are limited in scope, and are enforced poorly, if at all. Nevertheless, they are a beginning.

The first federal attempt to control noise of any kind was the 1968 noise standard for the certification of new aircraft (see box, page 722). This was soon followed by the amendment to the Walsh-Healey Public Contracts Act which regulates occupational noise exposure.

Many states have codes prohibiting excessive noise from transportation sources, mainly highways. Approximately 20 states pay workman compensation for hearing loss damage, but the awards are far from consistent across the U.S. In many cases, the state and local ordinances do not spell out actual decibel violation limits, and the mere existence of codes does not necessarily mean that they are enforced.

New York was the first state to adopt a highway antinoise statute in 1965. It defines excessive noise as 88 dBA at 50 ft. for a vehicle traveling at 35 m.p.h.

Perhaps the most comprehensive code is California's. It prohibits noise levels in excess of 82 dBA for passenger cars and 92 dBA for trucks and buses. There is also a California code requiring used cars be certified for noise worthiness before resale.

Noise reduction

There are essentially three ways to reduce noise. The first approach is to reduce noise at the source. Examples of this are the design and production of quieter aircraft engines, highway tires, industrial machinery, and home appliances.

A second approach is operational in nature. This approach is being followed by major airlines in their normally scheduled flights by following certain noise abatement takeoff and landing procedures at major airports in the country. The enclosure of machinery with sound absorbing materials is an example of the industrial operational noise reduction pattern already practiced by some industries.

The third is personnel protection

outlook

At home, at work, and every place in between, noise has joined filthy air, dirty water, and solid wastes as a major threat to health and sanity



through the wearing of devices such as ear plugs or ear muffs. In some cases, the second and third approaches are combined to reduce exposure to the lowest practicable levels.

Of course, the ultimate goal is to have remedies for the noise problems and to implement these by installation of new machinery, sound suppressing devices, and improved operational charges.

To attain this goal the federal government will spend approximately \$34.1 million for noise abatement programs in fiscal year 1971, up from \$32 million last fiscal year, when \$29 million went for aircraft noise reduction and \$3 million for all other programs.

Federal noise programs

Members of the federal noise club include the Departments of Commerce;

Health, Education, and Welfare (HEW); Housing and Urban Development (HUD); Interior; Transportation (DOT); Labor; and the National Aeronautics and Space Administration (NASA). The noise committee of the Cabinet Committee on Environment (ES&T, December 1969, p. 1249) has been actively studying the noise problem. Its goal is to formulate a federal policy on noise, but the proposed and long awaited policy had not yet been adopted at press time.

Commerce, the lead agency for noise in the Cabinet committee, has organized a Commerce Technical Advisory Board which is focusing on the technological, economic, social, and legal aspects of the problem. Jack E. Goldman, a vice president of Xerox Corp., is chairman of the advisory board whose report, "The Noise Around Us: A Program for Progress," will be released this fall.

Each federal department conducts an active research and development program. Not surprisingly, DOT has two noise abatement offices, one for transportation noises in general and another specifically for aircraft noise, in the Federal Aviation Administration (FAA).

Charles R. Foster, head of the DOT Office of Noise Abatement, notes that his office's prime interest is to find technical ways to reduce noise at the source. Foster notes that DOT has a program at the National Bureau of Standards directed toward the design of a quieter tire without sacrificing safety. Truck tires are noisier than those on passenger cars and are replaced more frequently. The so-called footprint configuration, the depth and

Federal regulations

P.L. 90-411. Effective July 12, 1968, commercial aircraft must comply with certain noisé levels before certification.

FAA noise standard. Effective Dec. 1, 1969, the standard applies to all new design aircrait of the turbofan variety. Does not apply to existing aircraft.

Walsh-Healey Health and Safety Regulations. Effective May 20, 1969, specifies a maximum allowable level of 90 dBA for a continuous 8-hour day exposure. Applies only to industries holding government contracts in excess of \$10,000.

Federal fundi (all figures in mi	ng Ilions)
NASA DOT HEW HUD Commerce Labor	\$22.31 8.85 1.40 1.01 0.50
Total	\$34.07

Noise—useful definitions Sound—Small local fluctuations in atmospheric pressure.

Frequency—The number of times a sound wave repeats itself in a unit of time. In acoustics, the unit of frequency is Hertz (Hz).

Human ear—Responds to the magnitude of these pressure fluctuations and to the rapidity with which the fluctuations occur. Human hearing ranges from 16-000 Hz.; it is most sensitive to frequencies from 500-6000 Hz., less sensitive to high and low frequencies.

Decibel (dB)—Unit of sound pressure level.

Decibel scale—Expresses magnitude of the pressure fluctuation, on a logarithmic scale.

C scale (dBC)—Gives a flat response across the entire sound spectrum.

A scale (dBA)—Places less emphasis on low frequency sounds; provides more weight to annoying high frequencies, and in general, correlates well with human response to a variety of noises.

Effective perceived noise decible-(EPNdB)—Unit developed specifically to rate aircraft noise.

EPNdB scale—Developed specifically as a measure of subjective reaction to annoyance of aircraft noise. It is similar to dBA scale but gives more weight to high frequency tones and includes adjustment for effective duration and discrete frequency components.

Sound level meter—Measures sound pressure levels but does not measure the qualities of sound to which humans respond. Octave band analyzer—An instrument equipped with filters to measure a band of frequencies one octave wide. For example, the 1000 frequency octave band extends from 707–1414 Hz. spacing of slits in the tire, might be redesigned to give better suction and, in essence, less noise.

DOT has contracted Serendipity, Inc. (Eastern Operations Div., Arlington, Va.) to attempt to come up with a noise pollution level for communities, which will include all transportation noises—aircraft, highway, and others. Serendipity is finding that the noise level from any individual source alone is not the real concern of the public. Rather, it is the incremental decibel change above the background that generally leads the public to complain.

John O. Powers, director of the FAA Office of Noise Abatement, concentrates on aircraft noise reduction and directs R&D to this end. Under an FAA contract, Rohr Corp. (Calif.) has performed a paper study to find the economic and operational impact of retrofitting (modifying the engine after initial production) aircraft to reduce noise. Reducing the noise level 5 dBA on takeoff and 10 dBA on landing is a difference that the general public would actually be able to notice. For a fleet of some 1200 planes, the cost approximates \$750 million. The final Rohr findings are to be released soon.

Eugene L. Newman, chief of Labor's Office of Training in the Bureau of Labor Standards, has long been associated with industrial occupational noise. But Labor's enforcement activities under the Walsh-Healey Act are headed by Robert D. Gidel.

Walsh-Healey covers all government contracts for the procurement of goods, supplies, materials, etc., in excess of \$10,000. Inspectors from the Department of Labor-safety engineers and industrial hygienists-inspected some 4000 locations in 1969, noise being one factor in their inspection. A status report of specific noise violations will be released this fall, along with a list of qualified consultants in the industrial occupational noise area. Newman points out that government contracts cannot be canceled on the basis of these inspections. But after serving notice of violation and failure to comply, Labor can be instrumental in preventing those companies from appearing on the list of eligible contractors for a period of three years.

Other noise abatement programs are in NASA, HUD, and HEW. Alexander Cohen, director of HEW's Bureau of Occupational Health and Safety (Cincinnati, Ohio), heads the federal programs dealing with health aspects of noise. A prime concern of the HUD program is reduction of noise nuisances in multifamily dwellings. NASA's program, the most costly in terms of the federal dollar, is a hardware development program ultimately aimed at the design of a quiet aircraft engine.

Industry's approaches

But the federal government does not stand alone in its noise abatement program, other organizations and industries also are involved. Another technical approach to reduce tire noises is spearheaded by John Carter, chairman of a tires subcommittee of the Society of Automotive Engineers. On the international scene, the Organization for Economic Cooperation and Development (OECD) plans to issue soon a report "Urban Traffic Noise."

Large industrial companies also are alerted to the noise problem, including Bell, Grumman, Du Pont, and Ford, to mention a few. To some, noise is not a new problem. Du Pont's audiometric testing of employees dates back to 1939. In 1965, Du Pont's Engineering Materials Laboratory began an extensive program directed at the fundamental aspects of structural and materials damping.

Some firms are establishing audiometric testing as part of an employee's routine prephysical examination. Not only does this type of information prove invaluable in hearing loss damage suits, but it also serves as a baseline against which hearing can be measured during periods of employment. The latter is particularly important because a number of young people already have a degree of hearing loss, according to one study. It might be the case that his employee's hearing would deteriorate more rapidly during his course of employment.

Future legislation

A coordinated federal approach to noise control is embodied in the proposed clean air amendments, S.3229, (Es&T, May 1970, p. 378), under which an office of noise abatement and control would be established. In time, this office probably will be set up; it could take a comprehensive look at the myriad federal noise programs now dispersed throughout the federal establishment.

Certainly little will be done to reduce noise pollution until the public becomes aroused. Then the public can bring about the necessary reduction through actions at the federal, state, and local levels. SSM

Air monitoring: How much is enough?

Pushed along by the needs of pollution control agencies, air quality measurement networks are proliferating nationwide

One phase of the nation's air pollution control program that is rapidly moving into high gear is the massive task of accumulating data to guide the implementation of control strategies. Local air pollution agencies throughout the U.S. have stepped up their surveillance programs, and relatively sophisticated monitoring and data telemetering networks have already been installed in major metropolitan areas such as Chicago, New York City, Los Angeles, and St. Louis. Regional networks also are emerging, as in the San Francisco Bay Area and Pittsburgh-Allegheny County and statewide programs have been established in New York, New Jersey, Maryland, and Delaware, to cite a few. At the federal level, six cities are participating in the National Air Pollution Control Administration's (NAPCA's) Continuous Air Monitoring Program (CAMP).

The reason for the proliferation of monitoring systems is obvious. The task of air pollution enforcement has been passed to the states and air quality regions under the Air Quality Act of 1967, and NAPCA is well along in its task of delineating such Control regions. agencies and NAPCA will need a fair amount of data to aid in the establishment and revision of standards and to gauge the progress of control programs. In fact, the Air Quality Act implies that each of the air quality regions to be designated will have some sort of monitoring system and established a grant program for federal funding.

How sophisticated?

But along with the initial rash of enthusiasm for establishing such monitoring systems, a few questions are arising to trouble control officials: Basically, how extensive should such networks be, and how complex, in terms of automatic operation and data transmission? The problem is particularly significant in view of the variety of sophisticated sampling and data collection techniques that are becoming available, and the relatively high cost of some of the more elaborate ones.

One clue to the justification for monitoring networks is the guidelines that have been established for processing federal NAPCA grant applications under the Air Quality Act. Generally speaking, the guidelines for the desirability and selection of network types are the same as for other phases of the local control programs: The monitoring networks should form an integral part of the overall control strategy by furnishing necessary data for its execution. Adequate provisions should be made in the control program for action to be taken on the basis of the data obtained.

Stated this broadly, the guidelines still leave a great many unanswered questions about what specific types of monitoring systems are called for. One attempt to answer such questions is a recent study conducted by the MITRE Corp., a nonprofit systems organization in McLean, Va. NAPCA's interest in contracting for the study was to serve as a guide for policy decisions on supporting air quality networks' research and implementation and evaluation of project grant applications. But the results of the study can also serve as an aid to local control officials on pertinent systems criteria and characteristics and in preparation of project grant applications.

MITRE'S Edwin Keitz and T. R. Mongan, two of the project workers, explain that the study involved an extensive survey of those NAPCA bureaus whose activities impinge on data acquisitions and processing, and visits to a representative sampling of about a dozen local control agencies where networks have been or are being established. Keitz points out that the study results show a definite need for



Surveillance. Six major U.S. cities are now included in NAPCA's network



Analyzer. D.C.'s Charles Bruno describes monitors in city's CAMP station

expansion of local (city and county) monitoring networks in highly urbanized areas. Furthermore, there are often operational needs for regional networks but only in the cases where air basins or airsheds are not completely contained within a single municipal jurisdiction.

Too many data

The MITRE study presents some specific warnings about the "data for data's sake" approach to monitoring. Keitz says, "Without a doubt, there are some cases where too much data are being accumulated without being used." Keitz stresses that the single most critical point in NAPCA's assessment of network project grant applications is assessment of the credibility of the applicant's proposed user action and evolving the most useful set of technical requirements for a network.

A well-planned, scientifically sound statistically data gathering function is acceptable as a valid user action, according to Keitz, but such usage can seldom serve as the only justification for elaborate and extensive systems that provide for rapid response or telemetered data transmission. Justification for such systems to be used for statistical data gatherings is largely one of economics.

For example, the MITRE study concludes that rapid response networks, regional or local, can be operationally justified only under limited circumstances. Such circumstances would occur when actions that can substantially affect the air quality of a region can be accomplished within a matter of hours after the receipt of data indicating imminent episode conditions or sudden industrial accidents. Typical of such control actions would be the imposition of preplanned emergency procedures, curtailment of nonessential industrial emissions, or switching to alternate fuels for power.

Other than a demonstrated need for real time data, the only other justification for rapid response network is one of cost-when necessary, data can be obtained by some mode of rapid response transmission cheaper than by slower modes. But here again, the comparison must be made only on the basis of transmission of the necessary data, says Keitz: "It's totally irrelevant whether or not a rapid transmissions system will transmit more data than are needed more economthan slower transmission ically mode." He concedes that the study uncovered no existing instances where immediate transmission is cheaper, but that it might be possible under certain circumstances.

Automated air quality data transmission, also, can be justified only if it saves money. One of the MITRE study's premises is that there is no air monitoring activity that requires a response so rapid that it could not be met, at least theoretically, by increased manpower. There are, of course, practical limitations of money and manpower. For instance, if a network uses unmanned stations, and the needed response time is shorter than the interval between routine maintenance, calibration, and inspection visits, automated transmission is called for. But even here, only that data for which the need exists should be telemetered; any other data transmission is useless, and the added sophistication usually results in increased installation and maintenance costs.

On a national level, the MITRE study could not uncover any clear-cut legal or operational needs for a national rapid response network. There may be political, public relations, or indirect legal needs for such a network, but such needs would involve a basic policy decision by NAPCA, and even here, the cheapest and simplest system should suffice.

Nationwide efforts

The MITRE study does endorse, however, the concept of an expanded federal air quality data bank, and a nationwide statistical air monitoring network, a conclusion which is seconded by John Bryant, chief of NAPCA's Air Surveillance Network Branch. The federal CAMP network, which now includes the cities of Cincinnati, Philadelphia, St. Louis, Chicago, Denver, and Washington, was originally set up to demonstrate the concept of continuous monitoring, to develop and field test analytical methodology, and to provide preliminary data for criteria and standards. CAMP has succeeded very well in this mission, says Bryant, but while the proliferation of local networks is one measure of success in this mission, it does not at the same time preclude the necessity for a continuing federal program. "The difference between the two types of programs," explains Brvant, "is that the local agency networks should direct toward enforcement activities. Meanwhile, the CAMP program is developing into an entirely different but equally valuable role."

The task now emerging for CAMP is a more research oriented one, in Bryant's view. The federal surveillance program can provide a uniform base throughout the country against which all other data can be verified, as well as measure pollutants, which are difficult to analyze, identify new or newly recognized pollutants, and conduct research in newer measurement tech-"As the nation's pollution niques. control program progresses, the relative importance of various pollutants will change and our methods of acquiring data will have to adapt accordingly," says Bryant.

But enforcement could be a factor in the CAMP program for some time to come, according to Bryant. The federal government still has a stake in the progress of local control programs and should have its own data input. Bryant foresees the need for expansion of NAPCA's surveillance program, perhaps through the use of mobile laboratories. This would permit NAPCA to evaluate control efforts in the regions and render assistance, especially in those interstate regions where the federal government could conceivably become a party to compliance proceedings. PJP

The great phosphorus controversy

Arguments over the controlling mechanisms of eutrophication have scientists—and politicians all hot under the collar

A furious controversy over the role played by phosphorus in the excessive growth of algae in lakes and streams is currently raging within a section of the technical community. Although the arguments bandied back and forth are scientific in nature, their implications go far beyond the laboratory. The issue involved is whether phosphorus is indeed the key element controlling algal growth; the assumption that it is underlies all current efforts to remove phosphorus from sewage and to replace the condensed phosphates in household detergents with a nonphosphate substitute (see ES&T, February 1970, page 101, and July 1970, page 544).

An accepted fact

For many years, the key importance of phosphorus (and of nitrogen) to the growth of aquatic algae was taken as absolute fact-and indeed the majority of water chemists and limnologists (scientists who study freshwaters) never did doubt that fact and do not do so now. Studies of the eutrophication (advanced biological aging) of bodies of water have for many years focused on the increased amounts of phosphorus and nitrogen entering the water, which, in practically all cases, accompanied excessive algal growth. The connection has been accepted as so obvious and proven that no argument was really expected.

First hints of the furor yet to come appeared in 1967, when Willy Lange, a chemist turned botanist at the University of Cincinnati, published in Nature a paper entitled "Effect of Carbohydrates on the Symbiotic Growth of Planktonic Blue-Green Algae with Bacteria." Lange's thesis was that algae always exist in association with bacteria and that the association is mutually supportive: the algae utilize carbon dioxide and sunlight to produce organic matter and oxygen by



Dieoff. Decaying algae disfigure Montrose Beach on Lake Michigan shorefront

photosynthesis; the bacteria use oxygen in the decomposition of organic matter to produce carbon dioxide. Lange's experiments proved to his satisfaction that it was the presence of large amounts of organic material in water that made the production of huge amounts of carbon dioxide available for algal growth.

Lange's contentions were picked up and given added currency in 1969, when L. E. Kuentzel, a Wyandotte Chemical Corp. physical chemist, reviewed the literature on eutrophication and concluded (without ever having performed an experiment himself, as his critics are quick to point out) that carbon, not phosphorus, is the element that controls algal growth.

Kuentzel followed Lange's reasoning that only bacterial action on dissolved organic matter could possibly produce the amounts of carbon dioxide needed for the algae to grow rapidly. According to Kuentzel, all the literature citations he studied pointed to the fact that there was sufficient organic matter present, together with phosphorus and nitrogen, to support his thesis concerning carbon dioxide production and utilization by algae. Furthermore, continued Kuentzel, in many reported cases of excessive growth, dissolved phosphorus levels were exceedingly small. So small, in fact, that they were in some cases less than the 0.01 p.p.m. previously suggested as the minimum phosphorus concentration needed for abundant growth, a criterion provided by University of Wisconsin sanitary chemist Clair Sawyer in the 1940's. Kuentzel's interpretations were roundly opposed by members of what has been called, with considerable risk of oversimplification, the phosphorus-is-the-key school of thought.

Then, at the 1970 Purdue Industrial Waste Conference, Pat Kerr, a plant physiologist at the Federal Water Ouality Administration (FWQA) Southeast Water Laboratory (Athens, Ga.), presented the results of work done by her and two colleagues from which she concluded that carbon was the controlling element. Miss Kerr's results were an extreme embarrassment to FWQA and to the federal government, who were gearing up (albeit somewhat tentatively) for a switch away from phosphates in detergents and were spending heavily on the development of processes for the removal of phosphorus from liquid

Two schools of thought clash on many points

Carbon-is-key school believes:	Phosphorus-is-key school believes:
Carbon controls algal growth.	Phosphorus controls algal growth.
Phosphorus is recycled again and again during and after each bloom.	Recycling is inefficient: some of the phosphorus is lost in bottom sediment.
Phosphorus in sediment is a vast reservoir always available to stimulate growth.	Sediments are sinks for phosphorus, not sources.
Massive blooms can occur even when dissolved phosphorus concentration is low.	Phosphorus concentrations are low dur- ing massive blooms because phos- phorus is in algal cells, not water.
When large supplies of CO ₂ and bicar- bonate are present, very small amounts of phosphorus cause growth.	No matter how much CO_2 is present, a certain minimum amount of phosphorus is needed for growth.
CO ₂ supplied by the bacterial decompo- sition of organic matter is the key source of carbon for algal growth.	CO ₂ produced by bacteria may be used in algal growth, but main supply is from dissociation of bicarbonates.
By and large, severe reduction in phos- phorus discharges will not result in re- duced algal growth.	Reduction in phosphorus discharges will materially curtail algal growth.

wastes. Swept along by wide interest in Miss Kerr's work and by a long, gutsy, and polemical attack on the whole phosphorus school in *Canadian Research and Development* magazine, battle lines were drawn. Lange, Kuentzel, and Miss Kerr were, once again for the convenience of argument, lumped together as the carbonis-key school, and their arguments were heatedly discussed by high level groups in FWQA and the Council on Environmental Quality (CEQ).

Counterattack

However, the phosphorus school counterattacked strongly and its arguments seem, at the moment, to have carried the day. Both the phosphorus and carbon schools agree that algae need, for growth, sources of inorganic carbon, phosphorus, nitrogen, and numerous other elements such as metals. Both schools further agree that algae and bacteria generally coexist, and the phosphorus school is willing to concede that the relationship may be symbiotic. But on almost all other points, they disagree (see table). At the very nub of the disagreement are two basic areas of contention:

• Precisely how much phosphorus do algae need for excessive growth.

• What sources of carbon are available to algae.

The carbon school maintains that only very small amounts of phosphorus are needed. It points to the low dissolved phosphorus concentrations found in the water of eutrophic lakes during algal blooms and believes that nutrients, including phosphorus, are recycled by organisms during growth and released for reuse during the periodic dieoff periods. Says the phosphorus school: On the contrary, algae require relatively substantial amounts of phosphorus and the incidence of low dissolved phosphorus concentrations during a bloom means that the phosphorus has been taken up by the algal cells.

The carbon school believes that the availability of utilizable carbon is the key and that diffusional processes are too slow to permit atmospheric CO., to support massive growth, hence its interpretation of the importance of bacteria-produced CO2. The phosphorus school points to the fact that algae can use, in addition to free CO₂, carbon dioxide produced by the dissociation of dissolved bicarbonates. Phosphorus supporters say that the dissociation occurs so rapidly that supply of carbon dioxide cannot possibly be limiting, and they pooh-pooh the carbon school emphasis on the need for respiratory supply.

It is very easy to convey the wrong impression that all scientists fall simply into one or other of the two camps. In fact, most probably see some merit in both sets of arguments. Phosphorus supporters, including University of Minnesota limnologist Joseph Shapiro, have told ES&T that they believe with Pat Kerr that carbon was indeed the controlling element in her studies. The reason for this, they say, is that Miss Kerr worked with the waters of several southern lakes in which dissolved bicarbonates are very low, and in a situation where nitrogen and phosphorus were very high. Miss Kerr herself is willing to concede that her results may not hold true "for all waters in all places at all times." She does feel, however, that removal of phosphorus but not of organic carbon from liquid wastes probably spells trouble. Phosphorus supporters continue to point out that most lakes, streams, and estuaries contain abundant supplies of inorganic carbon, and they stick with their belief that, in general, phosphorus is controlling. They do not believe that removal of phosphorus from wastes will halt all algal growth; they do believe, however, that growths will be much diminished.

Governmental bodies obviously are going along with the phosphorus school. In Canada, the federal government gave detergent manufacturers until August 1 to reduce the phosphate content of detergents to 20% (expressed as P_2O_5 —roughly equivalent to 35% expressed as sodium tripolyphosphate), and is aiming toward a total ban by the beginning of 1972. The U.S. government has not gone as far, however. Rep. Henry Reuss's (D.-Wis.) bill to limit phosphorus in detergents is languishing in a Congressional committee, but FWQA scientists are working on a crash program to evaluate the ecological effects of sodium nitrilotriacetate (NTA), the most likely present substitute for phosphate in detergents. And spokesmen for both FWQA and CEQ say that they are entirely convinced of the merits of the case against phosphorus.

Whether the current furor will testify to the supremacy of science over politics, only time will tell. But one thing is sure—man has been responsible for the advanced eutrophication of lakes through something he has added to them in the course of his technological and social progress. It is not unreasonable to hope that all the work that has been lavished on the role of phosphorus in eutrophication will eventually result in ways to remove that something, whatever it eventually turns out to be. DHMB

Asbestos: Friend or foe?

Common insulating material may be hazardous to health



New York City Regulations Governing the Spraying of Mineral Fiber Insulation

- Clean the area before and after spraying.
- Enclose the area in tarpaulins during spraying.
- Bag excess material in enclosed areas.
- Post warning signs when spraying. Provide workers with respirators
- and coveralls. Appoint a full-time spraying super-
- visor. Clean and seal sprayed surfaces in
- the ventilation system. Cease spraying if emission escapes
- occur.
- Notify Dept. of Air Resources before spraying.

Source: New York Department of Air Resources

in which the real pollution problem lies.

Delayed effects

Irving J. Selikoff at the Mount Sinai School of Medicine in New York notes that men engaged in insulation work over a period of time tend to contract fatal maladies including asbestosis (scarring of the lungs), lung cancer, and cancer of the gastro-intestinal tract. Selikoff's work in this Insulation Industry Hygiene Research Program is supported by the International Association of Heat and Frost Insulators and Asbestos Workers (the insulation workers' union) and the John Manville Corp. (J-M) with the consultative facilities of the Public Health Service (PHS). Unlike gaseous contaminants, asbestos is a cumulative pollutant, and once inhaled may be retained in the lungs. The problem is further complicated because exposure effects have a delayed appearance; diseases associated with current, initial asbestos exposure levels will not appear for another 20 to 30 years; unfortunately, precautions taken today will not be evident for 30 years.

TLV studies

In 1960 the Asbestos Textile Institute (ATI) initiated a study of the asbestos textile industry member com-

"Loose Asbestos Fiber Seen as Cancer Threat to Men in Building Trades" so reads a recent headline introducing an article about asbestos as an ingredient in sprayed mineral fiber insulation. Insulation workers, as well as their families and the passersby on the streets below, are being exposed to this fibrous material used in construction.

Asbestos, a general term applied to a number of fibrous inorganic minerals, is becoming more and more of a concern to scientists, the construction industry, and the general public because there is reason to believe that exposure to the fiber, under some circumstances, is associated with lung cancer, asbestosis, and other equally serious diseases. Chrysotile, hydrated magnesium silicate $[Mg_6(OH)_8Si_4O_{10}]$, is the most common form of asbestos fiber and is mined from serpentine rock for milling and manufacturing into a number of different products.

The asbestos industry is comprised of several industries in one: the asbestos cement industry, the asbestos textile industry, the asbestos electrical equipment industry, and, of course, the suppliers of the fiber to the various manufacturing industries. One of the key uses of asbestos is in its essential utilization in insulation and the construction industry. And this is the area



Dust-free. Mixing asbestos-containing cement in newly developed polyethylene bag reduces air fiber concentration to 1/10 of original level in work area

panies by requesting PHS to conduct environmental and epidemiological evaluations to determine a threshold level value (TLV) for dust in the textile industry and to determine the best method for measuring this dust. Currently, the ATI uses the membrane-filtered air sampling technique, says C. L. Sheckler, J-M manager of Accident Prevention and Health Administration, and chairman of ATI Environmental Study Committee. At present, there is no ambient air TLV for the country. A value of two to five fibers 5μ or greater length per milliliter of air are being discussed; Selikoff and other scientists believe any other level is much too high, that much disease has been found among workmen exposed to levels above this value.

Regulations

Various states have now issued guidelines and regulations calling for enclosed spray areas and spelling out procedures for handling asbestos waste materials (*see box, p. 727*). The National Air Pollution Control Association (NAPCA), advised by a committee from the National Academy of Science in regard to national standards and controls aimed at protecting the insulation worker as well as the general public, has study contracts with various institutions including Selikoff's group. "We would like nothing better than for the proper kind of regulations to be adopted, on sprayed fiber insulation particularly, and for the contractors to all abide by those regulations," emphasizes Fred Pundsack, vice president for R&D of J-M, the nation's largest supplier of asbestos fiber.

Problems and solutions

Insulation workers are exposed to dust-containing asbestos fibers during the mixing of asbestos cement, cutting asbestos pipe insulation, and application of sprayed mineral fiber insulation. When plasterers wet-spray the material on steel girders, small bits of "snow" drift th ough the construction site and down to the streets below as the wet slurry dries.

In the Insulation Industry Hygiene Research Program, one of the first things done was to survey dust counts on the actual construction sites and survey the typical activities in which an insulation worker engages. In this manner the dustiest jobs and thus the areas of greatest risks could then be identified.

In solving these dust problems, the J-M research lab in conjunction with

the Selikoff research team began studies on specific problem situations. First, when asbestos cement is dumped and mixed, clouds of dust are released. Now a polyethylene bag has been designed for the cement mixture. A spout at one end of the bag is for the introduction of the necessary water, and then kneading the mixture produces a wet slurry without dust. The dust released is reduced to 1/10 of the original level.

Sawing asbestos pipe insulation on the job site is quite often necessary, but cutting this low density material creates a dusty situation. By working with dust-collection equipment manufacturers and saw manufacturers, the research team was able to design an effective saw-dust collecting piece of equipment. Also, a process and product was devised to form elbows and other types of pipe insulation in the plant, rather than on the job. The dust level can therefore be reduced to 1/10,000 of the original dust level.

In some circumstances, industrial techniques cannot lower the dust count sufficiently, making use of a facial respirator necessary. Sclikoff stated that only 4% of the 13,000 insulation workers wore respirators during these job operations. The reasons: the masks are uncomfortable when fitted tightly to the face, thus the men will not wear them; also, conditions on a construction site are not controllable as in a factory, and changing the filter membrane is difficult or impossible. J-M developed a disposable respirator, currently being tested by the Bureau of Mines, and licensed the knowledge to manufacturers. A disposable respirator could be available within the next 12 months.

In regard to the spraying of the mineral fiber insulation, the contamination levels on the worksite and on the streets below can be reduced greatly by following spraying regulations, such as those initiated in New York (*see box*). If the regulations are followed, the hazard conditions are considerably reduced; if not followed, a potentially dangerous situation exists.

Cooperation among industry, government, labor groups, and scientists is yielding a wealth of data pinpointing the actual problem in the use of asbestos fibers and initiating studies resulting in control of hazardous situations. Granted, the obvious effect of controls and solutions today will not be readily evident for 30 years, but investment for the future is a must. CEK

Reclaiming solid wastes for profit

Hercules will build the country's first complete solid waste reclamation plant in Delaware

"Society must move in this direction; we're going to have to start recycling for the next generation and for future generations," says state representative Robert J. Berndt, chairman of the Governor's Committee on Solid Waste, in reference to the new \$10 million disposal plant for Delaware. Hercules, Inc., has received the bid to design, construct, and operate the solid waste reclamation plant in populous New Castle County.

From nine proposals and outlines submitted to the committee and Delaware Gov. Russell W. Peterson, Hercules was chosen. "(Hercules) has the talent to do the job," adds Berndt, explaining that the other proposals received offered only partial reclamation of wastes. Hercules' manager of New Ventures, John Hodges, stated that the plant, with 50 employees, will process 500 tons of domestic solid wastes and selected industrial wastes and 70 tons of sewage sludge (70% moisture) per day, based on an eight-hour day for five days a week. At present, these figures represent about one half of New Castle County's solid wastes; furthermore, this county is Delaware's most densely populated area.

Negotiations will be completed this month concerning the 15-acre site of the plant. After the location is determined, construction will start immediately if funds are available. There is hope of delegation of federal funds in the near future. The Solid Waste Resources Act of 1970, providing federal aid for such demonstration plants, is in Congress now. Sen. J. Caleb Boggs (R.-Del.), minority leader of the committee reviewing the bill, is enthusiastic because his state supports him in his efforts toward pollution control generally and solid waste control in particular. Pilot plants of this nature could receive up to 75% of construction costs as outlined in the bill.



Artist's conception. Hercules' plant will be constructed on a 15-acre site in northern Delaware and will treat about 570 tons of mixed solid waste per day

The state of Delaware has already appropriated \$1 million for the design and engineering of this project. If the additional money becomes available from the federal government, construction is scheduled to be completed in 22 months.

Self-sufficient

Once in operation the objective will be to bring the plant to a self-supporting basis with the return from the reclaimed products offsetting operational costs. No present landfill or incineration system achieves this. If the unit functions as planned, the plant's facilities may be expanded to double its capacity to 1000 tons per day. Expansion can also take place by creating a longer work week and double shifts; overhead costs would increase by 75%. Because of this planned expansion as well as constant upgrading of the plant's operation and quality of products in conjunction with advances in technology, George Dutcher, director of New Castle County Public Works, dubbed the new plant a "processes polymer."

Delaware has few acceptable sites for landfilling waste disposal as do other states. There are no quarries, mines, or canyons for burial. In most areas of the state the water table is only 5 to 6 feet below ground level, which limits the use of man-made pits. In southern Delaware the soil is sandy and poor for use in coverage. In the northern section of the state, the soil is clay-like with poor drainage. When wet, the water is retained in pockets and becomes stagnant; and when dry, the clay cracks, allowing rat infestation and fires. Remaining are the Delaware River, bays, and ocean, which provide no solution. "Delaware is ideally situated to be the pilot plant of the world," summarizes Richard Weldon, a member of the governor's solid wastes committee.

The solid wastes to be utilized in this scheme include domestic wastes, selected industrial and commercial wastes, and sewage sludge. If the unit size is eventually doubled and handles all of the county's wastes, initiation of plans for similar plants for the rest of the state will follow.

Flow Sheet of Proposed Plant



First receiving point

Solid wastes will enter the disposal plant at two receiving stations—one for household refuse and the other for selected industrial and commercial wastes. From the first receiving point, the domestic wastes will be dumped into a hopper and transported by conveyor to a pretreatment point where ferrous metals will be removed. These metals will then be sold. The remaining material will be shredded and pulped with sewage sludge, resulting in a mixture of 50% moisture.

After this step the design of the plant is based on three key elements:

· A digestor system, a controlled compost process patterned by the Fairfield Engineering Co., converts the incoming mixture of organic wastes and sewage sludge into a high quality pathogen-free humus product. When fed into the digestor, the 50% moisturized material is agitated with auger screws while air is blown in from the bottom. This system involves biological digestion processes utilizing aerobic, heat-loving bacteria already present in the mixture. No auxiliary organisms will be added. Sensors in the bottoms of the tanks automatically regulate the temperature and oxygen content, maintaining optimum conditions for the digestive procedure.

No unpleasant odors of air pollutants are produced by this system. A similarly constructed plant in Puerto Rico, operated by the Fairfield Engineering Co., handles 300 tons of solid waste per day. Following digestion, the nondigestable organic materials, including plastics, tires, shoe soles, rags, etc., and inorganic materials, are separated from the humus, using equipment and techniques developed in the mining industry. By-products of the digestive process are water, carbon dioxide, and the pathogen-free humus. After being pelletized, this clean humus has marketable uses as a soil conditioner, blend for fertilizer, substrate for systemic pesticides, and, in future development, animal food additive.

· Application of pyrolysis, a destructive distillation technique demonstrated by the Bureau of Mines (ES&T, Feb. 1969, p. 119) controls decomposition of the organic solid wastes. Pyrolysis handles automobile tires, plastics, and other materials posing disposal problems. The waste materials are subjected to high temperatures in the absence of oxygen, preventing ignition. This process provides good quality carbon products that will be marketed, hydrocarbon gases which are rich in hydrogen and can be used for fuel in the plant itself. and oils to be marketed as fuels or sources of such chemicals as styrene.

• A residue separation system applies techniques developed by the mining industry to separate ores. Inorganic residues, such as glass, grit, sand, and nonferrous metals, are sorted by screens, gravity tables, and other devices. Sand and grit will be used as landfill material, while the nonferrous metals will be sold. Until marketed more profitably, the glass mixture will be finely ground and useful for landfill or roadbed ballast.

Second receiving point

The second receiving station handles the selected industrial wastes. Paper coming into this point can be treated in various manners. If the paper is clean, it will be shredded, baled, and sold; or the paper can be conveyed to the digestor system and become an ingredient of the humus material. Otherwise, the paper can be sent into the destructive distillation unit along with plastics, rags, wood, and other industrial wastes to produce carbon. Rubber material, tires, industrial plastics, and other refuse are shredded and sent to the pyrolysis unit, which, as described in the preceding column, yields marketable products.

The waste disposal plant will follow a program of continuous, rather than batch, operation. The residue separation system will eliminate "handpicking," and the shredders are heavy enough to handle bedsprings, washing machines, chain link fences, and other equally indisposable materials.

New venture

This complete reclamation plant is unique in many respects. Hercules has drawn together and systematized equipment from other trades, plus industrial supplies that will have to be manufactured specifically for use in this system. Constant upgrading and application of new technological developments will mark the growth of the plant and improve the quality of the final products.

This project will be Hercules' first significant dealing with municipalities in the area of solid waste; however, the company has maintained an active program for handling its own solid waste problems and has conducted a company-funded program in the field of municipalities. Regarding this first venture with the public, "the area of solid wastes offers growth for products to be extracted. . . . If we can get the product in a form that the customer can use, he will buy," and this produces "a viable business in communities," states Hodges. Weldon remarked that the amount of research done in the area of marketing by Hercules had definitely impressed the governor's committee. Also, the plant will meet federal and state air and water pollution guidelines and regulations. The plant, says Berndt, "won't pollute air, water, or ground." This type of approach could be used for the entire country. CEK

Developing nations view environment

Interior official explains why other countries' concern for environment differs from that in the U.S.

Perhaps the No. 1 domestic goal for the U.S. is environment and while there is little doubt that the environment is important to all nations, other issues such as population growth, economic development, and military security are the top issues in other countries. Four countries with four different sets of conditions weigh these factors quite differently.

S. Fred Singer, deputy assistant secretary for scientific programs in the U.S. Department of the Interior, has had an opportunity to contrast U.S. priorities with those of three other countries—New Zealand, Iran, and Israel—when he visited them during a recent round-the-world trip.

New Zealand

"On the whole, the country has very little pollution," Singer says. With a favorable geographic situation, New Zealand consists of two long narrow islands with good crosswinds; consequently, there is not much air pollution. Secondly, the country generates its electric power by hydroelectric and geothermal means. Thirdly, there are relatively few people; although it has as much land area as Italy, New Zealand is sparsely settled and has less than 3 million people. New Zealand, a country that relies heavily on the export of agricultural goods for its foreign exchange, is faced nevertheless with development problems.

"If New Zealand decided to double or triple its population, environmental problems would become significant, and the country would have to plan for such growth rather carefully," Singer adds. "The country has essentially exhausted its hydro resources. It will have to increase electrical power by other means. One option is the import of fuel but the air pollution burden would then increase. So all these factors must be balanced



S. Fred Singer Round-the-world traveler

against the benefits of having a larger population, a larger economic base, and the higher standard of living."

Iran

The situation in Iran is quite different from that of New Zealand. "Iran also has a low population density, but a large fraction of its people is illiterate," Singer explains. "This same fraction has a high birth rate; the average family size is eight children. Iran's population is increasing at such a rate that its doubling time is 20 years. Within 20 years, Iran will increase from 30 to 60 million people."

The depletion of water resources is a critical problem. Fairly self-sufficient, it exports more than it imports. But it will need more water to grow food for the people. "Unless birth rate is controlled, Iran will never be able to catch up," Singer explains. "If population is not controlled, Iran will have to spend all of its development money on water resources, irrigation systems, and education of the illiterate segment of its rapidly growing population."

"Iran will probably make it because of its great wealth," Singer comments. "Some of the country's income from oil could be used for family planning. It's expensive, but worth it in the long term."

Israel

"The Israeli situation is highly distorted by military security problems," Singer says. "Natural resources are few, and the main problem is water. Israel has essentially used up all its water resources. Faced with the problem of increasing their numbers, the Israelis settle in desert situations where one would not otherwise normally settle in order to make the country's borders safe. This practice further worsens their water problem.

"To advise Israel to stop growing in population doesn't make sense," Singer comments. "National security is their No. 1 concern. The most sensible advice is complete reuse of waste water. The Israelis are well advanced in various water conservation schemes, particularly for irrigated agriculture; in the use of brackish water for fish farming; and in water management generally.

The analysis

Analysis of the environment and other costs of growing populations is essentially an economic analysis. Singer calls it the "populution problem." What are the environmental costs—the monies that have to be expended in one form or the other by the population as a whole—to maintain a good environment in face of growing population or growing consumption? Most nations now are performing such analyses. ssM James O. Evans U.S. Department of Agriculture Washington, D.C.

The soil as a resource renovator

"That which is used develops—that which is not used wastes away"

Hippocrates, 4th century B.C.

orticulturists. foresters, and agronomists view briars, bush, and weeds not just as nuisance vegetation but, more generously, as plants growing out of place-plants occurring where not wanted. Goats, however, reveal no intellectual bias among plants, and, as they pursue their hungry objectives, do not pause to segregate weeds from their bluegrass and clover neighbors. An analogy can be drawn concerning certain discarded residues and effluents. By way of illustration, an earth specialist-ecologist or a soil scientist-sanitary engineer, in contrast to most disposal engineers, can be expected to view treated sewage and many other wastes not as refuse but as valuable resources which happen to be at the wrong place, or in the wrong form, or in the wrong amount, or at the wrong time. Indeed, all resources,

whether animate or inanimate, are of limited value to man unless activated and properly utilized. For example, long ago the observation was made that muscles should be used for them to develop; otherwise, they atrophy—a wasteful process.

The value of human excreta and other animal wastes has been recognized if not understood—for many centuries. Historically, the Chinese and other early civilizations applied human organic wastes to the land to improve or maintain soil fertility. And there are numerous documented accounts of the common use of "night soil" in European countries. The following quote taken from Victor Hugo's immortal *Les Miserables*, published in 1862, is remarkably accurate, descriptive, and upto-date:



Costs of disposal methods for activated sludge

Do you know what these piles of ordure are, collected at the corners of streets, those carts of mud carried off at night from streets, the frightful barrels of the nightman, and the fetid streams of subterranean mud which the pavement conceals from you? All this is a flowering field, it is green grass, it is mint, thyme, and sage; it is game, it is cattle, it is the satisfying lowing of heavy kine; at night it is perfumed hay, it is gilded wheat, it is bread on your table, it is warm blood in your veins, it is health, it is joy, it is life.

Little can be said to supplement such eloquent testimony concerning a material that many people usually describe with a single, common, four-letter word.

A more ancient quote from the Old Testament, Eccles. 1:7, is instructive: All the rivers run into the sea. Yet the sea is not full; unto the place from whence the rivers come, thither they return again. This succinct and poetic description of the hydrologic cycle-the eternal reuse of water-illustrates a well-known but little appreciated fact that nothing is utterly consumed or wasted. Instead, substances simply change from one form to another and are recycled. The law of the conservation of matter not only is true-it must be lived by. An understanding of what this implies suggests that every effort should be made by man to: • develop economically feasible means of salvaging waste materials for reuse as salable products; · isolate particularly obnoxious, toxic, or otherwise troublesome industrial wastes at their origin so that they may either be subjected to neutraliz-



Spray. Three-year waste water irrigation tests at Pennsylvania State University showed significant increases in forest growth with no harmful effects

subjected to a compressed timetable. In our modern, extremely complex society-largely urban and industrial in orientation-no single waste treatment or disposal process is best suited to all conditions, and no perfect system will ever be devised. It is possible, however, through known treatment plant techniques to renovate completely waste waters into potable water. Advanced waste treatment processes have been developed and are being used by the Federal Water Quality Administration to allow effluent discharges from which absolutely no pollution would enter our surface or groundwaters. There is a cost consideration, of course, and proper disposal is required of the quantities of organic and inorganic sludge and ash materials separated from the effluent water during treatment.

Through treatment, sewage can be separated into two major components: · so-called sludge "solids," an inorganic and organic fluidized sludge material, almost all of which can be useful for fertilizing and soil conditioning, and • a liquid or water fraction. This liquid is not pure water, of course, and contains an appreciable amount of dissolved nutrients which also are available for plant use and growth. Not without reason, this nutrient content is viewed as excessive and undesirable when discharge to streams or lakes produces profuse aquatic growth and the resultant oxygen depletion, fish kills, and hastening of the eutrophication of lakes. And, until recently at least, most of the attention concerning treated sewage has been focused on the liquid portion. Furthermore, the importance of the

ing treatment or converted into useful products; • put the wastes to work as sources of energy.

The soil—a multifunctional system

All of our metals are derived from the earth, and the earth mantle is essential to the existence of land plants and animals. Any soil which promotes the growth and well-being of plants must be amply supplied with air, water, nutrients, and living soil organisms. A given soil may serve in a variety of roles-as a receptacle or absorbing agent, a storehouse or reservoir, a screening or filtering agent, a purifier or renovator, a vehicle for transmission and recharge, or as a foundation or supporting agent. Furthermore, a body of soil conceivably may serve each role simultaneously. Consider only one role for the moment. From the beginning of life on this planet, soil has served as a cleansing and renovating agent. It is no wonder (and no accident) that the microorganisms responsible for biological purification (i.e., degradation and stabilization) in sewage treatment plants have soil as their common origin.

Water recycling— a natural phenomenon

As implied by the hydrologic cycle, all water eventually is recirculated and reused by various processes and organisms. So-called waste waters, including all the dissolved and undissolved substances they harbor, are likewise recycled, gradually by nature and chance or more rapidly by man and design. Indeed, "waste water" treatment and reuse differ from natural water recycling only in dissimilarities in the rapidity and intensity of the time-treatment processes involved, the former being



water resource for industrial and domestic reuse in some areas is unquestioned, providing ample justification for use of the most advanced waste treatment techniques. There are many situations, however, where the disposal of solids, sludges, and effluents by land spreading or irrigation may offer the ultimate solution to waste disposal problems.

Land disposal

Land disposal can serve a variety of useful purposes. In an ecological sense, the partial restoration of the nutrient cycle afforded by land disposal of wastes in itself is a worthy endeavor. Although commercial fertilizers are relatively cheap and fertilizer application to crops and soils is accomplished, generally, with comparative ease, sewage and feedlot wastes usually are free of charge to farmers. And land disposal often is less expensive than any of the advanced waste treatment and disposal alternatives. Land disposal can be viewed if one prefers, strictly as a waste water treatment process. The method can be employed primarily for the irrigation water it supplies, for groundwater replenishment, for soil enrichment and improvement, or as a combination of each.

Modern-day disposal of treated sewage and other wastes (both raw and processed) by application to land surfaces is practiced in many technically advanced countries-England, France, Poland, Germany, and the United States, for example. The practice appears to be increasing in popularity in the United States. A survey made in 1967 revealed at least 29 municipalities in Pennsylvania alone were applying liquid digested sludge onto rural lands; whereas, in June 1963, there were one third fewer Pennsylvania municipalities using this disposal method. A survey made in 1965 by Bendixen revealed over 2400 landwaste disposal systems in use in the United States. (Disposal of solid wastes in landfills was not covered.)

Disposal of organic wastes to the land by industries is commonplace. Of the over 2400 systems mentioned above, about 900 were serving the food-processing industry. In this category, at least two installations are worthy of specific reference. Every year, Seabrook Farms Co. in New Jersey successfully sprays tremendous amounts of cannery wastes from a food-processing plant onto forested lands. Campbell Soup Co. in northwestern Ohio disposes of liquid discharges from tomato processing operations by application to land surfaces. In spite of soils of poor natural drainage, a combined spray irrigationgrass filtration system has been used successfully by the Campbell plant. The disposal of papermill waste water by crop irrigation and irrigation of forest lands is an established practice. Disposal of wastes from dairy plants through irrigation or other land application methods has been successfully used in several states including Wisconsin and Minnesota. Even hydrocarbons and oily sludge wastes can be effectively degraded by soil microorganisms in an aerobic environment and assimilated within the soil matrix. An industrial firm in France produces and sells protein synthesized by microorganisms growing on waste low grade petroleum. And since 1951, at the Houston, Texas, refinery of Shell Oil, almost all of the petroleum sludges and stable emulsion from tank bottoms, oil-water separators, sewer boxes, and ship ballast water has been consumed by a land disposal system.

Few would dare deny that the deliberate and orderly return by man of organic and inorganic wastes to the lands from whence they came is a good conservation practice. No one objects to the idea of systematic waste removal to areas where full utilization is possible without contamination of the environment or intrusion on the sensitivity of some group or individual; indeed, all will agree that this disposal practice is good whereas disposal to streams, lakes, open dumps, the air, the ocean, or even to so-called useless wastelands and deep underground cavities is either not so good or is unacceptable. Why then is time wasted talking about what is best rather than taking concerted action to make it a universal practice?

Negative factors

There are two major factors or obstacles to a more widespread application of what might be termed a wastes conservation-and-utilization concept. One obstacle is a lack of dedication or desire by too many people to see such a practice become universal. This is due mostly to ignorance and unfounded fears ignorance of the necessity for useful waste disposal and of its benefits, and muddled fears involving aesthetics (such as unpleasant odors or unsightly appearances) and disease or poisoning effects (i.e., contamination of animals, plants, soils, and groundwater with pathogens, excess minerals, or chemical poisons). Although these are valid and highly important considerations, my research investigations indicate such dangers are precluded if reasonable or commonsense precautions are used.

For example, deactivation, neutralization, effective incineration, or safe burial of certain highly toxic, obnoxious, or dangerous wastes may be necessary whenever such wastes occur in sufficient quantities or concentrations. Also, pasteurization or disinfection of human and livestock wastes prior to land disposal may become a recommended practice in some situations. In all cases, waste loading rates onto land areas must be adjusted to local soil, topographic, climatic, and land use conditions so that the soil environmental system is never overtaxed or loaded beyond its assimilative capacity. Continuing research, education, demonstration, and training are possible means by which the first obstacle may be overcome.

The second factor is more complex. but economics is at its core. Although it has been shown that some wastes can be hauled by truck or rail or piped economically over fairly long distances, and suitable disposal sites exist within a distance of 100 miles of almost all of our municipalities, costs must always be competitive with other treatment and disposal alternatives. Bouwer observed in 1968 that ultimate treatment and disposal of conventionally treated sewage by land application is considerably less expensive than costs of the most advanced wate treatment (tertiary) techniques available today. However, beneficial effects of the inexpensive replenishment which soils and land areas accrue from useful organic and inorganic waste materials must be compared with the relative cheapness and ease of application of commercial fertilizers to good agricultural land. And, of course, not all wastes can or should be applied to the land whatever the economic considerations. No intelligent and responsible individual would advocate discarding radioactive wastes, pesticide residues, or used car bodies onto the landscape. (Although such wastes as these also are either degradeable or reclaimable, they require special treatment and handling.)

Summation

Digested sewage sludge and sewage effluent are outstanding examples, however, of so-called waste products for which land disposal is a "natural." They are not useless, are not wastes, strictly speaking, and should not be wasted. They should be considered as resource materials and consequently as assets rather than liabilities.

Whenever agricultural land and crops are mentioned, one perhaps is apt to think of those common crops such as corn, soybeans, grain, or hay and the cultivated soils in which they are grown. Although the response of such crops to sewage application can be dramatic, cultivated soils need not be favored as disposal sites. Vast areas of range and forest lands also are available for waste disposal and utilization. Of course, transport distance would be a determining factor in some cases. A fact worthy of note is that forest soils, in general, exhibit superior water absorbing capabilities and can serve as excellent receptacles for the assimilation and utilization of fluid wastes. And, because of the high evapotranspiration rates exhibited by trees, forests can be very effective in removing excess soil moisture resulting from large waste water applications.

As an awareness of the usefulness, simplicity, finality, economy, and subsequent productivity associated with or resulting from the disposal of sewage and of many other processed "wastes" by application to land becomes more commonplace, a significant increase in the popularity of the practice can be expected. Conceivably, this popularity could be shared by everyone involved with disposal activities-by those needing to get rid of the waste substance and by those needing to get it, i.e., with treatment plant operators or disposal engineers and with land treatment operators or farm managers. Resource or refuse? It is what man makes of it.

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Variations in Phosphorus Uptake by Algae

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• Presented is a laboratory study of varying levels of P-uptake by algae under different environmental and physiological conditions. *Chlorella* and *Scenedesmus* were grown in synthetic feed as large-scale, continuous uni-algal-cultures. A photoelectric turbidostat apparatus and a rigorously controlled environment were used in culturing the algae. Physical parameters including light intensity, algal cell density, diurnal cycle, temperature, and mixing affected the mass rate of growth and the pattern and amount of P-uptake by algae. Three types of uptakes were demonstrated: the metabolic uptake for maximum growth, the storage or luxury uptake having no effect on growth, and the starvation uptake by P-starved algae. A phenomenon of partial 'unavailability' of phosphorus for algal growth was found at low cell densities and high temperatures.

Phosphorus is an essential ingredient in the conversion of solar energy to biochemical energy by plants. Continuous contributions of this element from domestic, industrial, and agricultural sources to the aquatic environment have resulted in enrichment of the system and thereby created increased levels of biological growth. As reviewed elsewhere (Azad, 1968), sufficient evidence relative to this phenomenon has been accumulated for environmentalists to believe that removal of this nutrient at the source could possibly result in better control of biological productivity in many receiving waters. The fundamental mechanism through which phosphorus acts to produce stimulation of primary producers is far from being thoroughly understood. As a result, a cost-benefit analysis justifying phosphorus removal on economic ground is not yet possible.

Specifically, the question is: what biomass would be produced by a given weight of phosphorus added to an aquatic ecosystem? Freshwater algae were analyzed (Krauss, 1963) for their phosphorus content and values ranged from 0.94 to 1.51% on a dry weight basis. Other observers report values well outside this range. Standing crop surveys have been widely reported along with the chemical analysis of the water. The results are too disperse to provide clues to the existing biochemical relationships.

Although algal blooms in many areas have attracted much publicity, little is known about the triggering mechanism. The persistence of sub-bloom algal densities and their relation to existing phosphorus concentrations are likewise not well understood. Laboratory studies have indicated that certain environmental factors are quite important in defining the algal mass growth rates. Among the significant variables are: light intensity, dark–light cycles, temperature, mixing, and the ratio of organism mass to water mass. Biochemically, the enzymes responsible for phosphorus transport from the media, and its subsequent phosphorylation on or within the cell, could possibly be activated or repressed by phosphorus concentrations in the substrate, depending upon the relative concentrations of this element in the aqueous phase and within the cell.

In addition to the permutations possible because of the above factors, certain less prominent parameters such as species requirements, algal-bacterial symbiosis, micronutrient requirements, cation complexation, and transport mechanisms, to mention only a few, could all play a part in algal growth.

The main objective of this research was to elucidate the cause and effect relationships that exist among the major factors that influence algal growth and the interaction of these with the existing phosphorus concentration in the aqueous environment.

Experimental

The green algae *Chlorella* and *Scenedesmus* were grown as large-scale, continuous uni-algal-cultures under rigorously controlled environmental conditions (see Azad, 1968 for photomicrographs of typical cells). A constant biomass was maintained during any given experiment by employing a photoelectric turbidostat apparatus (Azad, 1968; Gates and Borchardt, 1964). Chemical and physiological response patterns were generated by an orderly variation in the concentration of phosphates in the carefully prepared synthetic feed (Azad, 1968).

Total phosphorus determinations were carried out using

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the method described by Gales, Julian, *et al.*, 1966. Routine samples were taken from the reactor contents and from the effluent. In the latter case, algal cells were removed by filtration through a 1.2- μ membrane filter. Phosphate in the cells was calculated by subtracting the total PO₄ in the effluent filtrate from the total PO₄ in the reactor. The 24-hr. dry weight density measurement of algae and the cell counts were conducted in accordance with standard methods (APHA, AWWA, *et al.*, 1965). Gro-Lux fluorescent lamps illuminated the culture. Light intensity measurements were made with a Weston Model 756 illumination meter and a Weston illumination target equipped with a Viscor filter. The plexiglass reactor contained 26.25 liters of culture which were completely mixed by mechanical agitation. Further details on the methodology can be found elsewhere (Azad, 1968).

Physical parameters including light intensity, algal cell density, diurnal cycle, temperature, and mixing were investigated for their roles in determining the amount of phosphorus uptake by the specified algal cultures and accompanying growth. Enzymatic factors were studied through a reduction in the internal phosphorus content of the algal cells induced by a period of growth in a P-depleted medium and subsequent exposure of these 'P-starved' cells to P-rich substrate. Details of some of these experiments have already been published (Azad and Borchardt, 1969a; Borchardt and Azad, 1968).

The first portion of this study describes the response of the cultures to steady-state culturing conditions or to conditions where additional phosphorus is fed as a slug. The second portion describes the response of P-starved algal cultures to shock loading with phosphorus. Apparently in this



Figure 1. Effect of stepwise reduction of PO_4 on the mass growth rate of green algae at 2250 ft.-c.



Figure 2. Effect of stepwise reduction of PO_4 on the mass growth rate of green algae at 2250 ft.-c.

case the uptake process is largely independent of the previously enumerated major physical parameters.

Steady-State and P-Rich Culturing Conditions. It was anticipated that algae would store phosphorus above and beyond their usual metabolic needs to protect themselves against a possible subsequent shortage of this nutrient in their growth environment. In addition, it seemed logical that there must be some minimum steady-state phosphorus concentration required in the substrate for the maximum growth of algae under each set of environmental conditions and that below this concentration, the steady-state mass growth rate of algae must decline. This critical concentration of phosphorus was designated as *CCP*. Furthermore, it was expected that the *CCP* would vary with the major environmental parameters influencing growth.

Any amount of phosphorus incorporated by the cells above *CCP* would imply storage of the unused nutrient. This mechanism of storage was designated as *LUP* or luxury uptake of phosphorus. As in the case of *CCP*, the magnitude of *LUP* was also thought to depend upon the major environmental parameters and, likewise, the concentration of phosphorus in the reactor contents. As a net result, the effect of any given environmental factors on the growth of, and phosphorus uptake by, algae was considered to be closely related to these two basic concepts.

Light Intensity Effects. Without delving into the actual mechanism of photosynthesis, these studies circumvented the details and observed only end results. The overall response was observed and measured in terms of net growth of algal cell mass and removal of phosphorus from the aqueous phase.

Figures 1 and 2 illustrate the results of a typical experiment at a given value of light intensity measured as foot candles of illumination at the front face of the reactor. Average values of the significant environmental factors, measured routinely during these experiments, are noted on these figures as are the various concentrations of phosphorus expressed as PO_4 . Deviations from the reported mean values were small as evidenced by the consistency of the data.

It is apparent that a stepwise reduction of phosphate in Figure 1 from 2.0 to 1.5 mg. per liter PO₄ did not affect the steady-state mass growth rate of the culture. When the supply of phosphorus was further reduced, however, the rate of biomass growth declined. As can be seen in Figure 2, the critical level was 1.5 mg. per liter PO₄. Hence, this value is designated as *CCP*. When the concentration of phosphate in the reactor was one-third of the *CCP* value (0.5 mg. per liter), the rate of biomass growth rate $(1.14 \times 1/3 = 0.38 \text{ days}^{-1})$. Therefore, the mass growth of the culture would appear to be directly proportional to the concentration of total phosphorus in the reactor below the *CCP* level but independent of this value at any point above it.

Also, it should be noted that the difference of 0.5 (2.0 - 1.5) mg. per liter PO₄ was not detected in the effluent filtrate (Figure 1) and, therefore, must constitute *LUP*. This, however, does not represent the maximum limit of phosphorus storage by such cells. Other experiments indicate that, under similar conditions, the cells could contain up to a total of 10% phosphorus expressed as PO₄ by dry weight (Figure 3). Since the *CCP* from Figure 2 is 3% (1.5/51 × 100), it is obvious that this algal culture could normally store more than twice as much phosphorus for later use as was needed for their continuing metabolic needs, *CCP*. This additional phosphorus in the cells is not required for cellular growth. The rate of growth of the cell mass containing 10% PO₄ was exactly the


Figure 3. Phosphate removal and residual as functions of culture density

same as for cells containing only 3% PO₄ by dry weight under identical environmental conditions.

Similar experiments were conducted at other light intensities including 1200, 800, and 400 incident foot candles. The mechanism defined by *LUP* and *CCP* were confirmed in these tests. The magnitude of the luxury uptake of phosphorus, *LUP*, decreased with a corresponding decrease in light. *CCP* was also a function of light intensity as shown in Figure 4.

It should be noted that the abscissa of Figure 4 is not foot candles incident at the face of the reactor but an "effective average light intensity" (*EALI*). A method of transforming the former into the latter has been described in detail (Azad, 1968; Azad and Borchardt, 1969b). The *EALI* is a logarithmic mean intensity that takes into account the light absorption characteristics of a dispersed algal culture and likewise makes an allowance for respiratory needs. Illuminating test values of 2250, 1200, 800, and 400 ft.-c. (measured at the front face of the reactor) are represented by the four points showing net mass growth in Figure 4. The rate of mass growth of algae drops to zero at some finite light intensity where respiration and photosynthesis are just equal (the compensation point) as illustrated in this figure.

Within limits of experimental error, the mass growth rate of the algal culture appeared to be directly proportional to the *EALI* and each increment of 10 ft.-c. produced an additional 0.05 day⁻¹ growth under the experimental conditions noted in Figure 4. An average effect of light intensity on the critical concentration of phosphorus, *CCP*, was observed and the indirect proportionality appeared to deviate from linearity at about 200 ft.-c. It would appear from the slope of this straight line that each decrease of 10 ft.-c. demanded an additional 0.05 mg. phosphate per liter of the culture for supporting the maximum steady-state mass growth rate of algae under the systemic parameters used.

Since *CCP* increases as illumination decreases, one may speculate that a decrease in luminous energy not only would decrease the mass growth rate but also the efficiency of the algal cells for extraction of phosphate molecules from the solution phase. Conversely, the higher the level of light, the lower the concentration of phosphorus required for supporting the maximum growth of algae under these higher growth rate conditions. These observations are extremely interesting



Figure 4. Growth rate of and CCP for green algae as functions of average light intensity effective in net photosynthesis

and may provide the entering wedge in explaining the behavior of certain natural biological systems.

Cell Density Effects. At any constant level of illumination, a decrease in algal cell density would mean an increase in the effective average light available to the culture and vice versa. Also, a decrease of cell density in the reactor could possibly influence the CCP value by affecting the collision frequency of algal cells and nutrient particles. The cell density of an algal 'bloom' in a lake generally ranges from 5 to 20 mg. per liter dry weight of algae in the most active photosynthetic portions of the epilimnion.

Many experiments were conducted using cell densities ranging from 8 to 100 mg. per liter. The results of a typical low cell density experiment are illustrated in Figure 5.

These data reinforce the point that the storage of phosphorus by algae is a normal characteristic. The continuous culture was provided 2.5 mg. per liter PO_4 at time zero. After 9 hr., the cells contained 0.95 mg. per liter (8.6% by weight) PO_4 when less than 0.40 mg. per liter total PO_4 was present in surrounding growth medium. If this quantity were stored entirely as inorganic PO_4 by the cells, the concentration gradient of much more than 2 to 1 might tend to force the cells to leach their phosphorus out into the medium. Yet, all the evidence accumulated in these studies indicates



Figure 5. Determination of luxury uptake and *CCP* for algal growth at low cell density



Figure 6. The diurnal cycle effect on the growth and the PO₄ uptake process of predominantly *Scenedesmus* algae



Figure 7. Effect of a continuous decrease in PO_4 on the mass growth rate of and CCP for green algae at 30 $^\circ$ C.

that the phosphorus rich algae do not reject any of the phosphate once it is picked up from the substrate. Hence, either the cell must expend energy and adjust its ionic balance in some way to overcome the increased osmotic pressure or convert its inorganic phosphorus to some other form(s) such as AMP, ADP, ATP, polyphosphates, Phytin, guanidinophosphate, phosphorylated sugars, etc. Available evidence indicates that the latter course is adopted since the accumulation of phosphorus in these forms provides storage of energy usable at a later date (Kamen, 1963; Kandler, 1960).

A phosphate residual in the effluent filtrate at the *CCP* was detected only in the low cell density cultures. This characteristic as well as the *LUP* and *CCP* existing at various cell densities are summarized in Figure 3. Since the uni-algal-*Chlorella* and the uni-algal-*Scenedesmus* cultures showed a very similar response, the data points on this figure represent both types of culture. It should be noted that the scale for the total phosphate residual in the effluent filtrate is one hundred times expanded as compared to the total phosphate extracted scale. The data points at 100 mg. per liter dry weight algae should not be considered quantitatively rigorous since 1500 foot candles illuminated the culture at this density instead of the 2000 value noted for the rest of the runs.

It was apparent from many studies similar to Figure 3 that all such cultures studied required about 3% phosphate by weight to develop the maximum possible rate of mass growth under the given experimental conditions. Such cultures also extracted up to 10% phosphorus by weight from their growth medium when that amount of phosphorus existed. With the luminous energy at the source held constant, the available light decreased as the algal cell densities increased. Hence, the CCP value is seen to increase and LUP to decrease beyond 60 mg. per liter density. This observation is in good agreement with a similar factor illustrated in Figure 4.

At or above a cell density of 40 mg. per liter, the algae leave no detectable quantities of phosphates in the effluent filtrate as long as there is less than 10% PO₄ by weight of the microorganisms in the reactor. However, at lower densities than 40 mg. per liter, the phosphate residual rises very rapidly with a corresponding decrease in the dry weight density of algae. This phenomenon of the partial 'unavailability' of phosphorus at low cell densities, if validated for natural systems, should constitute a strong argument for justifying the approach of controlling eutrophication by limiting the supply of phosphorus.

Diurnal Cycle Effects. Light being the principal driving force for all photochemical reactions, its periodic absence from an algal culture would be expected to reduce the overall anabolic efficiency of these photosynthetic microorganisms. Phosphorus uptake reactions being endergonic, the metabolic uptake of this element should also decline, if not stop, during darkness.

Although continuous high intensity (more than 1000 ft.-c.) lighting of algal cultures destroys their natural periodicity, the original rhythms are restored simply by placing these cultures in the dark or in dim light (Giese, 1966). Some experiments were conducted to verify and define the impact of a light-dark (12:12) diurnal cycle on the growth of and P-up-take by unicellular green algae. The results presented in Figure 6 are typical of these tests.

There are several features of this figure worth noting. First, the mass growth rate and phosphorus uptake during darkness decrease to low levels as speculated. Second, the average rate of mass growth for the lighted period, after the first dark period, is higher than the previous maximum steady-state value. This factor apparently disappears after the second dark period since the average mass growth rate value of 1.01 days⁻¹ is identical to that of the maximum steady-state figure under continuous lighting conditions. Third, none of the phosphorus stored by algae leaches to the substrate during the dark period. At the onset of the first dark period for the case illustrated, the cells contained 9.5% PO4 by weight while the effluent filtrate contained relatively little of this element. Again, during the second dark period, the substrate contained only traces of phosphorus and the algae were composed of 6%PO4 by weight. In both cases, no stored phosphate leached out of the cells during the dark periods of little to no growth.

It may be concluded from these studies (Azad, 1968) that no net uptake or leakage of phosphorus occurs during darkness while the cell growth is greatly reduced. The overall efficiency of phosphate extraction by algal cultures would be lower in a natural light–dark environment than the normal high levels experienced under steady-state, continuously lighted conditions. Phosphorus removals would be in direct proportion to the reduction in the total growth. As a first approximation, a factor of 0.67 might be in order for green algae similar to *Chlorella* and *Scenedesmus* cultured under similar environmental conditions (Figure 6).

Temperature Effects. Temperature can affect the growth of microorganisms through its action either on the external medium or directly on the cells, or on both. The solubility coefficient of CO_2 is reduced from 0.76 to 0.36 and O_2 from 0.028 to 0.019 with a corresponding increase in temperature from 25° to 60° C. (Marre, 1962). Temperature acts directly on the cells by speeding up or slowing down the different biochemical reaction sequences.

Different experiments were conducted at 15° , 20° , 25° , and 30° C. to evaluate the effect of temperature on *CCP*, mass growth rate, and *LUP*. The results obtained from a typical run at 30° C are illustrated in Figure 7. Once again, it can be observed that the rate of mass growth is directly proportional to the concentration of phosphorus below the *CCP* and independent of it above this critical level. Also, traces of phosphorus were left in the effluent filtrate at *CCP* in Figure 7, while no such residual would have been expected at lower temperatures (Figures 1–3).

A summary graph of the effect of the temperature on the rate of mass growth of algae and *CCP* is presented in Figure 8. The scatter in the two growth rate values at 25° C. is at least partly due to the different light levels used. There was other conclusive evidence (Azad, 1968) on the basis of which the curve was passed through a growth rate value of 1.28 days⁻¹.

It is clear from this figure that *CCP* varies linearly with temperature irrespective of the response of mass growth rates. Within the range of 10° to 35° C., the 0.047 mg. PO₄ per liter per ° C. value may be used for approximate quantitative estimates of minimum concentration of phosphorus required for supporting the maximum growth of an algal culture under conditions similar to the ones in Figure 8. Similarly, 0.062 day^{-1} per °C. could be used for mass growth rate prediction purposes from 10° to 20° C.

Apparently, higher phosphorus concentrations must be present to grow the same mass of algae in nature at lower temperatures and conversely, much lower PO_4 concentrations would be needed at higher temperatures.

Mixing Effects. Mixing may affect the growth of algae in at least two important ways. One, it may enhance contact between the algal cells and the nutrient sources, thereby influencing the substrate utilization by the microorganisms. Two, the turbulence may expose the reactor contents to the luminous energy more effectively (this phenomenon is sometimes referred to as light integration). The changing levels of mechanical shear may have other consequences which are largely unknown at present.

Several different experiments were designed to discern the effect of the degree of mixing on the rate of mass growth of algae and the *CCP*. The algal cell densities in these experiments ranged from 34 to 100 mg. per liter, the luminous energy varied from 1600 to 1900 foot candles (at the face of the reactor), the pH was held in the range of 8.1 to 8.3, and the temperature was 25° C. throughout. Unfortunately, mixer impeller speed could not be increased beyond 1400 r.p.m. without interfering with the operation of the turbidostat in the particular equipment used. Reducing the speed of the mixer below 500 r.p.m. would not keep all the algal cells in suspension at all times and, therefore, provided unreliable results. Hence, the range of 500 to 1400 r.p.m. constituted the practical limits of the turbidostat apparatus without modifications in its design.

No definite effect of mixing on *CCP* and *LUP* could be observed during these experiments. A summary of the influence of turbulence on the mass growth rate of algae is presented in Figure 9. In spite of the several variables and the use of data normalization techniques, a line of best fit through the points calculated from different experiments clearly shows the trends. The rate of mass growth of algae appears to be a function of the degree of mixing even within the narrow region of high turbulence values reported in Figure 9. The value of 0.054 day⁻¹ per 100 r.p.m., however, is highly system specific and is not recommended for extrapolation to other systems. Further studies on mixing effects should prove highly fruitful.

Alternate P-Starvation of Algal Cultures. When there is a large excess of phosphorus in the growth medium, the algae pick up some maximum amount depending upon the environmental conditions, their metabolic, CCP, needs, plus a quantity for storage, LUP. These quantities seem well fixed and the question might be asked, why don't these cells pick up more phosphorus if there is an excess available? It may be speculated that an increased level of inorganic phosphorus in algal cells represses the biosynthesis of enzymes responsible for their P-uptake reactions. The higher the level of phosphorus, the greater the repression of these enzymes would be. Thus, in a P-rich substrate, the quantity of these specific enzymes would drop so low that no significant net transport of phosphorus would be possible from the medium. If some of the internal inorganic phosphorus was converted to organicand polyphosphates, etc., the level of this internal inorganic phosphorus would drop, the repression would be reduced, and additional specific enzymes would become avail-



Figure 8. Effect of temperature on the mass growth rate of and CCP for green algae



Figure 9. Summary of the effect of mixing on the mass growth rate of green algae



Figure 10. High PO4 uptake by P-starved algae at 2100 ft-.c. and 25 $^{\circ}$ C.

able for extracting more phosphorus from the substrate (Mahler and Cordes, 1966; Yoshida, 1955).

Reducing the internal phosphorus content of microorganisms below their normal metabolic needs for this element is referred to as phosphate starvation. A continuous culturing technique such as the turbidostat used in this study, when operated with a substrate containing little or no phosphate, will deplete the culture of its stored phosphate through cell growth and subsequent dilution. The time to produce any phosphate concentration in the culture can be predicted mathematically and checked experimentally. All phosphorus concentrations below the *CCP* in Figures 2, 5, and 7 illustrate a P-starved condition and the corresponding proportionate effect on the rate of mass growth of algae.

The degree of P-starvation of an algal culture may be determined by dividing the actual phosphate concentration, P_s , by the critical concentration of phosphate, P_c , *i.e.*, P_s/P_c . Since the value of the CCP for a relatively constant temperature, light intensity, and pH has been found to be about 3% PO₄ by weight of the algae, Pe would approximate the experimental cell density in mg. per liter multiplied by 0.03. With the dry weight density and the total phosphorus concentration of the culture, P_s , routinely measured and P_c computed, the degree of P-starvation of a culture, P_s/P_c , can easily be calculated. A value of 1.0 would mean no P-starvation, whereas progressively lower values would represent increasing degree of Pstarvation. The higher the degree of P-starvation of algae, the lower the rate of its mass growth (Figures 2, 5, and 7). Other methods including the observation of algal color, the spectrophotometric follow-up of the carotenoid or chlorophyll content, or enzymatic analysis for alkaline phosphatase content could be used for defining the extent of P-starvation (Azad, 1968; Azad and Borchardt, 1969a).

Figure 10 illustrates the response of a typical P-starved culture to a sudden slug of phosphates. It should be noted that the algae were fairly well starved ($P_s/P_c = 0.23$) at time zero and grew rather slowly until after containing 20% PO₄ by weight (7.2/36.0 × 100). When the maximum steady-state mass growth line is extrapolated back to the abscissa, the lag period for resuming maximum growth in Figure 10 is about 12 hr.

It is significant that a P-starved algal culture can extract



Figure 11. Characteristic high PO₄ uptake by P-starved Chlorella and Scenedesmus

more than twice as much phosphate as is possible by a Psatisfied culture under the most favorable conditions, *LUP*. If the algae were not P-starved at time zero in Figure 10, the maximum possible P-uptake could not have been more than 9 to 10% PO₄ by weight of the cells (Figures 3 and 5).

The magnitude of P-uptake by P-starved algae at various cell densities is summarized in Figure 11. It should be stressed that the variations in environmental factors noted on this figure do not materially affect the equilibrium value of phosphorus bound with the cells.

Figure 12 is an illustration of the effect of the degree of Pstarvation, P_s/P_c , on the magnitude of P-uptake and the lag period for resuming maximum growth. As the degree of Pstarvation increases, the magnitudes of both the P-uptake and the lag period increase at a decreasing rate up to the optimum starvation point, *OSP*. From this point on, the increasing degree of P-starvation probably has a genetically damaging effect on the cells (Azad, 1968; Azad and Borchardt, 1969a),



Figure 12. High PO₄ uptake by P-starved Chlorella and Scenedesmus as a function of the degree of P-starvation expressed as P_s/P_e

and the magnitude of P-uptake drastically decreases while the lag period sharply increases.

Based upon the visual observations of the algal cells at various degrees of P-starvation, the appropriate color notations are made on Figure 12. This can serve as a qualitative means of visually determining the degree of P-starvation and, therefore, assist in evaluating the potential for P-uptake and growth.

Discussion

The results presented in this paper would suggest that the chemical composition of a grab sample of the standing crop from a lake or river might easily range anywhere from less than 0.5 to more than 20% PO4 by weight -a 40-fold variation! Limiting the possibilities to the most common natural situations, this span might be narrowed to about 1 to 15%, depending upon the environment and the previous physiological condition of the algae. If we assume the existence of an excess of phosphorus, composition of algae should be around 10% PO₄ (or 3% P) by weight under circumstances corresponding to those in this study. As the supply of phosphorus in the environment decreases, the algae will contain less phosphorus without showing any effect on its growth up to the point called the critical concentration, CCP (about 3% PO₄ by weight in this research). Hence, 'normal' algae under similar conditions may generally contain 3 to 10% PO4 by weight.

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Received for review December 6, 1968. Accepted April 2, 1970

Water–Clay Interactions in North Carolina's Pamlico Estuary

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■ The pore to bottom water ratio of cationic equivalents measured at 20 stations increases systematically downstream from about 0.6 to 1.2 along a 50-mile profile in North Carolina's Pamlico River estuary. This trend is apparently controlled by entrapment of relatively saline water after northeasterly storms as the suspended load settles. Cationic concentrations generally decrease in the pore waters with depth, from a maximum 10-20 cm. beneath the sediment-water interface. Because top portions of the cores are from a zone of active sediment-water mixing and cores were taken at a time of near maximum salinity in bottom waters, pore water from deeper portions of the cores may reflect long-term mean salinities. An increase of K equivalent ionic fraction in the pore waters with depth may be related to H+ ion exchange with the sediments. A strong correlation between exchangeable Mg and chlorite, as well as exchangeable K and illite, was noted.

his paper presents information on the chemical relationships between the bottom water, pore water, and adsorbed cations on clay from sediments in a natural estuarine environment. The Pamlico estuary affords an opportunity to study interactions between these phases over a wide salinity range.

Freshwater enters the estuary through the Tar River with headwaters in the Piedmont near Durham, N. C., and flows eastward across the Coastal Plain through the cities of Tarboro and Greenville before becoming the Pamlico River at Washington, N. C. (Figure 1). Marine water flows into the sound through Hatteras Inlet and Ocracoke Inlet in the Outer Banks of North Carolina. The phosphate mine of the Texas Gulf Sulphur Corp., located near Aurora on the Pamlico River, was under construction during the period of collection of the samples used for this study; consequently, the samples were obtained before possible contamination of the estuary by phosphate rock tailings, although municipal waste is disposed of in the Tar River. Contamination from municipal waste, however, apparently does not invalidate the results of this study for overall trends in the data can be explained by systematic changes in the natural system unrelated to contamination.

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Figure 1. Map of the Pamlico River and Sound showing sampling Stations 1-20

Procedures

Bottom water samples and 25-35-cm.-long core samples of the bottom sediments were collected at 20 stations at intervals of about 2.5 miles beginning 2 miles southeast of Washington and continuing in the same direction down the middle of the river and on out into Pamlico Sound (Figure 1). They were collected during November 14-16, 1965. By staying in the middle of the river, we hoped that principally clay-sized sediments could be obtained by the Phleger corer. Sediment cores 50 mm. in diameter were extruded from the plastic core liners in the boat, sectioned, and placed in Desicoted glass bottles. Toluene was added to prevent bacterial metabolism; little or no toluene was observed to penetrate the cores. Immediately after returning to the laboratory the water was passed through a <0.45- μ Millipore filter to remove any particulate matter and acidified to pH 3 with glacial acetic acid. Several drops of formaldehyde were added to inhibit growth of mold. The water samples, about 300 ml. each, were returned to the polyethylene bottles in which they were collected and stored until ready for analysis.

The chlorinity of bottom water was determined by titration using the mercuric nitrate method (Kolthoff and Stenger, 1947). Salinity values were calculated from the chlorinity data by the standard formula:

S = 0.03 + 1.805 Cl

where Cl is the chlorinity expressed in %.

Cores were processed for analysis within 3 weeks after collection. After discarding the toluene and trimming off the disturbed outer portion of the mud core, we extracted pore water (1-5 ml.) from a 12-cc. mud sample, and placed it on Whatman No. 40 filter paper in a 5.5-cm. Buchner funnel, which was inserted in a 500-ml. suction filtration flask. After as much pore water as possible was removed, about 2-g. wet weight of the sample was placed in a centrifuge tube and washed with methanol three times to remove any remaining pore water and soluble salts. Neutral NH₄Ac (1N) was added in three separate leachings which were collected for analysis as the readily exchangeable cations (Jackson, 1958).

The remaining sediment from the filter cake in the Buchner funnel was separated by wet-sieving and centrifugation into coarse silt, fine silt, and clay-sized fractions. Each fraction was analyzed using a Philips X-ray diffractometer with a scintillation counter employing pulse-height discrimination to obtain a semiquantitative ($\pm 10\%$ of the total clay fraction) analysis. Samples with known proportions of kaolinite plus quartz and chlorite plus quartz were run to establish a calibration curve for estimating the amount of quartz in each fraction. Clay mineral percentages were calculated on the basis of peak area of the basal reflection and weighting factors assigned to each peak principally as a function of the mass absorption coefficients of the clay minerals and relative settling rates on glass slides during sample preparation (Gibbs, 1965; Freas, 1962). Freas used the following weighting factors: kaolinite, area under (001) X1; illite, area under (001) X3; montmorillonite, area under (001) X1. Because of the greater charge density and finer grain size of montmorillonite, it tends to concentrate at the top of a sedimented slide (Gibbs, 1965). Because of this, the following factors were used: montmorillonite X1; illite X12; kaolinite X4; "14 Å intergrade clay" X4. It should be pointed out that relative proportions of the clays among the various samples are more important than absolute amounts. Kaolinite and chlorite were distinguished according to the method of Biscaye (1964).

Analyses for the major alkali metals and alkaline earths in the water and the NH₄Ac leachate were performed on all solutions with a Perkin-Elmer Model 303 atomic absorption spectrophotometer. All analyses were checked for interferences by the standard addition method but no interferences were observed. Precision of the analyses is given in Table I.

Major Cations in Pore and Bottom Waters

Chemistry of the pore water compared with the bottom water is shown in Figure 2. Unless otherwise indicated, these



Figure 2. Plot of Na⁺ concentration in the pore waters (from the 2-6-cm. cuts of the cores) compared with bottom waters

Lines are fit by linear regression of y on x. Numbers on the inside of the abscissa on this and subsequent relevant plots refer to sampling stations



Figure 3. Plot of Na^+ concentration in the bottom waters and in the pore waters as a function of depth in the cores

Numbers along the top within the figure refer to sampling stations

Table I. Precision of Chemical Analyses^a

Na	K	Mg	Cl
1	9	3	6
4	8	7	
4	5	4	
	Na 1 4 4	Na K 1 9 4 8 4 5	Na K Mg 1 9 3 4 8 7 4 5 4

 $V = \frac{100s}{100s}$

where s is the standard deviation and $\bar{}_{s}$ is the arithmetic mean of 6 replicate sample preparations and analyses.

and all subsequent data from the cores are based upon measurements from the 2–6-cm. cuts. Chlorinity measurements of the pore water initially were made, but subsequently proved to be suspect at Stations 1–5 because of deviations from electroneutrality. The most abundant cation, Na, was plotted in Figures 2 and 3 because of its superior analytical precision (Table I) and its strong tendency to maintain conservative ratios with Cl in estuarine waters.

The trends in Figure 2 conclusively show that Na concentrations in the pore water are lower than bottom water values upstream and become increasingly greater than bottom water concentrations downstream. Trends of the other cations follow the Na trend quite closely. The Na pore:bottom water ratio farthest upstream at Station 1 is about 0.60; it steadily increases until it is doubled at a value of about 1.20 farthest downstream at Station 20. Moreover, an apparent pattern of cationic concentrations with increasing depth in the cores along a downstream profile is evident (Figure 3). Concentrations of pore water within cores taken at Stations 1 and 3 decrease with depth in the core. At Station 4 there is a slight maximum at about 20 cm. beneath the sediment-water interface, which in itself might be fortuitous, except that this same pattern is evident in most of the other cores farther downstream. A sufficiently close sampling of each individual core is not available to determine the exact position of this maximum in each core, but it seems to vary from 10-20 cm. beneath interface. Again, trends of the other cations follow the Na trend quite closely.

The phenomena of pore water salinities greater than bottom water salinities and salinity maxima in pore waters at shallow depths have been observed by other workers. Siever, Beck, *et al.* (1965) measured on the average slightly higher salinities in interstitial waters from modern oceanic sediments; however, pore to bottom water chlorinity ratios were generally 1.05 or less. They found that Na concentrations varied sympathetically with chlorinity and that seawater Na: Cl ratios were generally maintained. If we assume constant Na: Cl ratios in pore water of this study, which is the case with the bottom water, pore water from Pamlico Sound seems to be more concentrated relative to bottom water with respect to Cl than comparable ratios in the open ocean (about 1.2 in Pamlico Sound compared to 1.05 or less in the open ocean).

The most comparable situation to the present study, both from a geological setting and in terms of results, is in Aransas Bay and the Guadalupe River behind the barrier Matagorda Island, Texas Gulf Coast (Shepard and Moore, 1955). Some of the data from their cores reveal striking similarities to data from Pamlico Sound (see Figs. 70 and 71, pp. 1581 and 1582). For example, chlorinity values in core J72D (Fig. 71B) reach a maximum of 23% about 15 cm. beneath the interface and decrease with increasing depth. Maximum pore to bottom

Table II. Comparison of Bottom Water Salinities With Earlier Data (All values in %)

(All V	alues in %.)		
ations	8/25/64 (Hi	4 to 8/30/65 II, 1966)	10/13/65 to	
Equivalent station no. (this study)	Av. of 10 analyses	Range	10/16/65 (This study)	
5	8.0	5.3-13.7	11.8	
7	10.7	6.2-13.4	13.8	
10	11.4	6.7-14.3	14.1	
13	15.0	7.6-19.0	20.1	
18	19.2	14.8-22.8	23.9	
	(All v ations Equivalent station no. (this study) 5 7 10 13 18	(All values in %) %/25/6. Equivalent station no. (this study) Av. 5 8.0 7 10.7 10 11.4 13 15.0 18 19.2	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	

water chlorinity ratios vary from about 1.1 to 1.4. Maximum chlorinity values of pore water, however, occur at depths up to 60 cm., somewhat deeper than those observed in the Pamlico system.

Shepard and Moore offered no explanation for this phenomenon, and indeed, any explanation offered here must be speculative. Other facts must be explained here as well, and those are Na pore to bottom water ratios of less than one and the apparent lack of maxima at 10-20 cm. beneath the interface in the fresher water upstream. Siever, Beck, et al. (1965) suggested that since clays can act as ultrafiltration membranes at moderate to high pressures (300 p.s.i. or above), under pressure of compaction they could exclude ions and pass through fresher water, thereby concentrating the residual interstitial water in dissolved species. This process could not be operative in the pore water downstream in Pamlico Sound because: (1) pressures are not high enough in these shallow cores; and (2) Siever, Beck, et al. suggested that the water in the top few centimeters of the column might actually be fresher than the overlying bottom water because of the ascending excluded fresher water. This ultrafiltration mechanism at much greater depths than those from which these cores were taken (on the order of several hundred feet) could explain the pore to bottom water ratios of less than one upstream, as could relatively fresh groundwater recharge.

Emery and Stevenson (1957) pointed out that salinity of pore water depends on that of overlying bottom water, and as such, pore water salinity probably represents a median value of the salinity of the overlying water which flows past a point during the year. This does not seem to be the case for pore water in the top 20 cm. of the sediment column in Pamlico Sound, for the data in Table II clearly show that bottom water salinities were near a maximum for that year when the samples were collected. It may apply, however, to pore water from deeper levels in the sediment column. As shown in Table II, mean annual salinities are somewhat lower than those reported in this study, thus pore to bottom water cationic concentration ratios of less than one upstream in the fresher waters may be explained in part by Emery and Stevenson's hypothesis. Pore water at some unknown level in the cores may actually reflect mean annual salinities. It appears, therefore, that any or all of three factors may be involved in explaining the decrease in ionic concentrations with increasing depth: (1) relatively fresh groundwater recharge, (2) ultrafiltration at deeper levels in the sediment column and ascension of the excluded freshwaters, or (3) comparatively fresh pore waters from deeper portions of the cores reflecting longterm mean salinities. The third factor very likely may be the most important.

However, none of these mechanisms can explain either the concentration maximum or higher pore water cationic concentrations in the sound. During northeasterly storms there is



Figure 4. Mineralogical variations and variation in Ca-exchange capacity of the total sediment

Numbers in parentheses after each clay mineral refer to their average cation exchange capacities in meq./100 g. The numbers plotted for the clay minerals are moving averages calculated in each case from three adjacent values

considerable agitation of the bottom sediments in the shallow sound down to several centimeters (Duane, 1962). Moreover, because of the influx of normal marine seawater during the northeasterly storms, salinities in the sound, and to a lesser degree up the estuary, become abnormally high during and for some time after a major storm (Taylor, 1951). Then, an explanation for the phenomena described above might be higher salinities in the zone of sediment-water mixing, apparently confined in these cores to the top 20 cm. of the sediment column, which occurred during violent northeasterly storms. This would involve entrapment of comparatively saline water as the storm-derived suspended load of sediments settles to the bottom. This process could also explain the loss of the pore water concentration maximum upstream, since its effect would become increasingly negligible in that direction. Additional evidence for a zone of active sediment-water mixing in the uppermost portion of the sediment column will be presented in the discussion of equivalent ionic fractions. It follows that higher pore water cationic concentrations, and presumably salinities, may be essentially short-term paleosalinity indicators in this estuarine environment.

Clay Mineralogy

Clay mineral and quartz variations within the Pamlico Sound and estuary are shown in Figure 4, along with the Caexchange capacity for the total sediment. Chemical compositions of relevant clay minerals are given in Table III. The method of moving averages used for calculating the data points in Figures 4 (exclusive of quartz percentage and Caexchange capacity) and 5 is justified because of the semiquantitative nature of the clay mineral determinations. The trends are in general agreement with those reported by Allen (1964) in the Tar-Pamlico system, by Griffin and Ingram (1955) in the Neuse River estuary of North Carolina, and by Nelson (1963) in the Rappahannock estuary of Virginia. The term "14 Å intergrade clay" used in Figure 4 and Table III is synonymous with "diagenetic chlorite" and "dioctahedral vermiculite" of other writers (Rich, 1968). Two exceptions were noted to the general agreement: (1) Nelson (1963) found a decrease in "dioctahedral vermiculite" downstream; and (2) none of the other workers on the North Carolina estuaries reported the presence of montmorillonite. The diffractograms were carefully verified, however, and montmorillonite does exist in small quantities in the Pamlico system.

If we assume the majority of the clay minerals were detrital in this system, the trends in Figure 4 can generally be explained. Both detrital chlorite and kaolinite have smaller negative electrostatic charge densities and are coarser grained than the other clay minerals; therefore, they should flocculate out of the river's suspended load earlier and be concentrated relative to other clay minerals farther upstream. Conversely, montmorillonite has a greater charge density, is finer grained, and thus should flocculate farther downstream in waters of greater ionic strength. Characteristic initial settling rates of clay minerals in saline waters are given in Table IV. The properties of the 14 Å intergrade clay mineral are largely unknown and, as pointed out above, its trends in different studies are somewhat contradictory. The distribution of illite is more puzzling, for it should flocculate early. This has led Allen (1964) to suggest that illite may be forming in situ in Pamlico Sound by collapse and uptake of K⁺ ions in more saline waters by montmorillonite. As will be discussed in the section on equivalent ionic fractions, there is evidence against this in the chemistry of the pore water.

Although it is commonly believed that mineral percentages determined by X-ray diffraction are at best semiquantitative, it is encouraging to note the antithetic relationship between quartz percentage and the Ca-exchange capacity of the sediment shown at the top of Figure 4. The relationship is certainly expected because of the negligible exchange capacity of quartz and it bears out the precise, and hopefully accurate, quartz determination.

Table II	I. General Formulas for Clay Minerals ^a
Illite	K _{1-1.5} Al ₄ [Si _{7-6.5} Al _{1-1.5} O ₂₀](OH) ₄
Montmo-	
rillonite ^b	(1/2Ca,Na)0.7(Al,Mg,Fe)4[(Si,Al)8O20]
	(OH) ₄ · <i>n</i> H ₂ O
Chlorite	(Mg,Al,Fe)12[(Si,Al)8O20](OH)16
Kaolinite	$Al_{4}[Si_{4}O_{10}](OH)_{8}$
14 Å intergrad	le
clay ^c	$(Al,Fe,Mg)_{2}[(Si,Al)_{4}O_{10}](OH)_{2} \cdot nH_{2}O$
^a From Deer, e	t al. (1966).

^b Although all these formulas should be taken as approximate, this particularly holds for montmorillonite. ^c Summarized from Rich (1968).

Table IV. Characteristic Settling Rates of Clay Minerals

	(1	meters/day) ^a	
Salinity (%)	Kaolinite	Illite	Mont- morillonite	Chlorite
0.9	11.5	12.9	0.03	12.7
1.8	11.7	14.3	0.05	12.8
3.6	11.8	15.1	0.11	12.8
10.9	11.8	15.8	0.58	12.8
21.7	11.8	15.8	1.1	12.8
32.5	11.8	15.8	1.3	12.8

^a Data from Whitehouse, *et al.* (1958); Fig. 12, p. 33, and Table 13, p. 34; pH ranged from 7.5 to 8.5, temperature at 26° C.



Figure 5. Theoretical summation of exchangeable cations and measured summation of exchangeable cations

The numbers plotted are moving averages calculated in each case from three adjacent values

Water-Clay Interactions

At the outset of this discussion it should be pointed out that although Ca concentrations were determined in all phases, they are omitted from consideration in this study. There are small but varying amounts of skeletal CaCO₃ detritus in all these sediments that would affect the exchangeable Ca concentrations and possible pore and bottom water concentrations as well. The effect of dissolution of CaCO₃ on the Ca concentrations in the aqueous phases is somewhat conjectural, as it is dependent upon varying conditions of pH, but the solubility of CaCO₃ in neutral 1 N NH₄Ac is ample reason for excluding Ca from the exchangeable data. Inasmuch as one of the purposes of this study is to compare equivalent ionic fractions of the various phases, it was decided to exclude Ca from all the data.

Relationships between exchangeable cations and clay mineralogy are summarized in Figures 5 and 6 and Table V. Figure 5 is a plot of theoretical summation of exchangeable cations, as estimated from the clay mineral percentages and average exchange capacities for different clay minerals (Weed and Leonard, 1963) and the measured summation of major cations excluding Ca. It is not surprising that the theoretical exchange capacity curve does not coincide with the measured exchange capacity curve. The theoretical curve is based upon semiquantitative clay mineral determinations and exchange capacities for the various clay minerals estimated from the literature (Weed and Leonard, 1963). Indeed, the fact that both curves reach a maximum near Station 13 is encouraging.

The equivalent ionic fraction of K increases systematically downstream while Mg decreases, although the Mg trend is more diffuse (Figure 6). Inasmuch as the summation of the cations is recalculated to 1.000, the law of constant sums holds and the inverse relationship between Mg and K is not surprising; however, the fact that these antithitetic trends correlate with position in the estuary is significant. The principal Mg-bearing clay mineral in the estuary and sound is chlorite, while the main K-bearing mineral is illite (Table III). As shown in Figure 4, illite content increases downstream while chlorite decreases. The relative change in K equivalent ionic fraction downstream is approximately equal to the change in the percentage of illite, considering the limits of error in the semiquantitative clay mineral analyses; likewise the relative change in the Mg equivalent ionic fraction is



Figure 6. K^+ and Mg^{2+} equivalent ionic fractions in the 1 N NH₄Ac leachate

Table V. Mean Equivalent Ionic Fractions for All Twenty Stations ^a				
Solution	Na	К	Mg	
Bottom H ₂ O	0.777 ± 0.004	0.022 ± 0.001	0.200 ± 0.004	
Pore H ₂ O				
2-6 cm.	0.779 ± 0.010	0.027 ± 0.002	0.194 ± 0.011	
8-14 cm.	0.791 ± 0.011	0.028 ± 0.003	0.180 ± 0.010	
17-22 cm.	0.791 ± 0.008	0.027 ± 0.003	0.181 ± 0.006	
29-34 cm.	0.787 ± 0.014	0.032 ± 0.004	0.181 ± 0.013	
Sea H ₂ O	0.801	0.017	0.182	
Exchange-				

0.191- 0.288 0.096- 0.177 0.698- 0.557 ^a Plus or minus values are expressed as one standard deviation. The equivalent ionic fraction for Na, for example, as calculated in this paper is Na/Na + K + Mg, all concentrations being in equivalents. Data on exchangeables are from the 2-6-cm, cuts and are given as the range, rather than mean and standard deviation, since they vary systematically with pacifican in the schurzy (Figure 6). The pore water equivalent ionic with position in the estuary (Figure 6). The pore water equivalent ionic fractions, however, vary randomly with position in the estuary.

ables

similar to the change in chlorite content. It would appear, then, that the correlation between exchangeable Mg and chlorite, as well as K and illite, must involve removal of these cations from exchange sites or possibly actual dissolution of these minerals during NH₄Ac extraction. Probably no sharp line demarcates "exchangeable" and "nonexchangeable" ions in the clays of an estuary. A more appropriate term might be "readily leachable" ions, those that are available for any given extraction technique. Although considerably more erratic, the Na equivalent ionic fraction reaches a maximum toward the center of the profile, corresponding to the montmorillonite maximum, the principal Na-bearing clay (Table III).

The effect of amorphous or organic material in the sediments is impossible to ascertain here and may be quite significant with regard to the exchangeable fraction. McCrone (1967), for example, has shown that 75% of the exchangeable capacity of the sediments in the Hudson estuary can be accounted for by the organic fraction. However, the correlation between clay mineral distributions and "exchangeable" ions in the Pamlico estuary indicates that clay mineralogy exerts the primary influence upon the chemistry of the NH₄Ac leachate.

The fact that K may have been preferentially leached relative to the other cations during the sediment's residence time in the estuary is suggested from the data on average equivalent ionic fractions shown in Table V. The K equivalent ionic fraction in the pore water is distinctly higher than that in the bottom water and still higher than the value for normal marine water. This fact seems to be evidence against Allen's (1964) suggestion that montmorillonite may be collapsing in situ and extracting K from the pore water to make illite. Weaver (1967) has suggested that mildly weathered stripped illite (e.g., degraded illite) may satisfy its demand for K in the rivers on the way to the ocean. The higher K equivalent ionic fractions in the pore waters indicate that this process is not operative in interstitial waters of the Pamlico system.

Siever, Beck, et al. (1965) found lower Na:K ratios in interstitial waters from recent deep sea sediments than normal marine ratios, which is in general agreement with this study. They attributed these lower ratios to the fact that Na does not become incorporated in silicate minerals on the ocean floor to any significant extent, but K is liberated by hydrolysis of detrital K-feldspar (KAlSi₃O₈) in situ. They felt that clay minerals would tend to adsorb K rather than desorb it but that the ubiquitous K-feldspar would be out of its stability field and tend to dissolve. Minute quantities of K-feldspar were occasionally noted in the coarser fractions of the Pamlico sediments, and this explanation is a possibility.

Powers (1954) also reported an increase in K relative to the other ions with depth in the sediments of the James River estuary, Va. He attributed this to the desorption of K from the clays rather than dissolution of K-feldspar. Like Siever, Beck, et al. (1965), however, we feel that clays would tend to adsorb K rather than desorb it. He also found a decrease in Mg with depth; a hint that this may occur in pore waters from the Pamlico system is offered in the data of Table V. He found no systematic trends in ionic ratios as a function of position in the estuary, nor were any observed in this study. Deviations around the means for the equivalent ionic fraction data of the aqueous phases are quite small (Table V).

Perhaps another explanation for the increase in the K equivalent ionic fraction with depth may be found in the work of ZoBell (1946). He found minimum pH values 15-20 cm. beneath the sediment-water interface. This has been later substantiated in studies that have found lower average values for pH in the muds close to the interface than in the overlying water (for example, McCrone, 1967, Table 2). Tentative results are similar for the Pamlico system. The kinetics of exchange reactions involving clays and ionic species in water may be sufficiently rapid so that equilibrium exists between a clay particle in the suspended load of the river and cations in the water. When the clay particle settles to the bottom it will eventually encounter a lower pH environment. The mass action effect then will be such that there could be an exchange reaction set up between K⁺ ions in the interlayer positions and H⁺ ions in the interstitial waters until equilibrium is reached. The result would be an increase in K in the interstitial waters compared to ions less available for exchange. The Na⁺ ions would undoubtedly be involved in this exchange as well, but because of the high equivalent ionic fraction of Na, the effect is less obvious. The decrease in the equivalent ionic fraction of Mg with depth in the cores might simply be explained by the fact that the Mg²⁺ ion is less available for exchange. Presumably the pH will increase in the sediments at some depth lower than the cores taken for this study (Zo-Bell, 1946) and the compositional trends in the interstitial water seen in Table V will reverse. It should be pointed out that the above implications of cause and effect are quite speculative and further research is required in these areas.

As stated earlier, in the text, there is additional evidence to

active zone of sediment-water mixing. This is shown by the data in Table V, which indicate that Mg equivalent ionic fraction in the 2-6-cm. cuts of the cores is much more similar to bottom water values than those from deeper cuts. It is interesting to note that the Mg equivalent ionic fraction in the pore water from the deeper cuts is closer to seawater values than are those from the bottom waters. This may demonstrate the importance of the role clay-water cation exchange reactions play in affecting the ultimate composition of seawater.

suggest that the uppermost portions of the cores are in an

Acknowledgment

The authors wish to acknowledge the helpful suggestions and discussions of Gale K. Billings and Robert C. Harriss during the latter phases of the work. The constructive criticisms of Bruce W. Nelson, Roy L. Ingram, Ray E. Ferrell, Jr., and Daniel A. Textoris are appreciated.

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Received for review July 25, 1967. Resubmitted May 20, 1969. Accepted April 22, 1970. Presented in part at the Division of Water, Air, and Waste Chemistry, 152nd Meeting, ACS, New York, N. Y., September 1966. Also presented at a symposium on the geochemistry of sediments held at the annual meeting of the Geological Society of America, Mexico City, November 1968. This study was supported in part by the North Carolina Div. of Mineral Resources, Dept. of Conservation and Development, and the U.S. P.H.S. The atomic absorption unit was purchased through a grant by the North Carolina Board of Science and Technology. The data in this paper are from a dissertation submitted by David A. Dobbins in partial fulfillment of the requirements for the Ph.D. degree, University of North Carolina at Chapel Hill. ESE Pub. No. 214.

Concentration of Trace Metals by Solvent Extraction and Their Determination by Atomic Absorption Spectrophotometry

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• A simple solvent extraction procedure for concentrating trace metals for subsequent determination by atomic absorption spectrophotometry is described for aluminum, beryllium, cadmium, cobalt, copper, iron, lead, nickel, silver, and zinc. Different kinds of organic solvents were examined. A solution of diphenylthiocarbazone, 8-quinolinol, and acetyl acetone in ethyl propionate has been found to be useful. Interference effects of thirty-four diverse ions and compounds were studied and the procedure developed is highly selective. With the exception of aluminum, all of the metals can be determined when present at the low parts per billion level in an aqueous solution. Sensitivity for aluminum is $0.1 \ \mu g$. per ml. The procedure is well suited for environmental studies and is significant because it includes the majority of the inorganic carcinogens.

Solvent extraction techniques have proved to be very use-ful for preconcentration of traces of metal ions to the levels where they can be easily and accurately determined by atomic absorption (Mansell and Emmel, 1965; Mulford, 1966; Sachdev, Robinson, et al., 1967; Slavin, 1964; West, West, et al., 1967). Various complexing agents such as diphenylthiocarbazone(dithizone), dithiocarbamate, cupferron, and 8-quinolinol(oxine), can be used for the extraction of a large variety of metal ions. Conditions for extractions into solvents such as chloroform or carbon tetrachloride have already been reported (Morrison, 1957; Sandell, 1959), but chlorinated solvents are undesirable for atomic absorption methods because of the use of flame for atomization. Recently, the extraction of silver into ethyl propionate containing dithizone was reported (West, West, et al., 1967). The silver-dithizone complex was found to be stable in ethyl propionate for several days. These studies have since been extended and conditions for the simultaneous extraction and spectroscopy of seven important metal ions have been reported (Sachdev and West, 1969).

The present paper describes conditions for the extraction of various metal ions into an 8-quinolinol-ethyl propionate solution. By combining dithizonate, oxinate, and acetyl acetonate extractions into ethyl propionate, as many as ten different metal ions (Ag⁺, Al³⁺, Be²⁺, Cd²⁺, Cu²⁺, Fe³⁺, Ni²⁺, Pb²⁺, and Zn²⁺) can be concentrated by a single extraction step. The conditions for such an extraction are described together with pertinent information on the atomic absorption spectroscopy of the metal extract system.

Experimental

Apparatus. Atomic absorption spectrophotometer (Perkin-Elmer Model 303), HETCO burner with triflame burner head (Jarrel Ash Co.), gas flow meter (Hokes Model 993), hollow cathode lamps for the metals to be determined and a pH meter (Leeds and Northrup).

Reagents. Diphenylthiocarbazone (Eastman Kodak), 8quinolinol, ethyl propionate, acetyl acetone, ammonium tartrate, and tartaric acid. All reagents used were analytical grade. Standard solutions for metal ions were prepared by dissolving appropriate amounts of pure metal into minimum quantity of nitric acid and then diluting to a known volume using double distilled water.

Extraction Solutions. Diphenylthiocarbazone, 0.1 g.; 8quinolinol, 0.75 g.; and acetyl acetone, 20 ml. were dissolved in ethyl propionate and the volume was made up to 100 ml.

Choice of Solvents. Solvents such as n-butyl ether, methyl isobutyl ketone, methyl isopropyl ketone, ethyl propionate, and isoamyl acetate were examined for their suitability for the extraction of metal complexes, for the stability of the extracted species, and for their combustion characteristics for atomic absorption spectroscopy. The extractability of metal complexes was poor in n-butyl ether. Ketones such as methyl isopropyl ketone and methyl isobutyl ketone showed good extractability, but the complexes of dithizone are not stable in such solvents. Both of the esters, ethyl propionate and isoamyl acetate were found to be useful because the metaldithizone and metal-oxine complexes are easily extracted into these solvents and remain stable for many days. Although the solubility of isoamyl acetate in water is much less than ethyl propionate, the latter provides better spectroscopic sensitivity for the various metals involved.

Procedure for Extraction. An appropriate volume of aqueous solution was conditioned using 10 ml. of 1 *M* ammonium tartrate per 100 ml. of the sample and the pH adjusted to 6 ± 0.5 using ammonium hydroxide or tartaric acid solution. The solution was then transferred to a separatory funnel, shaken briskly for a minute with an extractant solution, and the two layers were then allowed to separate. The organic extract was then isolated and transferred into a small glass stoppered bottle for subsequent spectroscopic examination.

Effect of pH. The effect of pH on the extraction of metal ions by ethyl propionate containing 8-quinolinol was studied and the results are shown in Table I. The results indicate that Al^{3+} , Co^{2+} , Cu^{2+} , Fe^{3+} , and Ni^{2+} can be easily and effectively extracted. By adding diphenylthiocarbazone and acetyl acetone to the above systems, more than ten species of metal ions can be extracted. The presence of more than one kind of

	Table	I. Effect of pH	on the Extrac	tion of Metal I	ons by 8-Quino	linol in Ethyl l	Propionate	
pH	Al ³⁺ 25 µg./ml.ª	Be ²⁺ 0.5 μg./ml. ^a	Cd ²⁺ 0.5 µg./ml.ª	Co ²⁺ 5.0 µg./ml. ^a	Cu ²⁺ 5.0 µg./ml. ^a	Fe ³⁺ 5.0 µg./ml.ª	Ni ²⁺ 5.0 µg./ml.ª	Zn ²⁺ 0.5 µg./ml. ^a
1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3.0	0.0	0.0	0.0	0.0	17.5	3.0	0.0	0.0
4.0	7.0	0.0	0.0	20.0	36.0	42.0	30.0	5.0
5.0	17.5	0.5	0.0	30.0	40.0	42.6	33.0	12.4
6.0	17.4	1.0	3.0	30.0	25.0	42.6	33.5	16.0
7.0	15.6	7.0	7.0	30.0	22.5	42.0	33.0	2.6
8.0	13.5	7.0	3.0	28.0	6.5	40.5	22.2	5.0
9.0		15.0	0.0	18.0	5.0	41.5	5.0	6.5

^a Percentage absorption for metals at their respective absorption wavelengths.

Table II. Effect of pH on the Extraction of Metal Ions by Extractant Solution^a

	Act	A 13+	Do2+	C-12+	Co2+	C1.2+	Eo3+	NI: 2+	Dla 2+	7-2+
	Ag	Ale	DC-	Cur	0.0-	Curr	FC.	INI	P0-	ZI
	0.05	2.0	0.05	0.05	0.05	0.05	0.1	0.05	0.1	0.05
pH	μg./ml. ^b	$\mu g./ml.^{b}$	μg./ml. ^b	$\mu g./ml.^{b}$	μg./ml. ^b	μg./ml. ^b	μ g./ml. ^b	$\mu g./ml.^{b}$	μ g./ml. ^b	μ g./ml. ^b
1.0	5.9	0.0	0.0	0.0	0.0	9.0	0.0	0.0	0.0	0.0
2.0	6.0	0.0	3.2	8.6	0.0	9.0	2.2	0.0	0.0	3.0
3.0	6.6	2.0	15.4	11.2	0.0	9.0	5.0	2.2	3.5	21.0
4.0	6.6	8.0	18.0	11.5	5.6	9.0	6.0	6.2	6.9	32.4
5.0	6.6	15.9	25.0	11.6	6.2	9.0	14.2	6.5	9.3	32.8
6.0	6.6	15.9	25.0	11.6	6.2	9.0	14.2	6.5	9.6	33.0
7.0	6.5	14.8	22.7	11.6	6.2	9.0	14.2	6.5	9.7	33.0
8.0	5.6	13.8	19.8	11.6	6.2	8.9	14.2	6.5	9.6	31.5

^a Composition of extractant solution is described along with the reagents on page 749 ^b Percentage absorption for metals at their respective absorption wavelengths.

ligand has been reported to enhance the extraction (Freiser, 1968) and may provide a broader range of pH for optimum extraction efficiency in many cases. Thus, pH conditions were studied using a mixture of diphenylthiocarbazone, 8-quinolinol, and acetyl acetone in ethyl propionate. The results, as given in Table II, show that all metals ions studied can be extracted between pH 5 to 7. Any change of pH within this range has no significant effect on the extraction.

Stability of Metal Complexes. Although the solvent and the complexing organic molecules are completely destroyed in the flame, their stability is a very important factor controlling the efficiency of production of metal atoms in the flame and enhances the sensitivity and reproducibility of the procedure. The metal ions were extracted into the extractant solution and the absorption of each of the metal ions was measured at its respective wavelength. The extract was stored in a glass-stoppered bottle and after every 4 days, the absorption readings were compared with those of a fresh extract under identical conditions. The absorption readings for each of the metals were found to remain essentially constant over a 20-day period, indicating that the extract remains stable and can be stored for at least 2 to 3 weeks.

Optimum Flame Conditions for the Determination. The rate of aspiration, composition of the flame, and the position of the burner are the three important parameters in the spectroscopy of the respective metals. The rate of aspiration of about 3 ml. per minute provides the optimum sensitivity. This rate can be easily achieved by connecting a polyethylene capillary tube of 0.015-in. i.d. and 2.5 in. length to the capillary of the burner. Slight variation in the length of capillary may be required depending upon the burner used. The position of the burner should be adjusted so that the light beam passes through the flame about a centimeter above its base. The opti-

mum flame conditions, spectral slit width, lamp current, and appropriate wavelengths for the absorption lines are shown in Table III.

Interference Study

Method for Testing Interference. Interference effects of various ions were studied by the following procedure. A stock solution was prepared containing 0.05 μ g, per ml. each of beryllium, cadmium, copper, silver, and zinc; 0.1 μ g, per ml. of cobalt, iron, and nickel; 0.2 μ g, per ml. of lead; and 1 μ g, per ml. of aluminum. A 100-ml. portion of this mixture was extracted with 10 ml. of the extractant solution to provide reference values and to confirm the mutual extractability of each ion from the complex mixture. A similar solution containing all of these metal ions together with interfering ions (one at a time), as listed in Table IV, was extracted in the same manner as described above. All of the ions listed in Table IV were added at 100 μ g. per ml. level except for VO₈⁻, Sn⁴⁺, Bi²⁺, Cr³⁺ Si²⁻, and TeO₃²⁻ which were added at the 10 μ g, per ml. level.

Results of Interference Studies. Most of the ions listed in Table IV had no effect on the determinations. The presence of 100 μ g./ml. of HPO₄²⁻, HAsO₄²⁻, and MoO₄²⁻ lowered absorption readings for lead by 50%. A lower concentration of 10 μ g./ml. of these ions, which is still 50 times more than Pb²⁺ concentration, had no significant effects. As would be expected, large concentrations of halides lowered the absorption for Ag⁺; but, 100 μ g./ml. of Cl⁻, 10 μ g./ml. Br⁻, and 10 μ g./ml. I⁻ can be easily tolerated. Fluoride forms strong complexes with Al³⁺ and Be²⁺. A fluoride concentration, but only free (uncomplexed) aluminum can be determined by this procedure.

	Table III. Optimum	Conditions for the De	eterminations and	d the Range for L	inear Calibration (Curves
Metal	Wavelength (Å)	Spectral slit width (Å)	Lamp- current (mA)	Acetylene flow ^a	Sensitivity ^b µg./ml. for 1% absorption	Range for linear calibration curves $\mu g./ml.$
	Ai	r-acetylene flame air	$flow^a = 10 \text{ or}$	air pressure $= 3$	5 p.s.i.	
Ag^+	3281	2.0	12	2.2	0.002	0.0-0.25
Cd ²⁺	2288	6.5	8	2.5	0.001	0.0-0.10
Co ²⁺	2407	2.0	20	2.0	0.004	0.0-0.20
Cu ²⁺	3247.5	2.0	10	2.0	0.002	0.0-0.25
Fe ³⁺	2483.3	2.0	12	2.5	0.004	0.0-0.40
Ni ²⁺	2320	2.0	14	2.5	0.004	0.0-0.30
Pb ²⁺	2170	6.5	30	2.0	0.005	0.0-0.60
Zn ²⁺	2138	2.0	15	2.0	0.001	0.0-0.10
	Nitrous	oxide-acetylene flam	e, N ₂ O flow ^{a} =	10, N ₂ O pressure	e = 35 p.s.i.	
Be ²⁺	2348.6	2.0	20	21	0.002	0.0-0.10
Al ³⁺	3092.7	2.0	15	21	0.100	0.0-10.0
^a Flow units a ^b Sensitivity is	re arbitrary scale units or given for aqueous solution	Hokes flowmeter mode	el 993.			

Table IV. Interference Study

Group I Li+, Na+, K+ Group II Mg2+, Ca2+, Sr2+, Ba2+, Hg2+ Group III BO²⁻, B₄O₇²⁻, Ce³⁺ Group IV CO32-, Sn4+, SiO32-Group V NH4+, NO3⁻, HPO42⁻, Sb5+, HAsO42⁻, VO3⁻, Bi 3+ Group VI SeO₃²⁻, Cr₂O₇²⁻, Cr³⁺, TeO₃²⁻ Group VII F⁻, Cl⁻, Br⁻, I⁻, Mn²⁺ Miscellaneous: oxalic acid, citric acid, and detergents (Tide and Dreft)

Analytical Procedure

Calibration Curve. A stock solution containing 0.5 μ g./ml. of each of Ag⁺, Be²⁺, Cd²⁺, Cu²⁺, and Zn²⁺; 1 μ g./ml. of each of Co²⁺, Fe²⁺, and Ni²⁺; 2 μ g./ml. of Pb²⁺; and 20 μ g./ml. of Al³⁺ was prepared. Different volumes of this solution from 5 to 50 ml. were diluted to 100 ml. To each of these 100-ml. portions of solutions, 10 ml. of 1 *M* ammonium tartrate solution were added. The pH was adjusted to 6 \pm 0.5 by adding a few drops of dilute ammonium hydroxide, and the metal ions were then extracted according to the procedure described for extraction. Atomic absorption measurements were made at the optimum conditions as detailed in Table III. The range for linear calibration curve is also shown in Table III.

Determinations. Take 100 ml. of aqueous solution into a 250-ml. beaker. Add 10 ml. of 1 M ammonium tartrate, adjust the pH of solution to 6 ± 0.5 by adding dilute ammonium hydroxide or tartaric acid solution, whichever is necessary. In many samples, the addition of 10 ml. of ammonium tartrate-tartaric acid buffer of pH 6.0 may automatically adjust the pH of sample to about 6.0. Transfer the solution to

a 150-ml. separatory funnel, and add 10 ml. of extractant solution. Shake the solution briskly for 1 min. then allow to stand (about 3-5 min.) until the two layers are separate. Drain out the aqueous layer, dry the stem of the funnel from inside with a piece of rolled up filter paper, and pour the organic phase into a glass-stoppered bottle. The organic layer should be free of any aqueous droplets. Measure the atomic absorption for each of the metal ions using the conditions as shown in Table III. The reagents used such as tartrate or 8quinolinol may contain traces of metal salts; therefore, a blank should be carried out with each set of samples. Either the absorbance for the blank should be subtracted from that obtained for the respective metal ion or the instrument should be adjusted to read zero absorbance when the blank is being aspirated into the flame. By measuring the absorbance for the respective metals, their concentrations can be easily calculated by the use of calibration curve.

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Received for review March 4, 1970. Accepted May 11, 1970. This investigation was supported by U. S. Public Health Service Research Grant AP 00128, National Center for Air Pollution Control, Bureau of Disease Prevention and Environmental Control.

The Atmospheric Thermal Oxidation of Nitric Oxide in the Presence of Dienes

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The promotion of the atmospheric thermal oxidation of nitric oxide by conjugated dienes has been suggested as being partially responsible for the nighttime conversion of nitric oxide to nitrogen dioxide in polluted atmospheres. In this reaction, studied using long-path infrared spectrophotometry, the order of observed reactivities was: 2,3-dimethyl-1,3butadiene > isoprene > 1,3-butadiene. The addition of nitrogen dioxide to the diolefin was found to be the initial step in the overall reaction. The experimentally determined order of reactivity in this reaction is the same as that in the oxidation reaction. The diene-promoted photooxidation of nitric oxide was 7 to 25 times faster than the corresponding thermal oxidation. The thermal oxidation is therefore unimportant in polluted atmospheres during the day. Application of the data of this present study and typical pollutant concentrations showed that the diene-promoted thermal oxidation of nitric oxide is also unimportant at night.

n a recent investigation (Glasson and Tuesday, 1963) of the atmospheric thermal oxidation of nitric oxide, several olefins were shown to have no effect on the oxidation rate. Large concentrations of dienes, however, were reported in a study of gum formation (Jordan, Ward, *et al.*, 1934) to "catalyze" the oxidation of nitric oxide to nitrogen dioxide. On the basis of this observation, Leighton (1961) has suggested that in polluted atmospheres dienes may be partially responsible for the conversion of nitric oxide to nitrogen dioxide, particularly at night. To determine the importance of this atmospheric thermal oxidation of nitric oxide has been investigated.

In this investigation, the effects of nitric oxide, nitrogen dioxide, oxygen, and diene concentration on the rate of nitric oxide and diene oxidation have been studied. The dienes investigated were: 1,3-butadiene; 2-methyl-1,3-butadiene (isoprene); and 2,3-dimethyl-1,3-butadiene. Several experiments were also performed with 1,4- and 2,3-pentadiene and 1,5-hexadiene.

Experimental

Apparatus. Analyses were made with a 3-m. base path multiple reflection cell used in conjunction with a modified Perkin-Elmer Model 21 infrared spectrophotometer. A path length of 120 m. was routinely used in this study. A description of the irradiation system and the cell has been given previously (Tuesday, 1961).

Chemicals. Matheson prepurified nitrogen and extra dry oxygen were routinely used. The 1,3-butadiene and isoprene were Phillips research grade reagents. The 2,3-dimethyl-1,3-butadiene was a product of the K and K Laboratories. The 1,4- and 2,3-pentadiene and 1,5-hexadiene were API standard samples. These chemicals were used as received without further purification.

The nitric oxide was a Matheson product which was purified by passage through an Ascarite tube and subjected to repeated trap to trap distillations. Nitrogen dioxide was prepared, as needed, by the oxidation of nitric oxide as described previously (Tuesday, 1963).

Procedure. The reactions were carried out in air at 760 mm. Hg pressure at a temperature of 23 ° C. Details of the experimental procedure and the methods for determining the rate of formation of nitrogen dioxide have been given elsewhere (Glasson and Tuesday, 1963). The rate of diene oxidation was determined by measuring the increase of the carbonyl stretching absorption at 5.83 μ . Concentrations are given in parts per million (p.p.m.) (v./v.).

Product Identification. A special procedure was employed to obtain enough products for identification and to reduce spectral interferences from the diene and nitrogen dioxide. High reactant concentrations with nitric oxide in excess were used so that conversion of the diene to products would be complete. The large amount of nitrogen dioxide formed during the course of the reaction was removed by circulating the contents of the reaction chamber through a trap filled with mercury. Product spectra obtained before and after nitrogen dioxide removal indicated that no substantial change in the concentration of the other products occurred due to this treatment.

Results

A typical plot of the concentration of nitrogen dioxide as a function of time is given in Figure 1 for the system isoprenenitric oxide-air. The corresponding plot of the normal thermal oxidation reaction (no diene) is also included. In the presence of the diene, the nitric oxide oxidation rate increases with time indicating that the reaction is autocatalytic. Since the concentration of nitrogen dioxide increases to a maximum value and then decreases, the nitrogen dioxide formed apparently reacts with isoprene or a reaction product.

An organic product was formed during the course of the nitric oxide oxidation with an infrared absorption at 5.83 μ . A typical plot of the absorption at 5.83 μ vs. time is also given in Figure 1. The formation of this product parallels the formation of nitrogen dioxide and ceases when the maximum concentration of nitrogen dioxide is attained. Product identification studies have indicated that this absorption is due to



Figure 1. The thermal oxidation of nitric oxide in the presence of isoprene

the carbonyl stretching mode of formaldehyde, methyl vinyl ketone, and methacrolein (2-methyl-propenal). If the distribution of these products is independent of changes in concentration of the reactants, the 5.83- μ absorption can be used as a measure of diene oxidation. Hereafter, the initial rate of formation of the 5.83- μ absorption will be referred to as the carbonyl rate. Since there is some uncertainty as to the actual distribution of the indicated products, the carbonyl rates cannot be converted into concentration rates.

To understand the mechanism of the diene-promoted oxidation of nitric oxide, the kinetics of nitrogen dioxide formation and the accompanying diene oxidation have been determined for isoprene.

The Effect of Initial Nitrogen Dioxide Concentration. The effect of the initial concentration of nitrogen dioxide on the initial rate of nitrogen dioxide formation has been investigated. The initial rate of nitrogen dioxide formation, calculated from the data of the previous study (Glasson and Tuesday, 1963) for the normal thermal oxidation (no diene), has been subtracted from the observed initial rates to give the

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Figure 2. Effect of initial nitrogen dioxide concentration on the initial thermal oxidation rate

corrected initial rate of nitrogen dioxide formation. The results are given in Figure 2. The data indicate a first-order dependence of the corrected initial nitrogen dioxide formation rate on the initial concentration of nitrogen dioxide with a rate constant of 1.8×10^{-2} min.⁻¹

The plot of carbonyl rate as a function of the initial nitrogen dioxide concentration given in Figure 2 also indicates a first-order dependence.

The initial rate of nitrogen dioxide formation in the absence of diene is independent of nitrogen dioxide concentration (Glasson and Tuesday, 1963). Since a first-order dependence on nitrogen dioxide concentration is observed for the diene-promoted oxidation, succeeding runs have been performed with initial concentrations of nitrogen dioxide to increase the rate of the reaction of interest.

The Effect of Initial Isoprene Concentration. The effect of initial concentration of isoprene on the corrected initial nitrogen dioxide formation rate has been determined and the results are given in Figure 3. The linear dependence obtained corresponds to a first-order rate constant of 1.4×10^{-3} min.⁻¹



Figure 3. Effect of initial isoprene concentration on the initial thermal oxidation rate



Figure 4. Effect of initial nitric oxide concentration on the initial thermal oxidation rate

The carbonyl rate data are also presented in Figure 3 and indicate a first-order dependence on the initial concentration of isoprene.

The Effect of Initial Concentration of Nitric Oxide. The effect of the initial concentration of nitric oxide on the corrected initial rate of nitrogen dioxide formation has been studied and the results are given in Figure 4. The rate increases with nitric oxide concentration at very low concentrations but becomes zero-order at higher concentrations.

The corresponding carbonyl rates are also given in Figure 4 and indicate a first-order dependence on the initial concentration of nitric oxide.

The Effect of Oxygen Pressure. The effect of oxygen pressure on the corrected initial nitrogen dioxide formation rate has been studied and the results are given in Figure 5. The rate increases with increasing oxygen pressure over the entire range studied. The effect of oxygen pressure is more pronounced at oxygen pressures less than 15 mm. Hg than above this pressure.

The carbonyl rates are also given in Figure 5. The results show that the carbonyl rate is essentially independent of the oxygen pressure at pressures greater than a few mm. Hg.

Summary of Kinetic Observations. The corrected initial rate of nitrogen dioxide formation, in the presence of isoprene, is first-order in nitrogen dioxide, first-order in isoprene, and zero-order in nitric oxide (for nitric oxide concentrations greater than 1 p.p.m.). The results given in Figures 2 and 3 have been used to calculate the second-order rate constant for nitrogen dioxide formation in the presence of isoprene at nitric oxide concentrations greater than 1 p.p.m., in air. The value obtained is $(1.3 \pm 0.1_2) \times 10^{-3}$ p.p.m.⁻¹ min.⁻¹

The carbonyl rate is first-order in nitrogen dioxide, nitric oxide, and isoprene and zero-order in oxygen (at oxygen pressures greater than a few mm. Hg).

The Effect of Diene Structure on Reactivity. Several experiments were carried out with a series of dienes to determine their relative reactivities in promoting the thermal oxidation of nitric oxide. These data were obtained, in most cases, with no NO₂ initially present. Under this condition, the initial rate of nitrogen dioxide formation is merely the normal thermal oxidation rate. As a measure of the diene-promoted rate, therefore, the average rate to 25% oxidation of the initial concentration of nitric oxide was used. This rate is defined by Equation 1,

$$Rate_{Av.} = (NO)_0/4t_{1/4}$$
 (1)

where $t_{1/4}$ is the time necessary to convert 25% of the initial concentration of nitric oxide to nitrogen dioxide. The rate constants were calculated by assuming a first-order dependence of the average rate on the average concentrations of diene and nitrogen dioxide during $t_{1/4}$. The average concentration of nitrogen dioxide was taken to be 1/8 of the initial concentration of nitric oxide, while the average concentration of the diene was assumed to be equal to the initial diene concentration. In all cases, the average rate was corrected for the average rate of the normal thermal oxidation using the rate constant of Glasson and Tuesday (1963). The average nitric oxide concentration. The results are given in Table I.

The average values of k from Table I are 1.2, $(1.1 \pm 0.1_4)$, and $(0.44 \pm 0.02_9) \times 10^{-3}$ p.p.m.⁻¹ min.⁻¹ for 2,3-dimethyl-1,3-butadiene, isoprene, and 1,3-butadiene, respectively. The



Figure 5. Effect of oxygen pressure on the initial thermal oxidation rate

average value of k, for isoprene, determined from initial rates is $(1.3 \pm 0.1_2) \times 10^{-3}$ p.p.m.⁻¹ min.⁻¹ as reported above. The agreement between the rate constants obtained by these diverse methods is considered encouraging. In order to ensure a constant basis for comparison, the rate constants from Table I will be used.

The relative reactivities of the conjugated dienes given in Table I disagree with the order reported by Fulweiler (Jordan, Smoker, *et al.*, 1935). These data are also reported by Leighton (1961). The disagreement may be due to differences in the experimental techniques used in the two studies. Fulweiler's reactivities are given as the "percentage of the nitric oxide oxidized under a standard procedure." Because of the reaction of nitrogen dioxide with dienes, the relative reactivities derived from the above definition are dependent on the nature of the standard procedure employed.

The Reaction of Dienes with Nitrogen Dioxide. The kinetics of the reaction of nitrogen dioxide with dienes have been studied briefly. The data were obtained by two methods: measurement of the decrease in the nitrogen dioxide concentration with time in the system nitrogen dioxide-diene-air, and measurement of the decrease of the nitrogen dioxide concentration with time after the peak nitrogen dioxide concentration in nitric oxide oxidation runs. In both methods the reaction was assumed first-order in nitrogen dioxide and diene and the diene concentration was assumed equal to its initial value. The rate constants were obtained from the slopes of the plots of -ln (NO2) vs. time. The results obtained by the two methods were consistent if the decrease in the nitrogen dioxide concentration did not exceed 15% of the initial diene concentration over the period of measurement. The results are given in Table II.

Cadle (Cadle, Eastman, et al., 1952) has reported a rate constant for the reaction of 1,3-butadiene with nitrogen dioxide determined at reactant pressures of 0.4-12 mm. Hg in N₂-O₂ mixtures at total pressures of 100-700 mm. Hg. This data have also been reported by Leighton (1961). The reported rate constant is 76 liter mole⁻¹ sec.⁻¹ (1.9 \times 10⁻⁴ p.p.m.⁻¹ min.⁻¹ at a total pressure of 760 mm. Hg) at 25° C. Reference to Table II indicates that the value obtained in the present study is 2.3 times the literature value. The information in this reference indicates that the rate constant was determined by measuring the disappearance of either nitrogen dioxide or 1,3-butadiene. In this regard, a limited number of experiments indicated that in the reaction of isoprene with nitrogen dioxide, 1.5-2.0 molecules of nitrogen dioxide reacted for every molecule of isoprene reacted. If similar stoichiometry is followed in the reaction of 1.3-butadiene and nitrogen dioxide and Cadle used hydrocarbon disappearance to determine the rate constant, then his result would be in reasonable agreement with the value given in Table II.

Product Identification. An experiment was performed with 15 p.p.m. isoprene and 20 p.p.m. nitric oxide, in air, with successive additions of nit.ic oxide such that a total of 50 p.p.m. nitric oxide was added and the isoprene initially present was completely reacted. The nitrogen dioxide was then selectively removed from the reaction chamber (see *Experimental*) and a product spectrum was taken.

The major products and the infrared absorptions used for identification were: methyl vinyl ketone (5.8, 8.0, 8.5, and 10.5 μ); methacrolein (5.8, 9.7, and 10.7 μ); formaldehyde (3.6 and 5.6 μ); and organic nitrate (7.8 and 11.7 μ). Minor products were: carbon monoxide (4.6 and 4.7 μ); carbon dioxide (4.3 μ); formic acid (9.1 μ); and possibly nitro-compounds (7.3 μ).

Table I. The Kinetics of the Atmospheric Thermal Oxidation of Nitric Oxide in the Presence of Various Dienes

(Diene) ₀	(NO) ₀		<i>t</i> _{1/4}	$k \times 10^{3}$ (p.p.m. ⁻¹
(p.p.m.)	(p.p.m.)		(min.)	$\min(-1)$
		Isoprene		
4.94	2.01		218	1.1
5.00	4.00		147	1.2
5.00	5.99		116	1.1
5.00	10.0		81	1.0
15.1	1.99		94	1.2
15.0	4.00		79	1.2
15.0	6.01		67	1.2
25.0	2.00		62	1.1
25.0	4.00		55	1.1
25.0	5.98		49	1.2
		1,3-Butadiene		
5.00	1.99		311	0.50
10.0	2.01		248	0.42
9.94	3.99		169	0.38
10.0	5.99		126	0.41
14.9	2.00		191	0.44
15.1	2.00 (0.	51 p.p.m. NO ₂)	78	0.48
15.1	2.00(1.	00 p.p.m. NO ₂)	56	0.42
15.1	3.54 (0.	52 p.p.m. NO ₂)	94	0.44
	2,3-1	Dimethyl-1,3-butad	liene	
5.00	2.00		200	1.2
14.9	1.99		90	1.2
		1,4-Pentadiene		
5.00	2.00		500	0.04
		2,3-Pentadiene		
5.00	2.00		500	0.04
		1,5-Hexadiene		
5.00	2.00		500	0.04

Table II. Kinetics of The Reaction of NO₂ with Various Dienes

Diene	No. of determinations	$k \times 10^{4}$ (p.p.m. ⁻¹ min. ⁻¹)
2,3-Dimethyl- 1,3-butadiene	1	3.7
Isoprene	8	$(1.7 \pm 0.1_0)$
1,3-Butadiene	3	$(0.42 \pm 0.01_3)$
1,4-Pentadiene	1	0.03

Unidentified peaks in the product spectrum were noted at: 6.1 and 6.2 μ (may be due, in part, to residual nitrogen dioxide); 12.6 μ ; and 13.0 μ .

Product spectra from the system 1,3-butadiene–nitric oxide–air indicated the presence of acrolein (5.8 μ) and form-aldehyde.

A product analysis of the system isoprene–nitrogen dioxide– air was attempted with 10 p.p.m. isoprene and 10 p.p.m. nitrogen dioxide. The mixture was allowed to react for approximately three days, at which time virtually all the nitrogen dioxide and about 65% of the isoprene had disappeared. The following products were indicated: formaldehyde, methyl vinyl ketone and (or) methacrolein, formic acid, and organic nitrate. Un-



Figure 6. Oxidation of nitric oxide in the presence of TME

identified peaks were noted at 4.5 μ , 6.1 μ , 12.6 μ , and 13.0 μ . The products observed, however, accounted for no more than 20% of the reacted isoprene.

Altshuller (Altshuller and Cohen, 1961) has studied the condensed products of the reaction of isoprene with nitric oxide and nitrogen dioxide. He finds no substantial difference in the products from both systems. Since the product spectra were obtained in the liquid phase, the spectra are not directly comparable to those obtained in the present study. In general, however, the occurrence of carbonyl, nitrate, and nitro bands is common to both investigations.

Attempted Identification of Ozone as a Reactant Product. Although ozone was not found in the product identification study, its formation by Reaction 2 (Hanst and Calvert, 1959) was considered as a possibility, albeit unlikely, because of its endothermicity. Subsequent rapid reaction of ozone with

$$RO_2 \cdot + O_2 \rightarrow RO \cdot + O_3 \tag{2}$$

the diene would lead to the existence of a small steady-state concentration of ozone, which would be difficult to detect. The reaction of ozone with tetramethylethylene (TME) to produce acetone has been used (Hanst and Calvert, 1959) as a means for the detection of low ozone concentrations. This method was applied to our system.

The reaction of 15 p.p.m. isoprene, 2.0 p.p.m. nitric oxide, and 1.0 p.p.m. nitrogen dioxide was carried out in air at 760 mm. Hg pressure, containing 10 p.p.m. tetramethylethylene. The concentration vs. time plot is given in Figure 6. Acetone was formed after an induction period of 25 min. and its concentration leveled off at 0.30 p.p.m. at 70 min., the time required to oxidize all of the nitric oxide. Acetone was not observed when the latter experiment was performed in the absence of isoprene. Thus, the formation of acetone occurred only in the presence of nitric oxide. But ozone cannot coexist with nitric oxide at a significant concentration because of Reaction 3 (Johnston and Crosby, 1954).

Table III. The Photooxidation of NO in the Presence of Dienes^a

Diene	$t_{1/4^b}$ (min.)
1,3-Butadiene	20
2,3-Pentadiene	20
Isoprene	22
1,4-Pentadiene	30
2,3-Dimethyl-1,3-butadiene	32
1,5-Hexadiene	54

^a The reactions were carried out with 5 p.m. diene and 2 p.p.m. NO and a light intensity of 0.34 min.⁻¹(Tuesday, 1961). ^b The time necessary to convert 25% of the initial amount of NO to NO₂.

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{3}$$

Therefore, the oxidation of tetramethylethylene was not due to ozone, and hence Reaction 2 is not considered as being operative in our system.

It was noted that the initial rate of nitric oxide oxidation was significantly increased by the addition of tetramethylethylene to the diene–NO– NO_2 -air system (no effect was noted in the absence of isoprene). This effect can probably be attributed to an increase in the free radical concentration in the system due to the oxidation of tetramethylethylene.

Photooxidation of Nitric Oxide in the Presence of Dienes. The photooxidation of nitric oxide in the presence of dienes has been briefly studied to compare the relative importance of this reaction with the diene-promoted thermal oxidation. The results of this study are given in Table III.

The data of Table III can be compared with the appropriate data for the diene-promoted thermal oxidation of Table I. These results indicate the rates of photooxidation are 7 to 25 times faster than the corresponding rates for the thermal oxidation and the effect of diene structure on reactivity is markedly different for the two oxidation systems.

Discussion

Although the individual steps of the mechanism of the diene-promoted thermal oxidation of nitric oxide are not clear, certain conclusions seem warranted.

The first-order dependence on nitrogen dioxide and isoprene suggests that the initial step is Reaction 4, which is analogous to the reaction suggested

$$CH_2 = CH - C(CH_3) = CH_2 + NO_2 \rightarrow$$

$$CH_2 = CH - C(CH_3) - CH_2NO_2 \quad (4)$$

(Brown, 1957) as the initial step in the reaction of nitrogen dioxide with olefins. The relative rate constants for the addition of nitrogen dioxide to dienes (Table II) are consistent with the effect of structure on rate observed (Rajbenbach and Szwarc, 1959) for the addition of methyl radicals to dienes. Thus, the reactivity of conjugated dienes relative to nonconjugated dienes, in our work, is apparently determined by the rate of nitrogen dioxide addition.

Among the conjugated dienes, however, the rate of Reaction 4 does not entirely explain overall reactivity. Although the relative rates of Reaction 4 for 2,3-dimethyl-1,3-butadiene, isoprene, and 1,3-butadiene are 9:4:1, the corresponding relative rates for nitric oxide oxidation are 3:3:1.

From the rate constants for Reaction 4 and the corresponding rate constants for nitric oxide oxidation, the number of molecules of nitric oxide oxidized per initiation can be calculated. The values obtained for 2,3-dimethyl-1,3-butadiene, isoprene, and 1,3-butadiene are 4.2, 7.5, and 11, respectively, which suggest that the diene-promoted oxidation of nitric oxide is a chain reaction.

The diene-promoted oxidation of nitric oxide is a chain reaction initiated by the addition of nitrogen dioxide to the diene. The data are not sufficient to permit a detailed discussion of the mechanism. However, sufficient data are available to assess the significance of the diene-promoted thermal oxidation of nitric oxide in polluted atmospheres.

Importance in Polluted Atmospheres. Since the rates of the diene-promoted photooxidation of nitric oxide (Table III) are 7 to 25 times faster than the corresponding rates for the diene-promoted thermal oxidation (Table I), the dienepromoted thermal oxidation is relatively unimportant in polluted atmospheres during daylight hours.

To estimate the importance of this reaction during the night, the results of this study have been used to calculate the diene-promoted rate under typical conditions (Neligan, 1962) found in polluted atmospheres. The data of this reference indicate that 1,3-butadiene is the only conjugated diene observed in the Los Angeles atmosphere and that this diene, nitric oxide, and nitrogen dioxide occur at average concentrations of 0.004, 0.11, and 0.18 p.p.m., respectively. The rate constant used for the 1,3-butadiene-promoted oxidation of nitric oxide is taken from Table I. This rate constant applies to a condition of zero-order dependence of the rate on nitric oxide concentration. Although the indicated nitric oxide concentration would fall in the first-order range, the zero-order rate constant was used to yield the maximum possible rate for these concentrations. The normal and diene-promoted rates of nitric oxide oxidation under the above conditions were (4 and 0.3) \times 10⁻⁶ p.p.m. min.⁻¹, respectively. Thus, the diene-promoted oxidation is relatively unimportant in the atmospheric conversion of nitric oxide to nitrogen dioxide during the night as well as during the day.

Acknowledgment

The authors wish to acknowledge the valuable assistance of Jerome Zemla in obtaining the data and preparing the manuscript.

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Received for review August 25, 1969. Accepted April 20, 1970. Presented in part at the 147th National Meeting, ACS, Philadelphia, Pa., April 10, 1964. This paper is a contribution from the Fuels and Lubricants Dept., General Motors Research Laboratories, Warren, Mich.

Potassium Formate Process for Removing SO₂ from Stack Gas

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A new process has been developed for removing sulfur dioxide from stack gas, and encompasses absorbent regeneration and sulfur recovery. In stack gas scrubbing, sulfur dioxide is adsorbed by a concentrated potassium formate solution at 200° F., producing thiosulfate. The spent scrubber solution is transferred to a regeneration unit where the thiosulfate is reacted with additional formate at 540° F. to produce hydrosulfide. The potassium hydrosulfide is stripped with carbon dioxide and steam to release hydrogen sulfide from which elemental sulfur is recovered in a Claus reactor. After stripping, the remaining solution of potassium carbonate and bicarbonate is regenerated to potassium formate by reduction with carbon monoxide at a pressure (including steam) of 1000 p.s.i.a. at 540° F. The formate solution is then recycled to the scrubber. Advantages include an all-liquid recycle system, no gas reheat, and mild conditions for regeneration and sulfur recovery.

n recent years, as numerous methods were being developed for SO₂ removal from stack gas to reduce air pollution, the physical characteristics preferred for commercially practicable processes became increasingly evident. First, a liquid absorbent system is desired to obviate problems attendant with solids handling, such as mechanical or attrition losses and the more involved operations in solids transport and control. Second, the liquid absorbent should be operable at temperatures sufficiently above ambient to provide for plume rise from the stack after gas-scrubbing, without requiring reheat. With these requisites in mind, it was decided to attempt to develop an SO₂ absorption system based on an alkaline molten salt or a molten mixture of alkaline salts as the reagent. Potassium formate was selected for the prime molten salt role because of its relatively low melting point of 333° F. and thermal stability at the melting point.

The early exploratory experiments on SO₂ absorption were conducted with minor quantities of K2CO3 dissolved in molten KOOCH at 350° F. to fortify the alkaline nature of the

KOOCH. These experiments showed that SO₂ was very efficiently absorbed by such a mixture and also incidentally showed that the absorption proceeded well beyond the capacity of any carbonate-SO₂ reaction. Also, the absorption capacity for SO₂ greatly exceeded the additional amount that might be anticipated from KOOCH acting only as an alkaline reagent, that is, acidic SO2 reacting with alkaline KOOCH to produce bisulfite and formic acid until the acid neutralized the alkalinity of KOOCH. Clearly, the formate had to be involved in the SO₂ absorption and by some reaction other than acid-base combination. Experiments with pure KOOCH next proved that molten KOOCH by itself was indeed a very efficient reagent for absorbing SO2; the carbonate was unnecessary for absorption. Studies were then directed to the development of molten KOOCH itself as an SO₂ absorption reagent, including the possibility of regenerating the reagent.

Analyses identified the product from the SO₂-plus-formate absorption reaction as almost all potassium thiosulfate and not potassium bisulfite. Although it is possible that the initial absorption occurs by way of an acid–base reaction to form transiently the bisulfite, it in turn must be very rapidly converted to thiosulfate by the formate acting as a reducing reagent.

Since formate was found to be a sufficiently powerful reducing agent to reduce SO_2 (or KHSO₃) to thiosulfate form, it was reasoned that formate might also reduce thiosulfate even further at other conditions to yield sulfides in the form of K₂S or H₂S. Laboratory experiments established that such a reaction between formate and thiosulfate did indeed proceed at more elevated temperatures. In fact, at 540° F. and ambient pressure, this highly exothermic reaction was found to generate H₂S and CO₂ with almost explosive violence. The thiosulfate was reduced completely to K₂S and H₂S. The potassium from the consumed formate appeared as potassium carbonate.

An overall route for SO₂ scrubbing and formate regeneration became apparent. SO₂ scrubbing with potassium formate could be extended to a point where just enough formate is left to reduce the scrub-product thiosulfate. Then, this product mixture could be reacted at a separate location at 540° F. to produce mostly K₂S and K₂CO₃ with some H₂S. The K₂S can, by known reactions, be stripped with CO₂ and water to complete the release of all sulfur in the form of H₂S from which elemental sulfur is easily recovered via the well-known Claus process. Other than elemental sulfur, the net product following the reduction and stripping reactions is K₂CO₃ and (or) KHCO₃. The carbonates are susceptible to reduction to formate by such reducing gases as carbon monoxide or hydrogen-carbon monoxide mixtures. Therefore, broad developmental studies were undertaken to find a method to control the formate-thiosulfate reduction reaction, to prove the CO₂ stripping of K₂S or KHS for collection of all sulfur as H₂S, and to find the optimum method of regenerating potassium formate from the carbonate.

In the course of these studies, it was recognized that use of concentrated aqueous solutions for every stage in the regeneration scheme, instead of a molten formate solution or suspension of intermediate products, possessed certain potential advantages. With aqueous solutions, reduction was manageable, stripping of KHS was complete and final KOOCH regeneration with CO proceeded at a reasonable rate, all at relatively mild conditions. It only remained to show that concentrated aqueous potassium formate would function as an SO₂ scrubber as well as the molten formate. Tests proved that 85% aqueous formate at 200° F. was an even better SO₂ scrubber, having two distinct advantages over molten formate. The scrub

product had a greater percentage of $K_2S_2O_3$ with a smaller quantity of the minor side products, and traces of H_2S were not produced during scrubbing as was produced when molten formate was used at 350° F. Even slight H_2S release into stack gas is, of course, undesirable. The lower stack gas scrubbing temperature of 200° F. is still deemed as sufficient for plume rise, especially for the cleaned stack gas.

Thus, all stages toward sulfur recovery and formate regeneration, as well as the scrubbing stage, were demonstrated successfully for the system based on concentrated aqueous potassium formate and with aqueous solutions throughout the regeneration scheme. This process has one distinct advantage which distinguishes it both from the molten formate process as well as other SO₂ scrubbing processes using aqueous reagents. Conditions are such that no troublesome precipitation of intermediate products occurs in any stage. The aqueous solutions can be handled throughout every step of the recycled scrubbing and regeneration process as homogeneous solutions.

The resultant process is described in the following section. In the interest of brevity, single operating results near the optimum for each stage are presented, as selected from a variety of intermediate routes and ranges of conditions that were examined experimentally. Supporting experimental data, as relevant to each stage of operation, are presented in the results section.

Since it is specifically the formate ion which reduces SO₂ to remove it from stack gas, compounds as ammonium formate and the other alkali metal formates have been found to react similarly and may also be used for SO₂ scrubbing. However, ammonium formate is thermally unstable, and the other alkali metal formates do not have the very high solubility in water as required to provide for operations at temperatures as high as 200° F. without serious water evaporation losses. The potassium formate, by virtue of its high solubility and chemical stability, is the preferred aqueous reagent for SO₂ scrubbing.

General Description of Process

The sequence of essential chemical reactions that complete the recycle of KOOCH in the SO₂ removal process, as based on concentrated aqueous solutions, is given below:

$$Scrubbing reaction 2KOOCH + 2SO_2 \rightarrow K_2S_2O_3 + 2CO_2 + H_2O$$
(1)

Regeneration reactions

 $4KOOCH + K_2S_2O_3 \rightarrow$

 $2K_2CO_3 + 2KHS + 2CO_2 + H_2O$ (2)

$$2KHS + CO_2 + H_2O \rightarrow K_2CO_3 + 2H_2S$$
(3)

$$K_2CO_3 + 2CO + H_2O \rightarrow 2KOOCH + CO_2$$
(4)

The only difference for the molten salt system would be that K_2S rather than KHS would appear in Equations 2 and 3. KHS appears in aqueous solution because of its high ionization constant. The net reaction for the overall process, *i.e.*, Equations 1–4, which eliminates the recycled formate–carbonate, is:

$$SO_2 + 3CO + H_2O \rightarrow H_2S + 3CO_2$$
 (5)

Many alternatives and combinations can be written for Equations 2–4 and indeed, other reactions do coexist. For instance, bicarbonate as well as carbonate coexist in equilibrium with available CO_2 , particularly in stripping Reaction 3. H₂S is also released in the stripper by Reaction 6 below:

 $CO_2 + CH_4 = 2CO + 2H_2$ (8)

$$CO_2 + H_2 = CO + H_2O$$
 (9)

Any excessive buildup of incidental impurities (gases other than CO₂, CO, H₂) in the gas loop that includes the synthesizer and reformer is alleviated *via* the purge line from which the CO₂ and fuel values are recovered as shown in Figure 1. Operations of the "hot K_2CO_3 " plant and the methane reformer are based on conventional, well-developed technology and thus require no further discussion.

Even after recovery of CO_2 from the Claus plant and formate synthesis streams, the net process requires supplementary CO_2 when the methane reformer is included in the scheme. This is seen by combining Equations 7–9 to show the gas requirement for the whole regeneration including the ancillary methane reformer. The resultant equation is:

$$K_2S_2O_3 + \frac{3}{2}CH_4 + \frac{1}{2}CO_2 \rightarrow 2KOOCH + 2H_2S$$
 (10)

This proportion of CO_2 , in excess of that which derives from the CH₄, is supplied by scrubbing CO_2 from flue gas in the "hot K₂CO₃" plant as shown in Figure 1.

If the CO gas for formate regeneration were supplied by gasification of a hydrogen-deficient fuel such as coal, then an external supply of CO_2 would not be required. As a matter of fact, a surplus of CO_2 would then be generated.

Tests have shown that nitrogen oxides do not react with the formate solution. Their presence in stack gas has no effect on the process.

In actual plant practice, it is expected that loss of KOOCH, as such, would be negligible because KOOCH has no significant vapor pressure. Entrainment losses can be maintained at an acceptably low value by the use of conventional demister equipment. There is the recognized possible minor loss of potassium value with the K_2SO_4 incorporated with residual fly ash that may be filtered from the scrub solution. If the filter cake is washed only with the amount of water required as make-up for the overall process, the potassium lost as K_2SO_4 and other residual unleached salts would add a cost of 2ϕ to 3ϕ per ton of coal (3.5% sulfur). After removal of the sulfate as CaSO₄, the wash solution of potassium salts would be returned to the process for regeneration.

Experimental Methods

The SO₂ scrubbing step and two of the three individual regeneration stages, namely reduction and formate syntheses, have been conducted in bench-scale continuous units. The remaining CO_r -H₂S stripping stage has been demonstrated only in a batch unit. However, sufficient equilibrium and solubility data were obtained to supplement the literature data available for more dilute solutions to predict the performance of continuous multiple sieve-tray strippers.

All equipment was constructed of 316 stainless steel since corrosion studies showed it to be suitably resistant to solutions of formate and the sulfur compounds at all conditions used here.

Scrubbing. The scrubbing chamber was a 4-in. diameter cylinder, 39-in. high, containing a jiggling glass marble bed near the bottom with 36 in. of free space above for foam disengagement. A double layer of 0.5-in. glass marbles on the screen was used. Recycled liquid absorbent was poured in at the top of the chamber, falling as a stream to the marble bed. High velocity recycle of absorbent was necessary to maintain a flooded condition over the marbles. The pool depth over the

Table I. Conditions and Results of 16-Hr. Run on Continuous Scrubbing of SO₂ from Stack Gas^a

Simulated stack gas	0.386% SO ₂ , 13.1% H ₂ O,
composition	10.4% CO ₂ , 3.5%O ₂ ,
	72.6% N ₂
Absorbent	Aqueous KOOCH (85.0%)
Temperature	200° F.
Liquid feed rate, g./min.	20.2
Liquid recycle rate, liter/min.	3.00
Scrubbed gas rate, s.c.f./hr.	636
Scrubbed gas velocity, ft./	
sec.	2.72
Pressure drop, inch-H ₂ O	2.90
Run duration, hr.	16.0
Total SO ₂ fed, g.	2816
Av. absorption/pass	88.35%
Total scrub product wt., g.	19,409
Total H ₂ S made, g.	0.00
Solute content of product	83.5%

Scrub product analyses (% of the dry salt)

S content via SO ₂ absorbed	8.66
S content via Σ S-forms	8.22
S as $K_2S_2O_3$	7.43
S as K ₂ SO ₃	0.52
S as KHS	0.00
S as K ₂ SO ₄	0.27
K_2CO_3	1.62
Load of all S-compounds	
in salt product	26.09
Residual KOOCH	72.29

 a Scrubber = 4-in, i.d. shallow jiggle-bed of 0.5-in, beads; weir height above bead bed = 1.0 in.; liquid residence time in scrubber and recycle system = 60 min.

marbles was 1 in. as set by an overflow pipe position. Fresh formate solution was fed continuously to the recycle loop at a feed rate selected to give the desired proportion of SO_2 absorption products in the withdrawn spent-formate product. Continuous withdrawal was automatically matched to the feed rate by a weir vessel in the recycle loop.

Simulated stack gas was fed to the scrubber in countercurrent fashion at a velocity high enough to prevent drainage of the pool down through the shallow marble bed. This gas velocity also causes the marbles to jiggle about and rotate. The attendant attrition would prevent any accumulation of absorption products in the scrubber which might otherwise choke it should there be any tendency toward precipitation. As it developed, precipitation was not a problem at desired levels of formate–SO₂ absorption products. Still, this form of scrubber was kept for the experimental work because of its demonstrated efficiency with a low gas pressure drop across the bed in our system. This type of scrubber resembles a commercial one marketed by National Dust Collector Corp., however, other types are also usable for scrubbing stack gas with formate solutions.

Supply and control equipment was available for providing the simulated stack gas feed which was made-up out of the individual components to have the composition shown in Table I. All the other conditions pertinent to operations of the scrubber are also listed in Table I.

Analyses of the sulfur compounds formed by scrubbing were made by conventional "wet-chemistry" techniques. To determine scrubbing efficiency, cleaned stack gas was analyzed for low levels of SO₂ by passing a metered off-gas side stream slowly through hydrogen peroxide in scrub bottles. The resultant sulfuric acid was analyzed colorimetrically to a sensitivity of 1 p.p.m., which also translates to a 1 p.p.m. accuracy for SO₂ in cleaned gas.

Reduction

Reduction. The continuous reduction unit for bench-scale studies was built around a 1-liter, stainless steel, stirred reactor rated for up to 3000 p.s.i.g. operations at up to 1000° F. Spent formate, from a feed reservoir tank kept at 220° F. to maintain solubility of sulfur products, was pumped continuously into the reactor and overflowed from it via a standpipe into an equally pressurized receiver tank. Product could be drained from the receiver at will. Though a gas feed system was available, it wasn't needed. Self-generated gas pressure was sufficient for reaction control. Make gas from the reduction reactor was released through a back-pressure control valve, the quantity monitored and sampled for analysis by gas chromatography. The flow, pressure, and temperature conditions that were found to be near the optimum are listed in Table II. Operationally, the reactor system was prepressurized with 500 p.s.i.g. of nitrogen at the start of a run. As the spent-formate was pumped into the reactor held at 540° F., the gases made by the reduction reaction supplanted the initial nitrogen as the gases were bled-off while maintaining 500 p.s.i.g. of pressure. No gas supply was needed during continuous runs. Runs at varied conditions were usually operated for 4-hr. periods after lineout.

Without a back pressure of about 500 p.s.i.g., this highly exothermic reaction proceeds too violently to control in continuous operations without specially designed injection and reactor equipment.

The danger of heating mixtures of a thiosulfate with any formate must be emphasized. Glass or open vessels must never be used. The reaction becomes explosive as 500° F. is approached. Only high-strength, high-pressure tolerant steel reactors should be used.

CO₂-HS₂ Stripping. Equipment used here only to confirm expected ease of H₂S stripping was quite simple, consisting of a heated, 1-liter, cylindrical, stirred vessel containing a batch charge of 500 g. of reduced solution. Tests were conducted at atmospheric pressure. CO₂ was bubbled into the solution at various controlled rates, with only mild dispersion of gas through the solution. Refluxing returned evaporated water. The off-gas stream was sampled periodically and analyzed for H₂S and CO₂ by gas chromatography.

KOOCH Regeneration. Two magnetically stirred reactors, having 3000-p.s.i.g. ratings, were used alternatively in the continuous regeneration unit. The smaller, 1-liter reactor (9 in. \times 3-in. i.d.) was used to obtain kinetic data on Reaction 4. The effects of extent of conversion as well as the effects of temperature, pressure, and stirring speed on reaction rate were studied. The larger reactor (4 ft. \times 2.63-in. i.d.) was used to provide sufficient residence time to demonstrate nearly complete regeneration at conditions defined as favorable by the kinetic study in the small reactor. This long reactor had six stirrers on an axial shaft. In both reactors, gas and liquid feed were pumped into the bottom of the reactor, flowed upward concurrently, and were withdrawn by an overflow pipe into pressurized receivers. The gas, separated in the receivers, was bled-off via a back-pressure control valve, sampled, and analyzed. Receiver temperature was kept at 220° F. (some CO₂

Table II. Continuous Reduction of Aqueous Spent Formate to Provide Sulfur in Sulfide Form (Equation 2)

Run conditions	For simulated spent- formate	For actual spent- formate
Temperature, ° F.	540	540
Pressure, p.s.i.g.	500	500
Stirrer speed, r.p.m.	825	825
Solution feed rate, g./hr.	4140	4370
Reactor inventory, g.	1070	1120
Reaction residence time, min.	15	15
Feed analysis, wt. %		
$K_2S_2O_3$	24.0	20.23
KOOCH	56.0	52.13
H_2O	20.0	22.06
S as $K_2S_2O_3$	8.09	6.82
S as K_2SO_3	0	0.19
S as KHS	0	0.32 ^a
S as K_2SO_4	0	0.73
Product solution analysis, wt. %		
$K_2S_2O_3$	1.42	0.50
K_2CO_3	42.01	42.43
KHCO3	10.68	5.04
S as $K_2S_2O_3$	0.48	0.17
S as K_2SO_3	0.22	0.09
S as KHS	5.77	5.80
S as K ₂ SO ₄	0.19	0
Product gas analysis, vol. $\%$		
H_2S	34.40	37.51
CO_2	64.50	61.77
CO	0.10	0.30
\mathbf{H}_2	1.00	0.42
^a Generated by aging. None in fresh sp	ent-formate.	

reabsorption by residual K_2CO_3 , if any) and the formate product solution could be drained at will.

Experimental Results

Scrubbing. All the conditions, results, and scrub-product analyses for a typical continuous run on SO_2 removal from stack gas are presented in Table I. The SO_2 contents of the stack gas before and after scrubbing, as sampled for 2-hr. intervals throughout the run, appear in Table III. Also shown are the SO_2 absorption or removal efficiencies for the intervals for the single-stage absorption in the shallow jiggle-bed contactor. An average SO_2 removal of 88.4% was achieved throughout this 16-hr. run made with 85% aqueous formate solution.

The ratio of gas: absorbent feed rates for the scrubbing was such that a load of sulfur compounds of 26% of the scrubproduct salts was obtained, which is near the desired proportion for the follow-up stage of reduction to sulfides as discussed in the next section.

As seen in Table I, the major portion (90.4%) of the absorbed sulfur is in K₂S₂O₃, which is a consistent finding for all runs made with formate. The balance of product sulfur is in

Table III. SO₂ Removal Throughout 16-Hr. Scrub Run^a

	Vol. %	SO ₂ in gas	
Scrub time (hr.)	Into scrubber (%)	Out of scrubber (%)	SO ₂ absorption (%)
2	0.392	0.0511	87
4	0.380	0.0399	90
6	0.404	0.0641	84
8	0.387	0.0464	88
10	0.387	0.0468	88
12	0.386	0.0456	88
14	0.367	0.0263	93
16	0.385	0.0450	89
			av. 88.4
a Absorber	nt = aqueous KOO	DCH (85%) at 200° F	

 $\mathrm{K}_2\mathrm{SO}_3$ and a trace of $\mathrm{K}_2\mathrm{SO}_4.$ Careful analyses showed no KHS.

Though the run was conducted with a load of sulfur compounds of 21.8% of the solution, no separation of insoluble compounds occurred and no operability problems were encountered. Liquid feed and recycle pumps operated smoothly at controlled rates. After the run, the scrub chamber was opened for examination of the bead bed. The beads were perfectly clean, with no precipitate collection at all in the bed.

Reduction. Numerous continuous reduction runs were conducted, first with simulated spent-formate solutions to determine the most favorable conditions, followed by demonstration runs with actual spent formate as obtained from continuous SO₂ scrubbing with aqueous KOOCH. The results proved that $K_8S_2O_3$, the major sulfur scrubbing product, was rapidly reduced by KOOCH in aqueous solution at 540° F., in accordance with Equation 2, with some secondary involvement of Equation 3. After developing the more favorable operating conditions, it was demonstrated that 96% reduction conversion of SO₂-scrub products to K_8S and H_2S was consistently achieved in continuous runs with a very low residence time of only 15 min., for both simulated and actual scrub products.

It was discovered that it was not necessary to apply CO:H₂ pressure to the continuous reactor for suppression of extraneous formate decomposition. Formate thermal decomposition was considered a possibility because early laboratory experiments showed that decomposition to K₂CO₃, H₂, and CO initiated at about 540° F., and accelerated to vigorous decomposition at 635° F. However, the reaction between K2S2O3 and KOOCH was found to be so much more rapid than thermal decomposition of KOOCH at 545° F. that reduction was essentially completed before significant decomposition could occur. By use of spent-formates that have just slightly more residual formate than the stoichiometric requirement for reducing K₂S₂O₃, reduction was still nearly complete, proving that there could not be much wasteful decomposition of formate. Measurements of KOOCH decomposition by measuring the hydrogen plus carbon monoxide produced as decomposition products in the off-gas stream also showed such loss to be very small. Thus, it was proven that aqueous spent-formate, produced from SO₂ scrubbing in such a fashion as to have just slightly more KOOCH than required for the reduction stage, can be utilized directly in the reduction stage without any alteration of its composition to achieve complete reduction to sulfides with very little extraneous loss of formate for remarkably low residence times.

Results and conditions of a typical continuous reduction

run with simulated spent formate and another with actual spent formate appear in Table II. The feed materials had only about 10% more formate than stoichiometrically required for reduction. The liquid product analyses showed that 94-98% of the thiosulfate was reduced, leaving most of the sulfur in the reduced form of hydrosulfide with only very small quantities of the other three forms of sulfur salts. The H₂S in the off-gas usually represents 5% to 10% of all the sulfur. Thus, the data prove that the formate reacts almost singularly with thiosulfate to yield KHS as shown by Equation 2 and a minor amount of sulfide is released *in situ* as H₂S *via* the reaction shown as Equation 3.

It is interesting to note that possible solvent water evaporation, if any, did not create any flow problems through the reactor, even though the temperature was 540° F. If serious evaporation were to occur in the reactor, in addition to consumption of the more soluble formate and production of less soluble salts, this stage would not be operable in a continuous fashion. No flow vehicle would be left. The reactor and offlines would plug with solids. Actually, operativeness was proven by the completion of over 20 runs, so that evaporation at 540° F. was not a problem. The relatively low equilibrium vapor pressure over the concentrated solutions used here apparently prevented excessive evaporation.

As seen in Table II, bicarbonate, as well as carbonate, appears in the liquid product analyses whereas it is unlikely that any actually exists in the reactor at 540° F. The reason is that both the gas and liquid products were withdrawn through the receiver which was at a lower temperature (370° F.). The reduced temperature permits reabsorption of the presurized CO₂ to produce the bicarbonate found in the product. Thus, the gas analyses also are not exactly representative of the off-gas directly from the reactor, but reflect the effect of CO₂ absorption in the cooled liquid product.

Stripping. Not much experimental effort on this regeneration stage was needed because of already available information. Only cursory batch tests of H₂S recovery from reduced products by CO2 stripping were performed to confirm the expected feasibility and the CO₂ requirement. Such tests simply verified that there are no unusual interfering agents in the materials to be stripped here. In addition to the batch stripping tests, some experimental data were obtained on the equilibrium for stripping Reaction 3 for the particular case of highly concentrated solutions. This was done to confirm the validity of extrapolating the literature data on more dilute solutions to the concentrated solutions used here. The results proved the extrapolation to be sound. Thus, more extensive, continuous operations of stripping were not necessary since the design of a commercial stripper could be based with confidence on the literature data on pertinent salt solubilities (Bocard and Mayland, 1962), equilibrium constants (Dryden, 1947; Mai and Babb, 1955; Astarita and Gioia, 1964), and practical reaction rates (Lemieux and Scott, 1969; West, Gilbert, et al., 1952; Cooper, Fernstrom, et al., 1944) for the mass-transfer controlled reaction involved here. The rate of Reaction 3 is likely controlled by CO₂ transfer into and through the solution.

As shown by the sample data in Table IV, stripping H_2S from the aqueous solutions of spent-reduced formate by passing CO₂ through the solutions has been demonstrated as feasible at 200° F. In very simple, stirred reactor equipment, complete H_2S recovery from the KHS in solution was achieved here in 2 hr.

The residence time required in the batch laboratory system used here has no direct bearing on the time required for commercial continuous stripping. This is because the ultimate limiting factor is the equilibrium in the stripping reaction which dictates the H_3S release in terms of the *quantity* of CO_2 supplied. Secondly, the reaction rate or approach to equilibrium depends primarily on the vigor of liquid-gas contacting supplied. Much superior contacting equipment would be used commercially as compared with the simple paddle stirrer used in this work, so more rapid stripping is expected. Commercially sized stripping equipment, such as multistage sieve trays, should provide about 3 to 5 times faster stripping so that a residence time as small as a half hour is projected.

As seen in Table IV, the solution for stripping is more dilute than the 15–20% water content solutions used in the scrubbing and reduction stages. This is due to the reduced temperature of 200° F. selected for stripping here which requires dilution to maintain complete solubility of the relatively low soluble carbonates. If stripping is done at higher temperatures and under pressure to prevent evaporation, the same higher concentrations could be utilized in the stripping stage as in previous stages. However, it should be noted that the lower temperature has a more favorable equilibrium, *i.e.*, the equilibrium H₂S:CO₂ ratio is increased as temperature decreases. This improved equilibrium favors more rapid stripping and reduces the CO₂ requirement.

KOOCH Regeneration. There are three potential reduction routes for regenerating KOOCH from K_2CO_3 , for recycle use in SO₂ scrubbing. One is the reverse of thermal decomposition, as

$$K_2CO_3 + CO + H_2 \rightarrow 2KOOCH$$
 (11)

For another, K_2CO_3 is converted to KHCO₃ by addition of CO_2 and H_2O and then hydrogenated, as

$$\mathsf{KHCO}_3 + \mathsf{H}_2 \to \mathsf{KOOCH} + \mathsf{H}_2\mathsf{O} \tag{12}$$

The third uses CO for reduction of an aqueous solution, as

$$K_2CO_3 + 2CO + H_2O \rightarrow 2KOOCH + CO_2$$
(4)

All three routes were investigated by conducting sufficient preliminary batch-type experiments to define the respective conditions necessary to produce KOOCH at reasonable rates. Results of such studies led to the conclusion that KOOCH regeneration by the third method, namely by the reaction in Equation 4, could be accomplished more rapidly, at a lower temperature and lower pressure than the other two routes. It is thus the most economically attractive one. Therefore, an extensive study was made of *continuous* regeneration of KOOCH by CO reduction of aqueous K₂CO₃ as the preferred route.

Table IV. Stripping H_2S from KHS in Typical Reduced Product Solution by CO_2 at 200° F.

CO₂ rate = 8 s.c.f./hr. per kg. of solution^a

n	Off-gas analysis	
(min.)	H_2S , vol. %	CO2, vol. %
5	25.19	74.81
10	22.11	77.89
20	17.94	82.06
40	15.14	84.86
60	9.96	90.04
90	5.00	95.00
120	2.01	97.99
150	0.00	100.00

 $^{\rm e}$ Feed analysis: 15.28 % KHS, 36.37 % K₂CO₃ equivalent, 48.35 % H₂O. Product analysis: 0.00 % KHS, remainder is carbonate and H₂O. (Some carbonate exits as bicarbonate and more so as CO₂ is added.)

Table V. Typical Continuous KOOCH Regeneration by CO Reduction of K₂CO₃, Using 4-Ft. High by 2.63-In. I.D. Stirred Reactor

Cor	ditions	
	Temperature	537° F.
	Total pressure	1190 p.s.i.g.
	CO partial pressure	700 p.s.i.a.
	K ₂ CO ₃ concentration in	
	feed solution	60%
	Feed solution feed rate	2570 g./hr.
	Feed gas	pure CO
	CO feed rate	29.5 s.c.f./hr.
	Stirrer speed	1200 r.p.m.
	Reaction residence time	108 min.
Res	ults	
	KOOCH production rate	1695 g./hr.
	Synthesis conversion	90.3%
	CO_2 in off-gas	35.9%
	CO in off-gas	61.0%
	H ₂ in off-gas	3.1%

The feasibility of continuous production of KOOCH was proven in both the small and large reactor systems referred to earlier. Studies of the effects of varied physical conditions showed that the synthesis rate increased with temperature, stirrer speed, and CO pressure. No optimum in the usual sense exists. Temperatures above 540° F. are not suitable, however, due to onset of thermal decomposition of the formate, and this was the highest temperature studied experimentally. In the experimental demonstration of the process, the maximum gas-liquid stirring possible within the limitations of the mechanical equipment was used. The maximum CO pressure used in the study was 700 p.s.i.a. since higher pressures would not be of interest for economic reasons.

Pertinent data and results of a typical continuous run and conditions used for KOOCH synthesis appear in Table V. Ninety per cent conversion was obtained for a reaction residence time of 108 min.

By use of the smaller reactor, a detailed study was made of the kinetics of the KOOCH synthesis Reaction 4, particularly of the effect of extent of conversion on reaction rate. Differential rates were measured on solutions representative of various extents of conversion. These rates were then integrated to yield the conversion curve in Figure 2. The rate was nearly independent of extent of conversion until 80% of the carbonate is converted to KOOCH, as is demonstrated by the linear region in the plot of cumulative conversion vs. reaction time presented in Figure 2. A more detailed presentation of kinetic data and more discussion of the kinetic behavior will be given in a separate technical publication, while the following generalizations will suffice here. The kinetics of the synthesis process generally conform to that of a first-order reaction. This behavior is in accordance with the concept of a mass-transfer controlled process where the rate controlling step is the diffusion of CO through a liquid film.

The data derived from measuring differential conversion rates in the smaller reactor, as presented in Figure 2, predict a 70-min. residence time for 90% conversion. The run described in Table V for the large reactor shows 90% conversion in 108 min. The lower conversion rate in this larger reactor is thought to be due to poorer gas dispersion with less gas-liquid contacting. The larger reactor had a somewhat smaller diameter



Figure 2. Conversion vs. reaction time for synthesis of KOOCH by $K_2CO_3 + 2CO + H_2O \rightarrow 2KOOCH + CO_2$



and deep pool, preventing much foaming relative to pool depth; whereas there was likely a large proportion of foam relative to the shallow pool in the smaller reactor which enhanced contacting.

Because the synthesis of formate via Reaction 4 has all the attributes of a mass-transfer controlled reaction, it is possible to design, for the cost analysis, a commercially sized reactor in which conversion rate can be predicted in terms of stirring power input, stirrer size and speed, and sparging gas rate. Such extrapolative techniques have been developed (Cooper, Fernstrom, et al., 1944; Yoshida and Miura, 1963) for mass-transfer controlled reactions. These authors have used experimental measurements on the rate of oxidation of aqueous alkali sulfite solutions and of the absorption of oxygen in water to develop their extrapolation methods. To apply their methods to formate synthesis, rate data were needed on one of their reactions conducted in our particular equipment. Thus, data on the rate constants for oxidation of aqueous potassium sulfite, as determined in the same equipment used for formate synthesis, are given in Table VI. These data on sulfite oxidation were used to "calibrate" our equipment for extrapolation to commercial design as will be discussed below. Also, shown in Table VI are the rate constants for formate synthesis obtained in the same equipment. The units of the rate constant K_G are moles of CO or O₂ reacted per liter per hour atmosphere of CO or O2, respectively. The volume term is the total in the reactor including dispersed gas which took up 30% of the reactor volume. The formate conversion was treated as having one first-order reaction rate constant at 0-80% conversion and another at 80-100% conversion, as shown in Table VI.

The literature data on sulfite oxidation (Cooper, Fernstrom, et al., 1944; Yoshida and Miura, 1963) in large reactors showed rates that were up to five times greater than the sulfite oxdation rates obtained in our equipment at 825 r.p.m. as discussed above (see Table VI). The design of a commercial reactor was then based on providing sufficient agitation or gas-liquid contacting to achieve the above fivefold increase on our observed experimental rate for sulfite oxidation. Since the rate of formate synthesis is also controlled by a similar masstransfer mechanism, it was also assumed that this same design will provide a conversion rate five times greater than the experimental values depicted in Figure 2. The costs and residence time were then determined for such a reactor for Figure 1.

Table VI. First-Order Rate Constants for 3-In. I.D. Reactor With 2.4-In. Pool Depth, Stirrer Speed = 825 R.P.M.

A. Conversion of 60% aqueous K₂CO₃ to KOOCH by Reaction 4 Date V D

	$Rate = R_G P_{CO}$	
	Av	K_G
Temperature (° F.)	For 0–80% conversion	For 80–100% conversion
482	0.10	0.06
536	0.18	0.09

B. Air oxidation of 0.2 N K₂SO₃ catalyzed with $6 \times 10^{-5} M \text{CuSO}_4$ 86 0.34 122 0.27

Table VII. Economic Analysis of Formate Process for SO₂ Removal^a

Power station load factor	57%	70%
Investment		
Total	\$17.7 mil.	\$19.4 mil.
\$/kW	13.6	14.9
Operating labor, man/shift	7	7
Treating costs, \$/ton coal		
Capital charges, 12%		
investment	0.80	0.72
Interest on working		
capital at 7%	0.02	0.02
Fuel costs at 40¢/MM		
Btu	0.56	0.56
Direct operating costs ^b		
(ex fuel)	0.70	0.61
Total	2.08	1.91
Sulfur credit, \$25/long ton	0.65	0.65
Net treating costs	1.43	1.26

^a Basis: 1300 mW station, 3.5 wt. % sulfur coal. Scrubbing section-equipment designed for 100% load factor. Regeneration section—90% operating factor with 24-hr. storage capacity for spent and regenerated

reagents. $^{b}1.5\%$ of investment included for property tax, insurance, and miscellaneous supplies.

Experimental work in large diameter reactors is now in progress to check this prediction and incident assumptions.

Economic Analysis

The economic analysis of the process was based on a detailed engineering layout expanded from the simplified flow sheet shown in Figure 1. A summary of results and basic assumptions of the calculations are given in Table VII. A detailed breakdown of investment costs is reserved for a future publication because of length.

Conclusions

The technology of all the steps in the formate process has been established by supporting bench-scale and laboratory developmental studies, including effective SO₂ removal from stack gas through to regeneration of KOOCH with sulfur recovery. The system does not require reheat of the cleaned stack gas and has no additional waste disposal problems other than the usual disposal of fly ash. Rather mild conditions suffice for all stages of regeneration. Regeneration is conducted with an all-liquid system and requires no solids handling equipment. No untried or radical commercial equipment would be required for a plant. Sufficient data now exist to design and construct a pilot plant to demonstrate the whole, integrated process.

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Received for review October 22, 1969. Accepted April 13, 1970. Presented at the Division of Water, Air, and Waste Chemistry, 159th Meeting ACS, Houston, Tex., February 1970.

Mercury in the Marine Environment

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Mercury levels in coastal marine organisms are several orders of magnitude greater than in comparable volumes of seawater. Also, higher values of mercury are found in sediments near sewer outfalls as compared to similar deposits further removed. The dispersion of this toxic pollutant by marine organisms and by man has already had serious consequences.

uman society, due to its immense variety of activities, sends mercury into oceans in amounts comparable to those introduced through weathering processes (Goldberg, 1970). Although the impact of such an entry has not as yet been observed, this study attempts a survey of the marine occurrences of mercury with the aim of obtaining general guidelines as to the potential reservoirs for this element in the oceans.

Production, Consumption, and Release

In 1966 the world production of mercury was estimated to be 9200 metric tons; slightly under 10% resulted from mining operations in the United States (Minerals Yearbook, 1966). The United States uses about 27% of the world output or threefold more mercury than it mines. Industry consumes a major proportion, principally in the electrolytic preparation of chlorine and caustic soda. Less demanding are the agricultural demands for fungicide and bactericide manufacture, which have steadily declined over the past decade. Intentional or uncontrolled discharge brings approximately 4000-5000 tons of mercury per year to the environment, which ultimately settle in the marine environment following release into the atmosphere or the rivers. This may be compared with 5000 tons per year of mercury transferred from the continents to the oceans by the rivers following continental weathering.

Several mass poisonings involving mercury attracted the general attention of the scientific community and resulted in legislation restricting the employment of mercurials in agriculture and industry.

In southwestern Kyushu, Japan, the inhabitants of the environs of Minimata Bay suffered an epidemic of neurological disorders, which were eventually related to a mercury poisoning from fish and shellfish. It was found each of the victims of the disease had eaten fish or shellfish from Minimata Bay. By the end of 1960, 111 cases were reported, and as of August 1965, 41 deaths had occurred.

The poisoning was due to methyl mercury chloride which was formed in the waste sludges of a plant that used mercuric oxide in sulfuric acid for acetaldehyde production. These solids were discharged to Minimata Bay where the organo-mercury compound was accumulated by fish and shellfish. Methyl mercury chloride, administered to cats, caused the various symptoms associated with the disease (Irukayama, 1967; Kurland, Faro, et al., 1960.)

Increased mercury concentrations in birds and fish from Sweden occurred in the 1940's and 1950's, a period coinciding both with the use of alkyl mercury compounds as fungicidal seed dressings and with an increase in mortality of wild birds. Analyses of bird feathers from museum specimens collected between 1840 and 1940 gave constant mercury levels, while a ten- to twentyfold increase was observed in more recent samples. For a study of metallo-organic mercury extracted from feathers see Berg, Johnels, et al. (1967).

Dispersion

Seawater. In the region of the Lamapo Deep off the coast of Japan (Hosohara, 1961), mercury concentrations in seawater increase from surface values of around 0.1 μ g./liter to 0.15–0.27 μ g./liter at greater depths. The analyses were based on spectrophotometric determination of the dithizone complex of mercury. The depletion of mercury in surface waters was attributed to its uptake by plankton and subsequent conveyance to depths by the biological activities of the marine food web. In Minimata Bay, a range of 1.6 to 3.6 µg./liter was found for total mercury, values ten times higher than those assayed in unoxidized samples (Hosohara, Kozuma, et al., 1961). These high values may reflect discharge of the industrial mercury waste mentioned previously. Stock and Cucuel (1934) found 0.03 µg./liter for mercury in North Sea water.

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In these experiments, mercury was coprecipitated from seawater with copper sulfide and subsequently deposited electrochemically on copper wire. Following distillation of the mercury from the wire into a capillary, the size of the globule formed was used as a measure of the mercury content.

Such experiments, if not subject to contamination from laboratory mercury or loss of mercury by volatilization, indicate mercury levels in the open ocean of tenths of μ g./liter. Further, they strongly suggest an involvement of mercury with biological processes.

Organisms. There is a marked enrichment of mercury in members of the marine biosphere over seawater. Raeder and Snekvik (1941) report that the algae *Laminaria hyperborea* and *Fucus vesiculosus* contain $3.7 \times 10^{-6}\%$ and $2.3 \times 10^{-6}\%$ by weight of mercury, respectively. Marine fish, analyzed by the same workers, contained 122 ng. of mercury/g. of fish, a factor of 4 higher. In general, fish indicate higher levels of mercury in tissues than other marine organisms in the food web (Stock and Cucuel, 1934). The limited data indicate mercury concentrations in fish to be a thousand to ten thousandfold higher than in seawater.

Sediments. Turekian and Wedepohl (1961) estimate 80–90 p.p.b. of mercury in basaltic and granitic rocks with sedimentary values in the range of parts per billion an order of magnitude guess according to the authors. Bostrom and Fisher (1969) found between 1–2 and 400 p.p.b. in pelagic sediments (on a calcium carbonate-free basis) on a traverse across the east Pacific Rise. The highest values occurred on the crest of the ridge in a zone of high heat flow; the low values in deposits on the flanks and adjacent to the ridge system. The authors suggest that a degassing of the mantle through volcanic activity governs this mercury distribution pattern.

Harriss (1968) found the mercury content of ferromanganese nodules quite variable, ranging from less than 1 to 810 p.p.b. Samples from the Pacific Ocean and a single sample from the vicinity of the Canary Islands in the Atlantic had much higher mercury contents than those from the Blake Plateau, Antarctic regions in the Atlantic, and the Carlsberg Ridge in the Indian Ocean. One sample from the Gulf of California contained less than 1 p.p.b. of mercury. Harriss suggested that the volcanic and hydrothernial activity of the region from which the nodules were obtained determined the mercury levels—higher levels (greater than 58 p.p.b.) come from tectonically active areas. Such a suggestion is not borne out in a comparison of the montmorillonite content of the clay-sized fraction of the associated sediment, a possible



Figure 1. Frequency distribution of the mercury content, on a dried weight basis, in marine organisms

Shaded area, La Jolla samples. Unshaded area, Palos Verdes samples

measure of volcanic input (Griffin, Windom, et al., 1968), and the mercury contents of the manganese nodules.

Atmosphere. Goldschmidt (1954) indicated the mercury found in air and rainwater to result in the main from burning coal. Condensing units in British gas works that consume coal accumulate mercury.

More recently, Williston (1968) monitored the mercury vapors in the air over the San Francisco Bay area and reports the winter concentrations to range from slightly over 0.5 to 25 ng. of mercury per cubic meter of air and the summer values from 1 to 50 ng. per cubic meter. The mercury concentration at a particular location appeared to depend chiefly on wind direction, wind speed, and seasonal temperature variations. The high mercury levels always covaried with high smog levels, indicting human factors may govern its abundance.

Mercury's dispersion about the earth can be affected not only by man but also by other members of the biosphere. Mercury is concentrated more highly in marine organisms than in seawater, a phenomenon which has as a consequence increased levels with depth in the water column. Such a situation has been previously and extensively described for other elements involved in biological cycles such as phosphorus, nitrogen, and barium.

The evidence associating mercury with such tectonic activity as volcanism and hydrothermal transport is less convincing. For example, the high mercury content in sediments on the east Pacific Ridge may be explained by high organic productivity rather than on the basis of vulcanism or hydrothermal activity. The enhancement of the primary production of organic matter in the oceans is chiefly related to the phenomenon of upwelling, which brings such nutrient salts as phosphate, nitrate, and silicate from deeper to surface waters. Bogorov (1967) points out that the biomass of plankton increases in the wind "shadow" of an island in the middle of the ocean, a situation emphasizing the importance of bottom topography in the mixing of deep and bottom waters and hence the productivity of a given area. If the east Pacific Ridge can act as a stimulator for upwelling, increased levels of heavy metals at the crest of the ridge could result.

To extend our knowledge about mercury in the marine environment, we have analyzed both organisms and sediments.

Experimental

Method. The analytical technique, modified from Brandenberger and Bader (1967), involves the electroplating of copper wire with an acidic solution of inorganic Hg(II). Prior chemical treatment of the sample converts all the mercury to the divalent ionic state. Hence, the method does not distinguish inorganic from organic mercury. The wire is then rinsed and placed in an optical cell passed through by the beam of a mercury hollow-cathode lamp. The spiral is heated by electrical current and the mercury volatilized as atomic vapor. The vapor slowly sweeps through the cell. The maximum absorbance read on the spectrophotometer, after correction for the reagent blank, is proportional to the concentration of mercury in the sample.

Results. The analyses were performed on the soft parts of 81 marine organisms most of which were epibenthic fauna, mainly from the Palos Verdes peninsula in about 20 m. of water, and some from La Jolla, Calif. (Figure 1). The average mercury level, on a dry weight basis (dried at room temperature under vacuum to minimize any mercury loss through volatilization), was 0.9 p.p.m. and the frequency distribution of mercury concentrations appears to follow log normal statistics. The variations in mercury levels between species



Figure 2. Mercury concentrations (in parentheses) in parts per million by weight on dried weight basis in surface sediment samples from the environs of the White Point sewer outfalls

Table I. Mercury Concentrations in Bottom Sediments and Organisms, Collected Off La Jolla and Palos Verdes (PV) ^a					nts	
	Station					
Sample	La Jolla	PV(I)	PV(II)	PV(III)	PV(IV)	PV(V
Sediment	0.02	0.3	0.2	1.0	0.3	0.2
Crab, Cancer anthonyi	0.8	1.0 1.1	1.2	0.5	2.3. 0.9	
Whelk, Kelletia kelletia	1.5 0.9 2.1	0.9	1.8	2.3 1.6	1.6 2.5	3.2
Rock scallop, Hinnites multirugosus	0.7 1.6	$\begin{array}{c} 1.0\\ 0.6\end{array}$	0.4			0.5
^a p.p.m., dry wt.	basis.					

were the same essentially as those within a species. The highest concentration was 21 p.p.m. in a cowry (Palos Verdes) and the lowest 0.4 p.p.m. in a sea cucumber (La Jolla). The concentrations in the dried sediments varied between 0.02 and 1.0 p.p.m. with the higher values close to a sewer outfall and the lower ones tens of kilometers away (Figure 2 and Table I). The mercury levels in the organisms near the outfall were comparable to those far removed.

To further examine the effect of a sewer outfall on the mercury content of marine sediments, sixteen bottom samples were analyzed from the regular coring program associated with the operation of the Hyperion outfall by the City of Los Angeles. Analysis of a single sample of the effluent showed a mercury concentration slightly below a μ g. per liter. Mercury concentrations in the sediments in the environs of the effluent are given in Figure 3. Near the outfall, the mercury content of the sediments is as much as fiftyfold higher than presumably uncontaminated sediments further away.

Discussion

The results confirm the biosphere's influence in determining the distribution of mercury on the earth's surface. Firstly, mercury levels in the sea animals appear to be five hundred or



Figure 3. Mercury concentrations in parts per million on a dried weight basis in surface sediment samples near the Hyperion sewer outfall, Los Angeles

The ellipse area is a measure of the mercury concentration

more times greater than those in comparable volumes of seawater, assuming the living organisms contain 90% water by weight. Man's influence is implied by the higher concentrations of mercury in sediments near sewer outfalls as compared to similar deposits farther removed. Secondly, the differences within the same species were the same or greater than the differences in content between different organisms.

Clearly, the industrial and agricultural dispersion of mercury compounds involves organisms by their ingestion of both compounds of this element, and of the element itself. Pollution studies involving mercury may benefit from the identification of indicator organisms in diagnosing man's impact upon his environment.

Acknowledgment

D. H. K. was supported by an National Science Foundation fellowship during the period of this work. Samples were furnished by W. Garber and J. Nagano (Hyperion Treatment Plant) and R. Kiwala and R. Grigg (Scripps Institution).

This work was carried out under an air pollution control grant, Department of Health, Education, and Welfare.

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Received for review January 15, 1970. Accepted June 18, 1970.

COMMUNICATIONS

Recovery of DDT and Dieldrin from Tissues of Coturnix Japonica Stepwise During Residue Analysis

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Recoveries were measured stepwise during a 5-part analytical procedure by counting carbon-14 labeled p,p'-DDT or dieldrin. The greatest losses occurred during concentration of eluates from Florisil columns or zones from thin-layer plates and were probably due to codistillation. Nonetheless, overall recoveries of 70-94% are possible.

or several years this laboratory has been analyzing tissues of field-collected bald eagles and other bird specimens for chlorinated hydrocarbon residues. A 5-part analytical procedure (Reichel, Lamont, et al., 1969) has been developed for isolating these residues from tissue lipids.

Stepwise, the wet tissues are chopped, mixed with sodium sulfate, and extracted for 6 hr. in Soxhlet with petroleum ether (30°-60° C., b.p.). The pesticide residues are grossly partitioned from the tissue lipids in hexane (60°-70° C., b.p.) by acetonitrile extraction. The remaining lipids are removed by Florisil column chromatography with elution of the residues by a 3:1 mixture of hexane: benzene. The residue mixture is separated into zones on a thin-layer plate (silica gel G, developing solvent-2% ethyl ether in hexane) with elution from each zone by boiling benzene (Mulhern, 1968) followed by analysis of the zonal eluates by gas chromatography (3% OV-17 on 100-120 mesh Gas Chrom Q in 6-ft. \times ¹/₄-in. glass column, operated at 197° C., 100 ml. N₂/min. gas flow).

To measure the percentage recovery for this analytical procedure, laboratory trials were conducted using tissues containing biologically incorporated carbon-14 labeled p,p'-DDT or dieldrin.

Experimental

Fifty-µc. p,p'-DDT-C14 (ring labeled) (New England Nuclear Corp.) were diluted with 90 mg. of the unlabeled compound in corn oil and fed by capsule at the rate of 3 mg. DDT per bird per day to three Coturnix quail for 10 days. Fifty- $\mu c.$ dieldrin-C¹⁴ (Amersham-Searle Corp.) were diluted with

150 mg. of the unlabeled compound in corn oil and fed by capsule at the rate of 4.25 μ g. dieldrin per bird per day to three Coturnix quail. This dosage proved fatal within 7 days to these and four replacements. Both living and dead birds were used to provide tissues for analysis.

To estimate the radioactivity in the tissues before Soxhlet extraction, two 100-mg. aliquots of each sample were solubilized in perchloric acid and hydrogen peroxide and counted according to the method of Mahin and Lofberg (1966). The entire sample of each tissue was then extracted and recoveries determined after each step in the following manner: for DDT, extraction, partition, and column elution solvents were evaporated to dryness, the residue redissolved in benzene and two aliquots, each equivalent to 100 mg. of sample before extraction, were taken for counting. For dieldrin, extraction and partition solvents were evaporated to drvness, the residue redissolved in hexane and aliquots taken for counting. Column eluates were concentrated to about 10 ml., transferred to graduated tubes, and made up to volume with hexane before taking aliquots for counting.

For separation of DDT and metabolites, the thin-layer plates were divided into four zones, the first zone extended to include the origin line. For dieldrin the plates were divided into five zones, four plus the origin line. Each zone eluate was counted separately and the compounds identified by gas chromatography.

Results and Discussion

The percentage recoveries of DDT and metabolites are given in Table I. By use of solubilized tissues as a reference base, petroleum ether gave complete extraction in Soxhlet of radioactivity from liver and brain tissue and nearly complete extraction from heart and breast muscle. The overly high recoveries from brain tissues after extraction and partition reflect the difficulties in sampling small-volume, high-activity extracts.

Residues of unextracted radioactivity in the muscular tissues may have been compounds in the protein-bound lipids which resist extraction by nonpolar solvents, or water-soluble

Tissue	Solubilized tissue	Soxhlet extraction	Acetonitrile hexane partition	Florisil chromatography	Zonal separation
Muscle	100	92.9	91.2	90.2	72.1
Liver	100	101.2	b	94.3	94.2
Heart	100	93.3	96.9	86.4	74.7
Brain	100	105.5	104.3	62.0	b
		Per	cent recovery of dield	rin ^a	
Brain	b	100	93.2	88.7	80.8
Liver	b	100	92.7	84.2	70.7
Heart	ъ	100	96.7	94.6	84.2
Breast muscle	Ъ	100	95.2	89.4	79.2
Shanks and toes	b	100	91.1	95.9	88.2
^a Average of two aliquots. ^b Not determined					

Table I. Per Cent Recovery of DDT and Metabolites^a

metabolites, although these have been previously reported only in liver and feces (Abou-Donia and Menzel, 1968). The lower recoveries obtained after Florisil and thin-layer chromatography illustrate the losses due to codistillation that can occur in virtually fat-free samples evaporated to near or complete dryness under an air stream (Burke, Mills, *et al.*, 1966). Scanning of the zone eluates by gas chromatography revealed p,p'-DDT as the principal compound present, with lesser amounts of p,p'-DDD and DDE.

The percentage recoveries for dieldrin are given in Table I. Depending on the tissue, duplicate variability in the counts of samples solubilized with perchloric acid and hydrogen peroxide ranged from 7-30%, and counts in an aliquot of Soxhlet extract exceeded those in an equivalent weight of solubilized tissue by 10-105%. Use of a quaternary base (Soluene) as a solubilizing agent did not improve recoveries. These results suggest that dieldrin was partially volatilized and lost during solubilization; thus, all stepwise recoveries are related in Table I to counts in the Soxhlet extracts rather than to those in solubilized tissues. As with DDT, some dieldrin was lost by codistillation during solvent evaporation after Florisil and thin-layer chromatography, but losses after Florisil were minimized by concentrating the eluates to about 10 ml. rather than to dryness. Scanning of the zone eluates by gas chromatography revealed only dieldrin.

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Received for review September 19, 1969. Accepted March 2, 1970, Presented at the Division of Agricultural and Food Chemistry 157th Meeting, ACS, Minneapolis, Minn., April 1969.

Preparation of Glass Fiber Filters for Sulfuric Acid Aerosol Collection

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• A method for reducing blank effects in the collection of H_2SO_4 aerosol on glass fiber filters has been developed. Treatment with hot H_2SO_4 followed by thorough rinsing permits the filters to be used to collect microgram amounts of H_2SO_4 aerosol without any significant irreversible loss of H_2SO_4 on the filter.

G lass fiber filters combine the desirable features of high retention efficiency of submicron particles with high flow rates, and so have found widespread use in the collection of particulate samples in air pollution studies. Such filters were used extensively for the collection of H_2SO_4 aerosol until it

was shown (Lee and Wagman, 1966) that atmospheric sulfur dioxide could be oxidized catalytically on the glass surface and thus seriously interfere with the determination of prevailing H_2SO_4 aerosol levels.

Difficulties encountered in allowing for blank effects when analyzing for H₂SO₄ aerosol collected on glass fiber filters have also been discussed. Dubois, Teichman, *et al.* (1967) report that many brands of these filters contained excessively high amounts of sulfate and have described extraction procedures by which these can be reduced. However, Scaringelli and Rehme (1969) said that the residual alkali content of the filter can result in sulfuric acid losses of 0.4 to 7.8 μ g. per cm.² of filter. Thus, there can be considerable variation in the chemical properties of glass fiber filters, and close attention must be given to blank effects when dealing with atmospheric samples containing microgram quantities of H₂SO₄. Recognizing this, Scaringelli, Boone, *et al.* (1966) described an acetic acid treatment for the removal of residual alkali from filters to be used for the collection of H_2SO_4 aerosol.

Work in this laboratory has required a method for the efficient collection and analysis of $<20 \ \mu g$. samples of H₂SO₄ aerosol. Collection on glass fibers filters, followed by analysis using the barium chloranilate method (Schafer, 1967), was selected as the most satisfactory combination. Preliminary calibration experiments using Gelman Type A glass fiber filters treated with acetic acid (Scaringelli, Boone, et al., 1966) indicated that approximately 50% recovery could be achieved when a solution containing 15 μ g. of H₂SO₄ in 2 ml. of H₂O was applied to a 47-mm. filter and subsequently extracted with 80% isopropanol. Attempts to increase this recovery by extracting the filter with boiling water rather than 80% isopropanol were not successful. Instead, this resulted in a slightly lower recovery of H₂SO₄ from the filter. This suggested that treatment of the filter, i.e., with excess hot H2SO4, followed by a thorough washing, might be a way to deactivate any surface contaminants which could be responsible for the apparent irreversible absorption of sulfuric acid. A procedure was developed in which filters are soaked in 20% sulfuric acid for 2 to 3 days at room temperature, brought slowly to a gentle boil for 10 min., and then repeatedly rinsed in distilled water, 80% isopropanol and, finally, acetone. Care is taken not to bend or fold the filters while wet to prevent permanent fractures. After the filters are air-dried, they are stored in a desiccator at a constant relative humidity of 45 %.

To test the effectiveness of this procedure in comparison with that of Scaringelli, Boone, *et al.* (1966), 2-ml. aliquots of standard H₂SO₄ solutions containing 3 to 9 μ g, H₂SO₄ were applied to filters treated in different ways and the measured recoveries are summarized in Table I. No losses of H₂SO₄ were observed with filters treated as described above, so that such filters can be used to collect microgram amounts of atmospheric H₂SO₄ aerosol for subsequent analysis by the barium chloranilate method.

The H_2SO_4 treatment would be expected to change only the surface of the glass fibers without causing any major disruption in the filter's fibrous structure which might result in a loss of retention efficiency. An H_2SO_4 -treated filter and a Millipore Solvinert filter (0.5- μ pore size) were used in series to collect H_2SO_4 aerosol having a mass median diameter of 0.6 μ . No significant amount of H_2SO_4 was detected on the Solvinert filter, confirming that the retention efficiency of the glass fiber filter was not decreased by the H_2SO_4 treatment.

Table I. Absorption of H ₂ SO ₄ by Glass Fi	iber Filters
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	H ₂ SO ₄ µg per 10 ml 80% isopropanol ⁴			
Filter treatment	Added	Found		
No filter	6.0	6.3 ± 0.4		
H ₂ SO ₄ treatment	6.0	7.0 ± 0.4		
No filter	14.8	14.8 ± 0.3		
HOAc treatment	14.8	7.2 ± 0.4		
HOAc treatment, w	ith			
refluxing	14.8	3.0 ± 0.5		
H ₂ SO ₄ treatment	14.8	15.2 ± 0.3		
No filter	18.0	17.9 ± 0.5		
H ₂ SO ₄ treatment	18.0	18.5 ± 0.5		
^a Average of at leas	t two determinations	s with the average devia-		

Earlier results (Lee and Wagman, 1966) indicated that SO_2 oxidation on glass fiber filters is surface-limited because of sulfate formation. Therefore, it is possible that the sulfuric acid treatment also reduces the catalytic activity of glass fiber filters, but any further investigation of this point was beyond the scope of the current program.

Acknowledgment

This work was carried out as part of a contract between the Air Management Branch, Department of Energy and Resources Management, Province of Ontario and the Ontario Research Foundation. The authors gratefully acknowledge permission of the Air Management Branch to publish these results.

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Received for review October 27, 1969. Accepted April 3, 1970.

industry trends

Chem-Trol Pollution Services, Inc., announces the debut of its new Blasdell, N.Y., liquid waste disposal and reclamation facility. The plant will process over 1 million gallons of liquid chemical wastes in accordance with state and federal pollution control codes.

Combustion Equipment Associates, Inc. (New York) has been given the contract for the design and construction of equipment to clean converter gas at the Black Sea Copper Works in Turkey, at the rate of 230,000 cu. ft. per minute. Recovered sulfur dioxide will be used in making sulfuric acid.

Water Pollution Research & Applications, Inc. (Washington, D.C.) has been retained by Illinois state attorney general William J. Scott to evaluate the state's litigation against U.S. Steel's South Works plant (Chicago) for pollution of Lake Michigan. The consulting firm is headed by J. I. Bregman, former deputy assistant secretary of the Interior for Water Quality and Research.

Cottrell Environmental Systems, Inc., a subsidiary of Research-Cottrell, will study air pollution and make recommendations for its control for a naval weapons industrial reserve plant operated by North American Rockwell in Columbus, Ohio.

Firestone Tire & Rubber Co. estimates that by fall, its synthetic fibers plant in Hopewell, Va., will have converted its only coal-fired boiler to oil. The project is part of a two-year, multimillion dollar antipollution program being conducted by Firestone.

Nardin Laboratory (Greenville, S.C.) has merged with Commonwealth Laboratory, Inc. (Richmond, Va.). The merger will expand Commonwealth's capabilities in air and water pollution research and control as well as drug, food, and feed analysis. Liberty Leasing Co., Inc., of Chicago will act as the national leasing representative for two manufacturers of air and water antipollution equipment: Keen Corp. (Aurora, III.) and Clean-Air-Ator Corp. (Oklahoma City, Okla.). Keen specializes in the process equipment utilized by municipal water pollution control plants and Clean-Air-Ator's equipment is geared to halt pollution originating from incineration.

Calgon Corp. (Pittsburgh, Pa.) will market its water pollution control system, products, and engineering services, including its water-soluble polymers and granular-activated carbons for water treatment, in Europe through its new subsidiary, Chemviron. Calgon also has acquired Technique et Distribution of Brussels (now the Water Treatment Equipment Division of Chemviron) which for the past three years has been the exclusive marketer of water conditioning equipment manufactured by Calgon's Bruner Division for the Common Market countries and Switzerland.

Corning Laboratories, Inc., a newly organized consulting and commercial testing laboratory, has been formed in Cedar Falls, Iowa. The new corporation specializes in testing and controlling air and water pollution and presently holds a federal grant for an air pollution study of Black Hawk County.

Seiberling Tire & Rubber Co. (Barberton, Ohio), a division of Firestone, has implemented its antidust pollution installation which automates and encloses the handling of carbon black, a component of tires. Earlier this year, the Seiberling plant reduced emissions by replacing its coal-fired stokers with oilfired boilers.

Ward & Associates (Caldwell, N.J.), was awarded the Army Corps of Engineers' contract for studying the sources of debris on the Hudson River and suggesting ways of cleaning it up.



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new products



Oil-on-water detector

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Monomer

Production of a new cationic methacrylate monomer, Sipomer Q-5, for applications in water treatment, textiles, plastics, industrial coatings, and latex paints. Sipomer Q-5 brings to 12 the number of commercially available monomers. Alcolac Chemical Corp. **63**

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available and are arranged so that air leads fuel when load increased and fuel leads air when load decreased. Analogous to cross-limiting in pneumatic systems and have generally been unavailable in low cost electric combustion control. These systems have been adopted by some of the major boiler and burner manufacturers. Reliance Instrument Mfg. Corp. 74

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new literature

Cooling water programs. Booklet explains factors and procedure involved in developing water cooling programs. Bulletin C-7 describes the control of cooling water problems of corrosion, scale and deposits, and microbiological activity. Nalco Chemical Co. **91**

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Chlorine. Two-page bulletin describes the properties of chlorine and provides brief information on packaging, shipping, handling, storage, and toxicity. PPG Industries, Inc. 94

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Environmental instruments. Catalog No. 8 lists instruments and systems for the atmosphere and environment. Devoted primarily to meteorological instruments, it also includes equipment of interest to hydrologists and air pollutionists. Science Associates, Inc. 97 **Dust filter.** A diffusion-type filter, consisting of a sealing flange, dry modocrylic synthetic fiber filter element, face grille, and retainer, is described in Bulletin No. 1511-2. The bulletin lists the features and characteristics of Dustfoe 35 and gives diagrammed instructions for mounting. Mine Safety Appliances Co. **98**

Air quality products. Brochure S-3200 presents a new particle mass monitor that, using solid state techniques, performs measurement of airborne particle mass concentration in less than 3 min. Range is to 100,000 μ g. per cubic meter. Brochures S-3000, S-3100, and S-3105 describe engineering data on an aerosol analyzer that determines particle size from 0.005-1.0 μ , an aerosol sampler, and other airborne particle research accessories. Thermo-Systems Inc. **99**

Cathodic protection. TP-40.15 describes the service plan for the Electro Rust-Proofing system of cathodic protection of water and waste water treatment structures. Points out the testing and inspection services offered and the advantage of such annual checkups. Pennwalt Corp. 100

Noise pollution. The 28-page booklet presents evidence compiled through medical research that noise constitutes a health hazard. Also defines the legal dangers of industrial noise pollution and the effects of antipollution legislation. AMF Beaird, Inc. 101

Air pollution control. Brochure outlines the capabilities and applications of the air pollution control systems in the lines of fluid, fabric, and dynamic pollution controllers. Applications are in the foundry, metalworking, woodworking, ceramics, chemical, stone, and other industries. Dollinger Corp. 102

Scrap and salvage materials. Four-page booklet describes the use of equipment and systems to automatically separate, upgrade, classify, and convey magnetic and nonmagnetic scrap and salvage materials. Equipment available for reclamation and upgrading includes magnetic, mechanical, and vibratory products. Eriez Magnetics 103 Solid state controllers. Folder describes three cooling water and one boiler chemical feed and blowdown controllers with schematic diagrams of typical installations, W. R. Grace & Co. 104

Waste oil report. The report recommends that greater use be made of used oil for heating purposes, indicating that where re-refining industry services are not available renewed attention should be given to burning as the optimum method of disposal. Also contains detailed data on tests conducted by oil companies. \$3.00. Publications Section, American Petroleum Institute, 1271 Avenue of the Americas, New York, N.Y. 10020 (Write direct)

Water pollution control. Two new reports covering applied techniques in water pollution control have been written by the Federal Water Quality Administration. "The Practice of Water Pollution Biology" (\$1.50) is for biologists inexperienced in techniques and data analysis, for sanitary engineers, chemists, attorneys, and administrators. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 (Write direct)

The other, "Spectral Analysis," is a handbook on advanced mathematical techniques new in water pollution control. Federal Water Quality Administration, Public Information Office, Washington, D.C. 20242. (Write direct)

Computerized water programs. Report 118 describes how advanced computer techniques dealing with mathematical modeling, data management, and operations research can be used in a systems approach to coordinated water planning. Texas Water Development Board, P.O. Box 12386, Austin, Tex. 78711 (Write direct)

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

The Politics of Pollution. J. Clarence Davies, III. xiii + 231 pages. Pegasus, 350 Third Ave., New York, N.Y. 10022. 1970. \$1.95, paper.

With an introduction by Sen. Edmund S. Muskie, Mr. Davies describes how government policy is made and analyzes the interests and ideas competing for dominance over pollution control. Pegasus states that this publication "makes clear that any hope for the improvement of environmental quality rests with public commitment and will require continuing pressure on the legislative and executive branches for greater commitments of resources to environmental problems."

Quantitative Analysis of Gascous Pollutants. Walter E. Ruch. x + 241 pages. Ann Arbor-Humphrey Science Publ., Inc., Drawer No. 1425, Ann Arbor, Mich. 48106. 1970. \$18.75, hard cover.

Designed as a quick reference source in the area of microchemistry of airborne gases or vapors, the book covers 176 pollutants and gives 376 methods for the quantitative analysis of gaseous pollutants. This reference is of value to anyone involved in air pollution or industrial hygiene.

Proceedings: Annual Tall Timbers **Fire Ecology Conference.** 292 pages. Tall Timbers Research Station, Tallahassee, Fla. 1969. Gratis, paper.

Papers compiled discuss ecological burning in all terrains and the effects, both detrimental and beneficial, on the environment and ecological development.

Man and His Urban Environment: A Sociological Approach. William H. Nichelson. xiii + 242 pages. Addison-Wesley Publ. Co., Reading, Mass. 01867. 1970. \$3.75, paper.

Advanced undergraduate and graduate level text illustrates, with examples of research, the interrelations of such concepts as life style, stages in the life cycle, social-economic status, values, and pathology with aspects of the physical environment in which people live.

Global Weather Prediction: The Coming Revolution. Bruce Lusignan, John R. Kiely, Editors. xi + 307 pages. Holt, Rinehart, and Winston, Inc. 383 Madison Ave., New York, N.Y. 10017. 1970. \$15.00, hard cover.

The book is a useful source of background information on the various aspects of a global meterological system, and according to the publishers, provides an overall description of a revolution which is beginning to take place in weather forecasting. Discusses the future behavior and prediction of such behavior of the atmosphere.

Marine Chemistry, Vol. 2: Theory and Applications. Dean F. Martin. xi + 451 pages. Marcel Dekker, Inc., 95 Madison Ave., New York, N.Y. 10016. 1970. \$9.50, hard cover.

Containing information for chemists, oceanographers, technicians, biologists, zoologists, geologists, and scientists in fields concerned with water, the book places considerable emphasis on the interactions of organisms, chemicals, and the environment.

Air and Water Pollution. Gerald Leinwand, General Editor. 160 pages. Washington Square Press, Inc., 630 Fifth Avenue, New York, N.Y. 10020. 1969. 75 cents, paper.

Book is the fifth volume in the "Problems of American Society" series. Mr. Leinwand, professor at Bernard M. Baruch College of the City University of New York, intends to stir an apathetic public to necessary action.

Active Carbon: Manufacture, Properties and Applications. Milan Smisek and Slavoj Cerny. xii + 479 pages. American Elsevier Publ. Co., Inc., 52 Vanderbilt Ave., New York, N.Y. 10017. 1970. \$30.00, hard cover.

This English edition presents a systematic basic review of the available information on the manufacture, applications, structure, adsorption properties, and testing of, as well as methods of research into, active carbon. Includes much relevant work from Russia and Czechoslovakia which has been virtually inaccessible.

Environmental Pollution, An International Journal. Kenneth Mellanby, Editor. About 80 pages per issue. Elsevier Publ. Co., Ltd., Ripple Road, Barking, Essex, England. 1970. \$15.60 (inclusive of postage), paper.

Journal is mainly concerned with the biological effects of pollution and includes papers on the ecological effects of all types of environmental pollution and pollution control. Published quarterly, it presents points of view from the international, political, economical, social, medical, managerial, planning, and engineering aspects.

Dimensions of Water Management. Proceedings of a conference. 133 pages. Ohio Section—AWRA, c/o Battelle Memorial Institute, 505 King Ave., Columbus, Ohio 43201. 1970. \$5.00, paper.

This book is a compilation of 12 papers presented at the 1970 Ohio Water Resources Conference. Topics discussed range from political dimensions to engineering and systems analysis dimensions. According to the publishers, the program did not include technical material but aimed at broadening the perspective of participants through clear, easily understood presentations.

Proceedings of the 1970 National Incinerator Conference. 330 pages. American Society of Mechanical Engineers, 345 East 47th St., New York, N.Y. 10017. \$19.50, paper.

The papers record the specialized findings and experiences of the authors concerning details of incinerator design, operation, and maintenance. A progress report of a technology that is advancing rapidly to assist in restoring the environment.

meeting guide

September 13-18 American Chemical Society

160th National ACS Meeting

Chicago, III.

Topics include biochemical responses to environmental stresses; atmospheric reactions; air analysis and control technology; solid waste chemistry; organic matter in natural waters; thermal pollution; and "Earth Day in Retrospect." Complete details: Chemical & Engineering News, June 29, 1970. Also, contact: Chicago Section, ACS, 86 E. Randolph St., Chicago, III. 60601

September 14-17 Association of Iron and Steel Engineers

Iron and Steel Exposition and Convention of Association of Iron and Steel Engineers

Cleveland, Ohio

Traditionally the steel industry's largest trade show, the Exposition will feature exhibits of pollution control-oriented devices and papers on pollution control at the technical meetings. 15,000 are expected to attend. Contact: Russ Robinson, Association of Iron and Steel Engineers, 1010 Empire Bldg., Pittsburgh, Pa. 15200

September 14-17 New Jersey Animal Waste Disposal Task Force

Agricultural Waste in an Urban Environment

Atlantic City, N.J.

First conference dedicated to finding a practical solution to the pressing national problems of agricultural waste. Will be special sessions on legislation, funding, research, and public relations. Write: Richard D. Chumney, N.J. Dept. of Agriculture, P.O. Box 1888, Trenton, N.J. 08625

September 21-24

National Assoc. of Corrosion Engineers; American Society for Quality Control; Instrument Society of America (Toronto Chapter); Assoc. of Consulting Chemists and Chem. Engineers; Chemical Industries Accident Prevention Assoc.; National Dairy Council of Canada; and the Filtration Society, Canadian Chapter

5th Canadian Chemical and Process Equipment Exhibition

Toronto, Ontario

Program features expertise from the seven sponsoring organizations on a wide range of subjects of interest to the process industries. Equipment of over 300 manufacturers will be displayed. Details: Richard Hardy, Press Officer, Canadian Chemical and Process Exhibition, P.O. Box 1010, Station B, Toronto 2B, Ontario

September 23-25 22nd Annual Convention and Operator's School, Western Canada Water and Sewage Conference Winnipeg, Manitoba

For full information, contact D. A. Shillabeer, Rm. 324, Administration Bldg., 109th St. and 98th Ave., Edmonton 6, Alberta

September 29-October 2

U.S. Department of the Interior

National Conference and Exposition on Environmental Pollution Washington, D.C.

Will cover 18 major environmental topics in more than 50 sessions. Pollution abatement equipment, techniques, and services will be displayed. More than 3000 attendees expected. More information: Suite 1040, Shoreham Bldg., Washington, D.C. 20005

September 30-October 2 The University of Michigan, and Michigan State University

International Conference on Environmental Mercury Contamination: Present Knowledge and Research Needs

Ann Arbor, Mich.

Participants will discuss distribution and transport of mercury in the environment and possible hazards associated with mercury exposures. Information: Conference Center, Extension Service, The University of Michigan, 412 Maynard Ave., Ann Arbor, Mich. 48104

October 4-9

Water Pollution Control Federation

43rd Annual Conference Boston, Mass.

Over 250 exhibits of water pollution control equipment, supplies, and processes. Program includes management, collection, treatment, and research of industrial wastes, oil pollution, sludge disposal, and estuaries and coastal waters. Write: Editor, Water Pollution Control Federation, Room N-400, 3900 Wisconsin Ave., Washington, D.C. 20016

October 5-7

Council on Environmental and Public Health of the American Medical Association

Air Pollution Medical Research Conference

New Orleans, La.

Conference will provide an up-to-date roundup of latest research findings in effects of airborne pollutants on human health. Further information: Frank Chappell, American Medical Association, 535 Dearborn St., Chicago, III. 60610

October 5-7 Cyrus Wm. Rice Division of NUS Corp.

Seventeenth Annual Water Seminar Pittsburgh, Pa.

Seminars for management, engineering, and operating personnel with water management and quality control. Registration fee \$300. Write: Cyrus Wm. Rice Division, NUS Corp., 1910 Cochran Rd., Pittsburgh, Pa. 15220

October 8 and 9

Mid-Atlantic Section of the Air Pollution Control Association, and Vehicular Exhaust Committee of the National Air Pollution Control Association

Harrisburg, Pa.

Examination of the problems of transportation and air pollution. Information: William O. Farley, Director of Public Information, Consolidated Edison Co. of New York, A Irving Place, New York, N.Y. 10003

October 8 and 9

West Coast Section of the Air Pollution Control Association

Fifth Technical Meeting

San Francisco, Calif.

Theme will be "Future Approaches to the Control of Air Pollution." It will be a workshop meeting in which audience participation will be encouraged. Attendance at the convention will be limited to registrants. Contact: John T. Donovan, c/o Bay Area Air Pollution Control District, 939 Ellis St., San Francisco, Calif. 94109

October 13 and 14 Purdue University

9th Annual Indiana Air Pollution Control Conference

Lafayette, Ind.

For further information, contact Dr. David L. Benchley, Conference Chairman, School of Civil Engineering, Purdue University, Lafayette, Ind. 47907

October 13-15

IIT Research Institute

Second International Conference on Ozone

Chicago, III.

Sessions include ozone generators, air and water treatment, sterilization, meteorology, effects on living organisms, and chemical reactions. Details: Mr. Charles K. Hersh, Assistant Director, Chemistry Research, ITT Research Institute, 10 W. 35th St., Chlcago, Ill. 60616

(continued on page 778)

October 13–15 European Chemical Marketing Research Association

Petrochemicals and their Raw Materials in Europe: Present Markets and Future Trends

Budapest

Delegates will attend the largest assembly yet (400) of Eastern Europeans concerned with such commercial activities as trading, planning, and marketing. After the conference, there will be an optional study tour, including a visit to the Hungarian Petrochemical Works of Leninvaros. Contact: Mr. E. Gaai, c/o Chemolimpex, P.O. Box 121, Budapest 5 or Mr. A. L. Waddams, European Chemical Marketing Research Association, Devonshire House, Mayfair Place, London WIX 6AY

October 19-23 American Industrial Hygiene Association

Industrial Toxicology Conference Detroit, Mich.

Sessions include scientific fundamentals and the practical applications of industrial toxicology. Industrial physicians, hygienists, nurses, engineers, public health officials, government and industrial personnel, chemists, and biologists are expected to attend. Registration fee \$250. Details: Program Registrar, Conferences and Institutes, Wayne State University, Detroit, Mich. 48202

October 19-23

International Gas Union, the International Institute of Refrigeration, and the Institute of Gas Technology

Second International Conference on Liquefied Natural Gas, LNG-2 Paris

Theme of LNG-2 will be "LNG-Gas International." Included are topics of developments in technology and trade and technical visits in France, Italy, and Spain. Contact: IGT-LNG Conference, B. Schukraft, Institute of Gas Technology, 3424 S. State St., Chicago, III. 60616

October 22 and 23

Chemurgic Council 32nd Annual Conference

Washington, D.C.

Theme is "Chemurgy–For Better Environment and Profits."

October 26-29

Instrument Society of America

25th Annual Conference and Exhibit on Instrumentation, Systems, and Automatic Control

Philadelphia, Pa.

Conference will focus on 25 years of advancement in instrumentation technology while also highlighting developments anticipated during the next decade. Contact: Public Relations Department, Instrument Society of America, 530 William Penn PI., Pittsburgh, Pa. 15219

October 26-30 American Water Resources Association

Sixth American Water Resources Conference

Las Vegas, Nev.

Technical sessions include topics of desalting water, water hydrology and quality, environmental issues, and water resources planning and problems. Contact: American Water Resources Association, P.O. Box 434, Urbana, III. 61801

October 28 New York State Action for Clean Air Committee

Symposium on Air Pollution and Respiratory Disease Albany, N.Y.

Symposium will be cosponsored by several local tuberculosis and respiratory disease associations and will be chaired by Frank M. Woolsey, M.D., of Albany Medical College. Emphasis will be on conditions in New York State. For details: New York State Action for Clean Air Committee, 105 E. 22nd St., New York, N.Y. 10010

November 2-4 Society of Engineering Science

Eighth Annual Meeting

Washington, D.C.

Theme of "Environmental Engineering" includes environments of major U.S. cities; mathematical and statistical models in pollution; ecological, social, and legal aspects of pollution; and systems analysis, problems, and progress in environmental engineering. Contact: Nozer D. Singpurwalla, School of Engineering and Applied Science, The George Washington University, Washington, D.C. 20006

November 2-4

Technicon Corp.

Technicon International Congress New York, N.Y.

Congress features a symposium with the theme "Pollution Control: Now or Never." Sessions to be held in ten different fields of concentration and feature exhibits of latest chemical analysis equipment. Contact: Martin H. Adelman, Manager, Environmental Sciences, Technicon Corp., Tarrytown, N.Y. 10591

November 2–6 IUPAC and the Federation of Swedish Industries

International Congress on Industrial Waste Water

Stockholm

The congress will deal exclusively with control of industrial water pollution by use of in-plant process or through waste water treatment. The program covers, one by one, the majority of industries with water pollution problems. Full details from International Congress, Drottning Kristinas väg 47, S-114 28, Stockholm, Sweden

November 4–7 IEEE, AEC, NASA, and NBS

1970 Nuclear Science Symposium New York, N.Y.

Program emphasizes the impact of nuclear energy on the environment, biomedical instrumentation, and nuclear reactor instrumentation. Further information: Melvin E. Cassidy, Local Arrangements Chairman, U.S. Atomic Energy Commission, 376 Hudson St., New York, N.Y. 10014

November 6-10

American Institute of Biological Sciences, and Federation of American Societies for Experimental Biology

First National Biological Congress Detroit, Mich.

Theme of the congress will be "Man and Environment." Morning sessions will deal with scientific topics but will appeal to both professional and layman. Evening symposia on the subject of man, environment, and public policy will bring together environmentalists and lawmakers. For full details: National Biological Congress, 3900 Wisconsin Ave., Washington, D.C. 20016

Courses

September 22-24

Toronto Chapter and the Chemica Division of the American Society of Quality Control

Short Course on Fundamental Concepts in the Design of Experiments Toronto, Ontario

Subjects to be covered include design, statistical inference, experimental design, and statistical analysis techniques. Contact: J. E. Willard, American Society for Quality Control, P.O. Box 221, Postal Station N, Toronto 14, Ontario

September 22-25

University of California

Short Course on Management of Solid Waste for Optimum Environmental Control

Berkeley, Calif.

Will deal with social, cultural, economic, and technological factors governing generation of solid wastes and with practical problems involved in proper management. Fee is \$200. Write: Continuing Education in Engineering, University Extension, University of California, 2223 Fulton St., Berkeley, Calif. 94720

October 5

Water & Wastewater Technical School Neosho, Mo.

Instruction in the 36-week course prepares students for careers in the water or waste water industries. Subjects include microbiology, mathematics, chemistry, stream sanitation, and waste water collection and distribution. Contact: Water & Wastewater Technical School, Box 370, Neosho, Mo. 64850

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