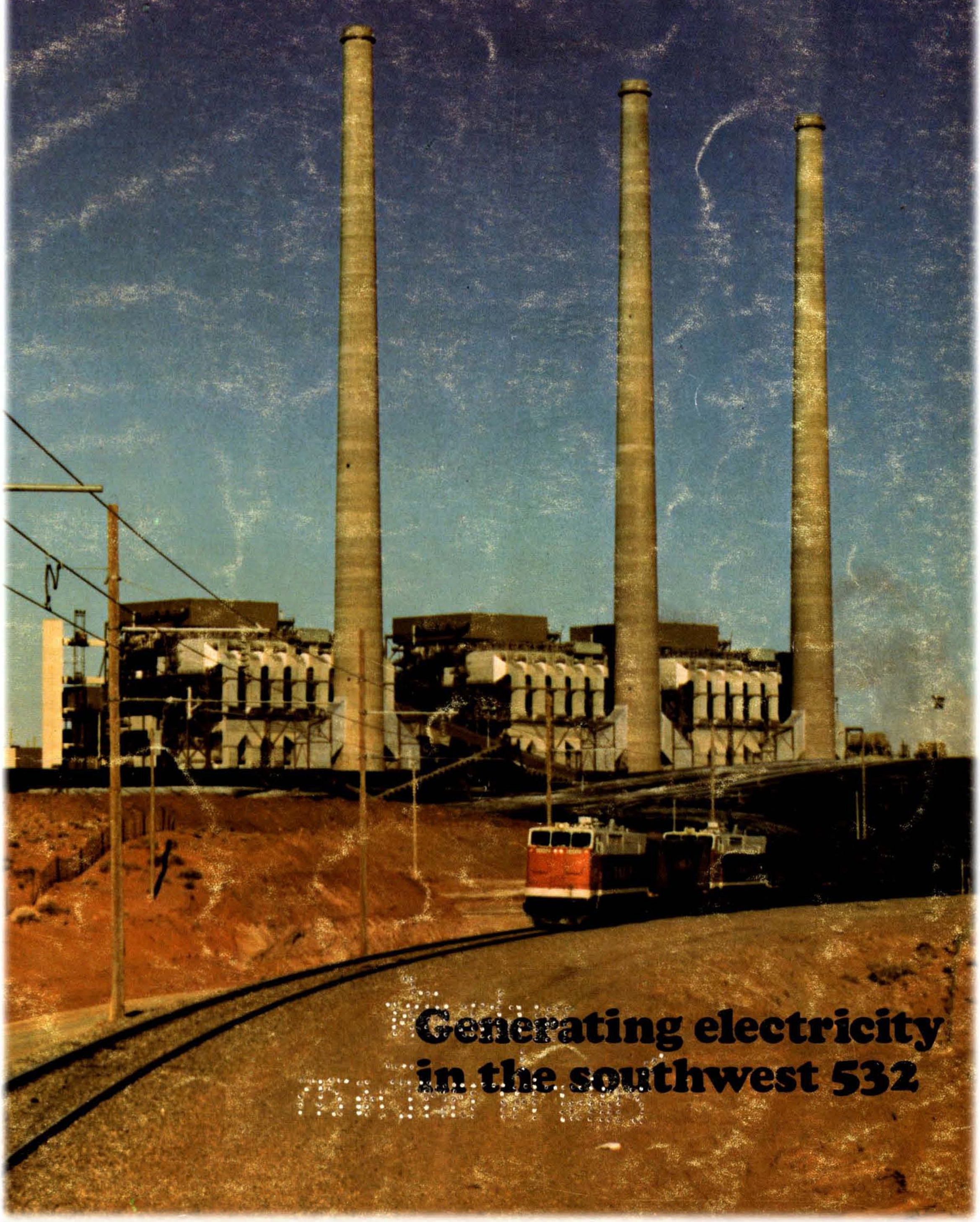
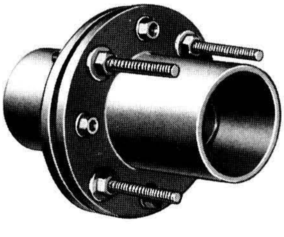
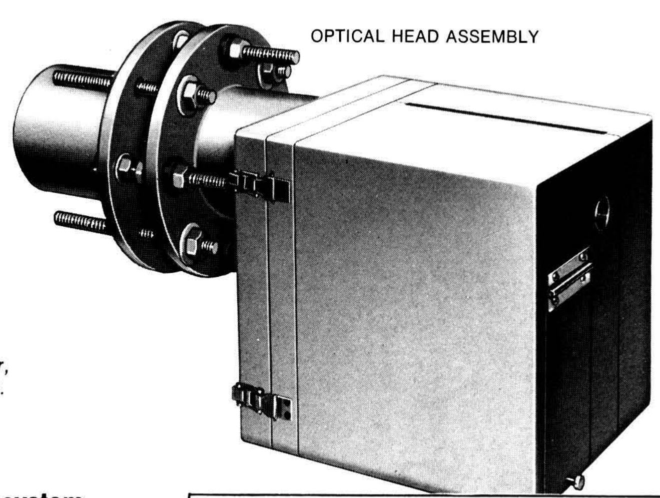
Environmental
Science & Technology
JUNE 1976



Generating electricity in the southwest 532

RAC on-stack transmissometer *

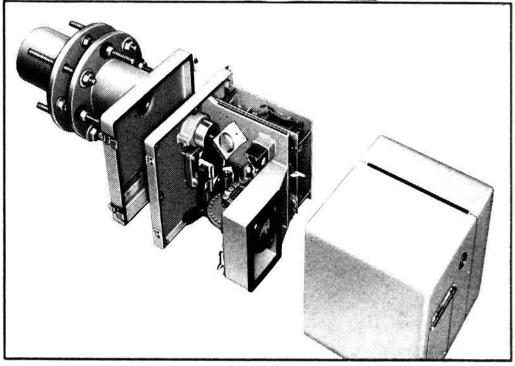

RETROREFLECTOR
ASSEMBLY

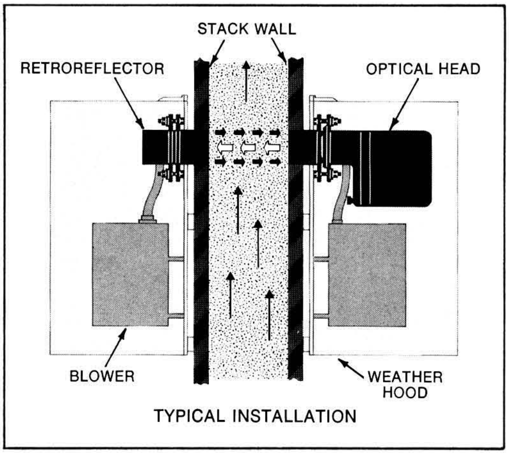

OPTICAL HEAD ASSEMBLY

* *Meets or exceeds all performance specifications outlined in the Federal Register, Vol. 40, No. 194, dated 10/6/75.*

This advanced electro-optical system measures from 0 to 100% opacity in stack gas streams . . . provides direct readouts with accuracy of ±3%.

The RAC on-stack transmissometer accurately measures stack gas stream opacity by means of a modulated light beam. A highly precise instrument, with patented design/operating features, this dual-beam monitoring device uses more simplified optic and electronic subsystems than competitive units. Its advanced design assures optimum optical performance . . . minimizes operating problems as well as normal service/maintenance requirements.





TYPICAL INSTALLATION

The RAC transmissometer features a unique chopper design and a solid-state automatic control circuit. These components make the system insensitive to ambient light, provide continuous recalibration (every 0.1 second), and automatically compensate for light and temperature changes as well as aging/drift in the electronics. In addition, the system's calibration can be verified easily, while the unit is operating, by a unique system response test kit with four NBS filters.

Once properly installed, this compact, lightweight (37 lbs) system normally requires no further on-stack adjustments. The optical head and retroreflector units, after fine alignment, are locked in position by external threaded connections to assure a vibration-free installation.

A variety of accessories—including blower units to protect the optics (when required), computer interfacing, remote strip-chart recorder, fail-safe shutter, remote control panel, linearizer-integrator, window soiling alarm, retro alignment tool, and a system response test kit with NBS filters—are available to enhance the RAC transmissometer's inherent capabilities for optimum performance with minimum attention.

For details, send for BULLETIN 2700.

STACK SAMPLING SEMINARS
Since 1970, RAC has sponsored an annual series of 2-day, technical, practical seminars on stack sampling parameters & procedures (EPA methods). **Write for descriptive folder.**

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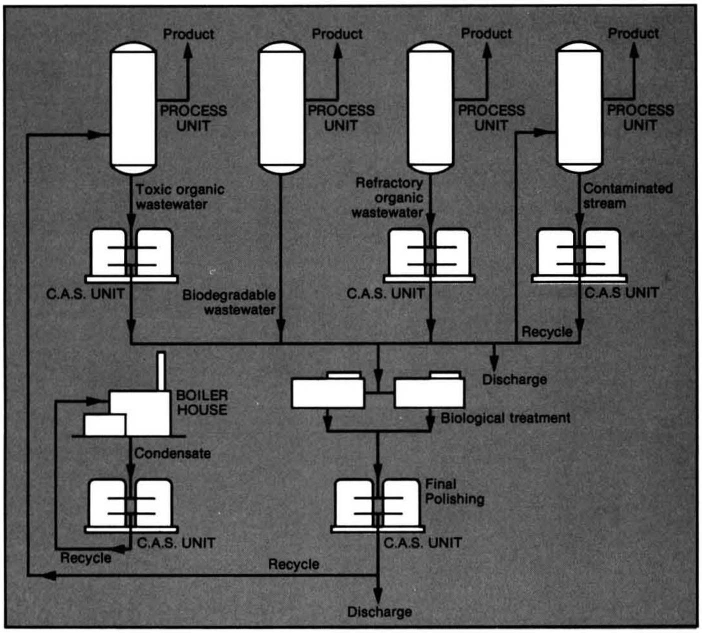
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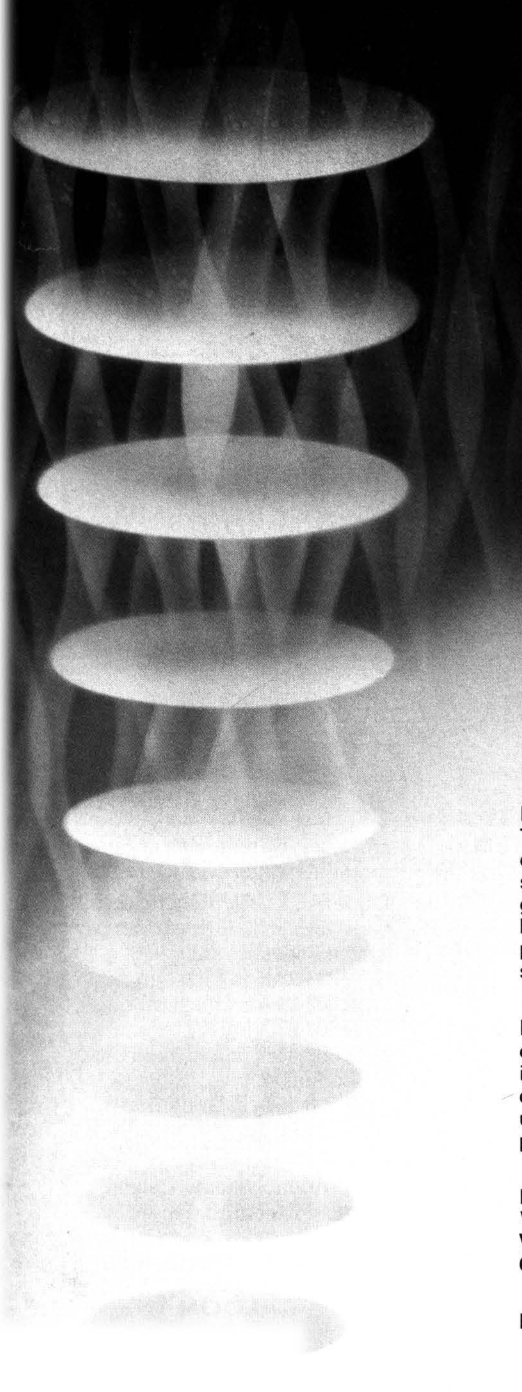

if you work in...

- *Air Pollution*
- *Wastewater Analysis*
- *Suspended Solids Analysis (EPA)*
- *Stack Sampling*
- *Gas/Liquid Purity Analysis*
- *Cell Harvesting*
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Environmental
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Volume 10, Number 6, June 1976

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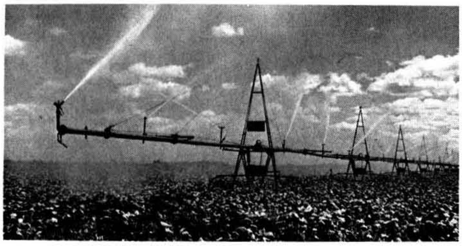
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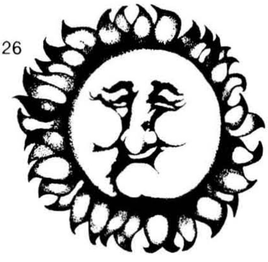
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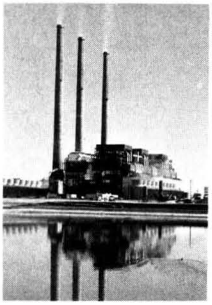
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Special report

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Those interested in joining the American Chemical Society should write to Admissions Department of Washington Office.

CURRENT RESEARCH

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L. H. Keith

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L. L. Smith, Jr.,* D. M. Oseid, and L. E. Olson

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W. A. Cronkright* and W. J. Leddy

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P. T. Roberts and S. K. Friedlander*

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D. C. Gordon, Jr.*, P. D. Keizer, W. R. Hardstaff, and D. G. Aldous

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H. E. Moore*, E. A. Martell, and S. E. Poet

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D. L. Flamm* and T. L. Wydeven

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R. Statnick*, R. Grote, and R. Steiber

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A. P. Altshuller

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T. S. Cox and D. N. Ingebrigtson*

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Cover: Salt River Project (Phoenix, Ariz.)

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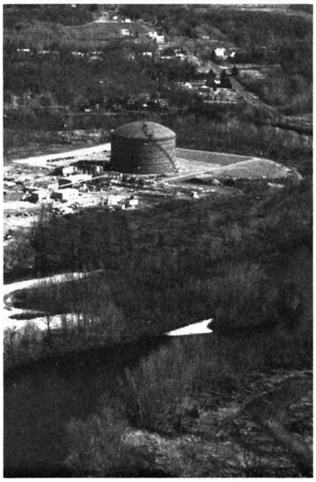
* To whom correspondence should be addressed.

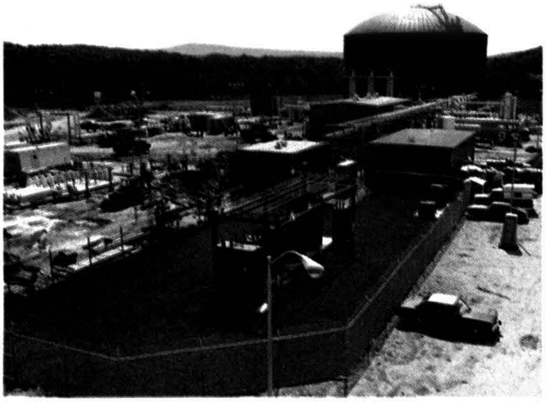
LEAKAGE PREVENTION = ENERGY CONSERVATION

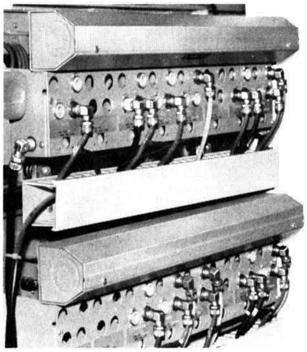
Bay State Gas Co., supplier of liquified natural gas to 12 communities in the Springfield (Massachusetts) area, insures leak-tight handling and control of precious LNG by using SWAGELOK Tube Fittings at critical connections throughout its storage facility in Ludlow, Massachusetts.

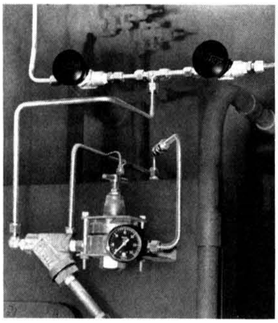
Control panels, recording and measuring instruments, dehydration and absorption equipment, gas analyzers and LNG pumps all demand the reliability and safety of SWAGELOK connections.

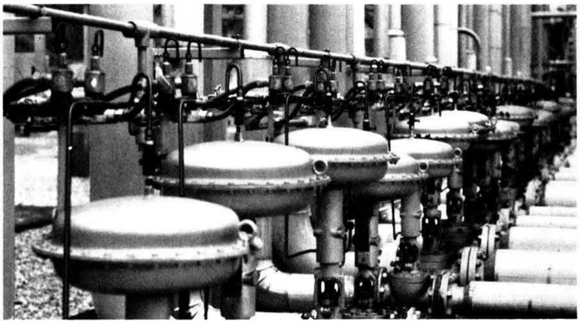
Valving is equally important...and WHITEY Valves with SWAGELOK end connections are used for exacting flow control functions. Three-way, air operated models are integrated with an alarm system which provides for automatic shutdown of the entire plant in case of emergency. Hand operated valves furnish positive on-off service for the plant's dew point moisture analyzer.











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CIRCLE 10 ON READER SERVICE CARD

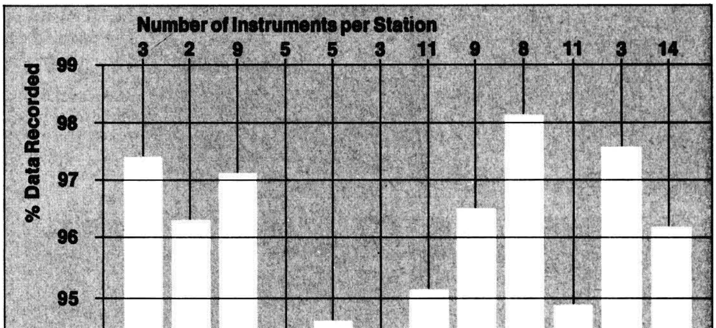
Philips SO_2 monitors: 90 days, 90%... 90 years?

1969

The first Philips SO_2 monitor is installed in the U.S.

1976

. . . over 60,000 data hours later this Philips SO_2 monitor is still on duty, still producing 90-95% *valid* data on an annual basis.



High quality means high performance: *95.9% average recovered data from a 12 station 83 monitor system. Record covers a 10 month period. The data above was validated by a multi-point external calibration using the following schedule: 24 hours, 7 days, 45 days.*

This is why . . .

Philips designed the monitor around a 90 day scheduled maintenance program

90 day unattended operation, together with 90 day scheduled maintenance establishes the basis for Philips unequalled field performance and for its broad acceptance. Implied by these tough field performance criteria are design standards of the highest level. Today, seven years after the introduction of the PW9700 SO_2 monitor, Philips remains the *only* manufacturer to offer 90 day standards for unattended operation and for scheduled maintenance—no one else is even close.

Design criteria that make the 90 day scheduled maintenance program possible include . . .

Highest quality components. Components selected for the monitor must pass a quality assurance program to satisfy the necessary MBTF for 90 day unattended operation. Success of this program is attested by the more than 2500 monitors now in the field worldwide and routinely reporting a 90% or better data recovery.

Automatic regeneration of reagent. A constant level coulometric cell with automatic regeneration of reagent provides for a 6 month life of the electrolyte.

Philips designed the monitor around a built-in data quality program

Continuous data validation. Automatic, daily systems zero[*] and dynamic span[†] checks are made

---

[*] An activated charcoal filter incorporated in the monitor provides a pure air sample to generate a system zero signal.

[†] In the PW9755 a thermostatted SO_2 permeation source, traceable to an NBS standard, is used to provide a known amount of SO_2 when a calibration command is received.

to assure continuously validated information from the monitor.

Philips monitors get off to a good start

The Philips monitor is installed and made operational at the customer's facility by a Philips service engineer. The instrument is released to the customer only after the system has been verified as meeting specifications. This service is provided to the customer as part of the purchase price.

Philips nationwide service organization assures prompt local support

Our 12 month field warranty brings prompt on-site service to the customer as required . . . and at no cost to the customer.

Philips highly trained service engineers operate from 14 service offices throughout the nation. On-going schooling programs for these engineers assure up to the minute competence in their performance.

Philips support assures continuing performance

At the time the equivalency document was published, our PW9700 SO_2 monitor had been superseded by the PW9755 (see below) and was no longer in production . . . Philips, nevertheless, embarked on a program, prior to the promulgation of the document, to bring the PW9700 in line with future requirements, and filed for equivalency on behalf of this instrument.

Philips listens to its customers

After extensive field experience and component design improvement programs, Philips, in 1976, introduced an updated version of the PW9700, the PW9755—even though the older model still has no peer for field performance.

1981

Philips has every reason to believe that its first U.S. monitor will be operationally effective in 1981, the year in which all monitors must be EPA equivalent. This is why equivalency for our 1969 model was important: we wanted those many companies and institutions who had purchased the PW9700 to be able to achieve the use that was originally built into this instrument . . . and this is why our present customers can be confident that in 1981 they will still be achieving 90-95% valid data on an annual basis.

2059?

Still in use? Probably not. But as the first 90 day monitor for the control of ambient air quality, the PW9700 will have long since earned its place in history.

1976 Valid year to purchase your first (or 90th) Philips SO_2 monitor. Call us today (914-664-4500) and ask for the EQP Group (Environmental Quality Products). They'll be glad to get things moving for you.

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PW9755

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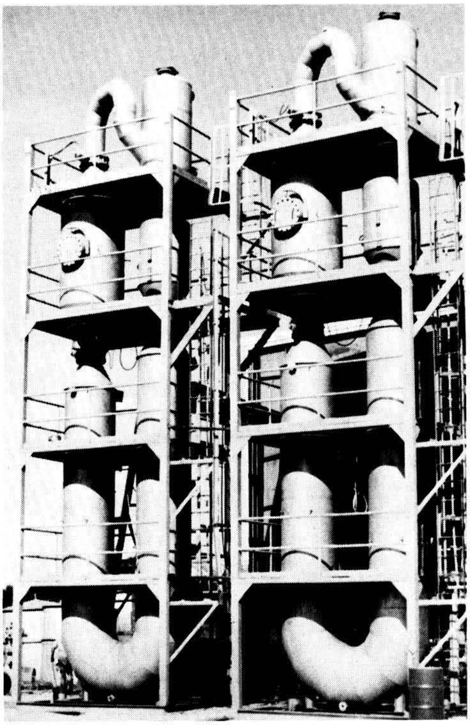

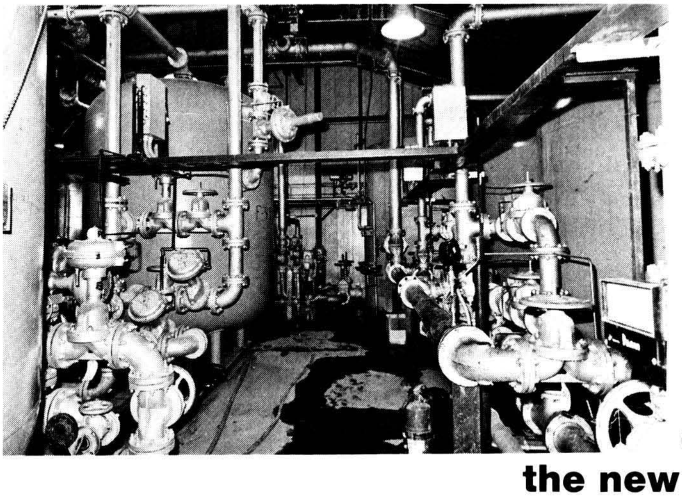

EDITORIAL

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Air standards' standstill

The Clean Air Act of 1970 mandated an inflexible sequence of events, to be accomplished within a rigid timetable. This was followed by the promulgation in 1970 of the present six air quality standards for carbon monoxide, hydrocarbons, nitrogen oxides, oxidants, particulate matter, and sulfur dioxide. The sequence involves (1) publication of air quality criteria and control technology documents, (2) publication of the proposed standard, (3) time for public response, (4) promulgation of the standard, and (5) the requirement that the states submit plans for their implementation to EPA for approval.

Although the first four of these steps are relatively rapid and painless, the last step has been long drawn out and traumatic. This trauma has made EPA so gun-shy of following the prescribed sequence and timetable for air quality standard promulgation and revision, that, since 1970, no new air quality standard has been promulgated and no major revision of the original six standards has been made, despite accumulating evidence that both these types of actions are badly needed.

The remedies for this situation are to

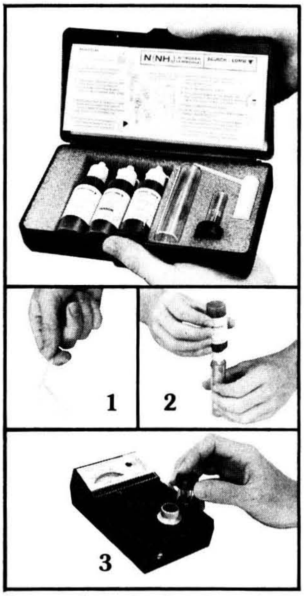
(1) force the Administrator to periodically update, and, where necessary, revise his air quality criteria and control technology documents, obtain public response, and repromulgate the air quality standards and

(2) make the required sequence and timetable more flexible by allowing the EPA Administrator to set the timetable.

The status of Congressional action on the Clean Air Act is that no change in the sequence or timetable is included in the proposed 1976 amendments, nor is there any provision that would force updating and review of present air quality standards. The prospect of a change in the amendments at this late date seems remote.

The EPA National Air Quality Criteria Advisory Committee has completed a chapter-by-chapter review of the six air quality criteria documents, noting which need updating or revision, and why; and has requested an EPA timetable for accomplishing such updating and revision. However, EPA has announced its intention to terminate this committee's activities by June 30, 1976. Therefore the prospect of a new look at our 6-yr-old air quality standards, and at their 8-yr-old supporting documentation, presently appears very dim indeed.

Arthur C. Stern
Chairman of the Air Quality Criteria Advisory Committee that advises the EPA



LETTERS

It's your health

Dear Sir: Your editorial (*ES&T*, December 1975, p 1101) was fresh and to the point. Your admonishment to read Assistant Editor Lois Ember's special report was well taken. She did a great job of amalgamating diverse and difficult subjects into a cogent, readable article. The theme "It's your health", the importance of toxic substances, and the apparent lingering interest of Congress may suggest the desirability or need for your kind of lucid reporting to focus attention on that complicated issue. Or have you already done so and I've missed it!

Industrial, commercial, and urban developments here have done much to improve economic and social conditions. The value of tourism, its impact on migration within the country, and developing environmental conflicts pose opportunities for societal choice. Establishing methodologies for environmental impact assessment, taking into consideration strong cultural concerns for littoral ecosystems, landscape, and historical monuments, makes fact finding for political action in this fast-developing country fun and hard work. Lois Ember's article will give us more help in assisting our Yugoslav colleagues to sort out issues and develop perspectives for environmental protection. A "message" on toxic substances would be welcome.

John T. Middleton
United Nations Development Programme
Istarska 6-51000 Rijeka, Yugoslavia

Ed: John T. Middleton was formerly the Commissioner of NAPCA, the National Air Pollution Control Administration, predecessor of the U.S. EPA.

Impact of chlorination

Dear Sir: After much thought reviewing all of the presentations at the Oak Ridge conference (*ES&T*, January 1976, p 20) there are two significant thoughts I would like to express.

The 15-minute chlorine demand of a raw water supply (potable) should be a water quality parameter. For example, if this chlorine demand is in excess of 5 mg/l the raw water should be rejected because it is too polluted.

As for the value of wastewater disinfection practices, many experts view this as a wasted effort. Not so! Several years of applying the disinfection requirement in California reveals that the value of a disinfection system as a pollution monitoring and control device is well worth the effort, in addition to the benefits from its value as a formidable barrier in the spread of waterborne disease.

Any wastewater treatment plant operator, when confronted with an effluent coliform requirement, soon finds out—usually to his great surprise—that the disinfection process is all but a complete failure unless all the treatment plant unit processes are functioning properly.

It is quite probable that the most important benefit of a wastewater disinfection facility is its value as a pollution monitoring device.

Therefore, one of the major benefits of wastewater disinfection is the fact that its efficiency is a measure of pollution control. If we cannot achieve disinfection efficiently, we are not solving waterways pollution.

Geo. Clifford White
San Francisco, Calif. 94118

Legal opinions

Dear Sir: John P. Hills has done an able job of summarizing existing legal decisions and opinions (*ES&T*, March 1976, pp 234–238), but has gone beyond his mandate and existing knowledge in adducing fluorocarbons as an example of infinite harm. Numerous people have tried to prove that the entire population of the Earth is at risk in this case. This is simply not so.

Even if the entire hypothesis is correct, the population at risk remains essentially the small group of fair-skinned blonds. If one adds to this the recent finding of John Eddy (reported in *Science* **191,** 1159, 19 March 1976) of several historical periods during which, if the theories to date are correct, the ozone must have been depressed to levels comparable with the forecast effects of continued fluorocarbon release for centuries, yet without any recorded biological impact, the whole matter becomes much too nebulous to warrant action at this time.

Finally, it should be noted that the incremental risk of waiting until better information is available has been shown to be trivial. I submit that this is not an example of a case in which immediate action is warranted, but rather of one meriting a Scottish verdict of not proven. Present talk of an enforced moratorium on fluorocarbon release is very little short of vigilante justice.

James P. Lodge
Consultant in Atmospheric Chemistry
Boulder, Colo. 80303

The specter of cancer

Dear Sir: In the Special Report (*ES&T*, December 1975, p 1116) the author cannot be blamed for mentioning that NCI scientists had reported that counties having copper, lead, or zinc smelters had higher than normal lung cancer mortality and that the scientists had suggested airborne arsenic might be the cause. She should also have noted, however, that the NCI authors cited no arsenic data, either for smelters or ambient air, to support their speculation.

The fact is that copper smelters account for most of the arsenic intake of the non-ferrous smelting industry. It is also a fact, derived from NCI data, that more copper smelting counties rank below the national average lung cancer death rate than above.

K. W. Nelson
ASARCO, Inc.
New York, N.Y. 10005

Groundwater

Dear Sir: In a recent issue (*ES&T,* March 1976, p 226) you noted enteric viruses from human wastes have been detected in ground water, apparently leachates from sanitary landfills containing disposable diapers.

In a recent year-long intensive study of California roadside and recreation area litter, the Institute for Applied Research survey teams found one or more disposable diapers in 3.4% of 324 roadside locations and 2.9% of 208 recreation areas. This rather high incidence was particularly disturbing in that some locations were close to streams or rivers that were direct sources of drinking water in downstream locations. Those concerned with quality assurance of groundwaters would do well to investigate the potential contribution of contaminants from roadside and reaction area litter.

Daniel B. Syrek
Institute for Applied Research
Carmichael, Calif. 95608

Groundwater

Dear Sir: I applaud the view expressed (*ES&T,* March 1976, p 226) that groundwater is one of this nation's most precious resources and must be protected from contamination and depletion. For many years our laboratory has been actively engaged in developing suitable methods for monitoring viral contamination and, indeed, for eliminating such contamination where it may occur. (See details in "Viruses in Water," Amer. Publ. Hlth. Assoc. Monograph, 1976.)

However, there is an error of fact. It is true, as mentioned in our feature (*ES&T,* December 1975, p 1124) that we have been concerned about the possible viral contamination of leachates of sanitary landfills [*Appl. Microbiol.* **28,** 232 (1974)]. In spite of our concern, we have not detected any viruses in such natural leachates in the small testing program done a few years ago. The available evidence on testing leachates generated from experimentally infected lysimeters in our laboratory as well as in Illinois by Englebrecht and in California by Cooper leads me to the belief at this time, that virus contamination of groundwater is unlikely. Nevertheless, the potential exists. However, much more widespread monitoring is required before we can say whether a problem of any significance exists from the disposal of virus-infected diapers in landfills.

Joseph L. Melnick
Baylor College of Medicine
Houston, Texas 77030

MSA INSTRUMENTS in the NEWS

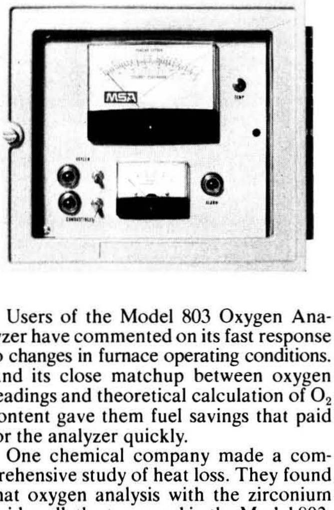
COMBUSTION CONTROL • HEALTH & SAFETY • ENVIRONMENTAL • PROCESS

New-generation oxygen analyzer for combustion control cuts emissions, pays itself off in months.

Unburned fuel going out your stack means pollution. But just as important, it means you are wasting expensive fuel. Accurate monitoring of excess air will permit you to save fuel and avoid the loss of Btu's up your stack.

MSA's new Model 803 Oxygen Analyzer was designed to solve many of the practical operating problems that you face in accurate monitoring of O_2 in hot, dirty flue gases.

The Model 803 sensor cell mounts directly on the stack for shortest possible sampling line. It operates hot to keep all gases above their dew points and minimize plugging. The stabilized fuel sensor measures oxygen—not an effect of oxygen—so it produces a high-level signal. It analyzes 0.1% to 21% O_2. The lower the oxygen concentration, the better the readability on its logarithmic scale.



Users of the Model 803 Oxygen Analyzer have commented on its fast response to changes in furnace operating conditions. And its close matchup between oxygen readings and theoretical calculation of O_2 content gave them fuel savings that paid for the analyzer quickly.

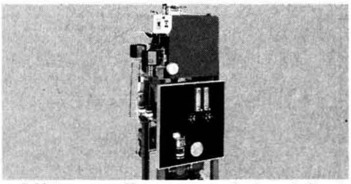
One chemical company made a comprehensive study of heat loss. They found that oxygen analysis with the zirconium oxide cell, the type used in the Model 803, overcame the operating problems and the need for frequent maintenance found in other types of sensors.

They also reported to their operating group that use of such an analyzer for excess air control could save about *$1,500 a month*, if the efficiency of a 200,000-lb/hr boiler was increased by just 1%. This calculation was based on 26¢ fuel oil, 335 days of 24-hour operation per year.

If you need a dependable, accurate oxygen analyzer that stays out of trouble and saves you fuel, get details on the Model 803.

Circle No. 37

SO_2, NO and CO analysis in stack gases made simpler, more accurate.



MSA now offers custom-designed Stack Analysis Systems which include a compact extractive sample acquisition and conditioning system. You have a choice of free-standing cabinets or wall-mounted housings, and provisions are available for single-point or multipoint sampling, or for one or more contaminants.

The analysis train starts with a specially designed 5-micron shielded-filter probe mounted directly in the stack. The heat-traced sampling line is maintained at a temperature high enough to keep the sample gas above the dew point, so that any water vapor remains in the vapor state. The sample is quenched quickly and dried after it enters the conditioning system, without any appreciable loss of SO_2 content. The entire sampling train is built of corrosion-resistant materials to minimize both maintenance and possible contamination.

The cooled gas sample then passes through a series of filters which removes the balance of the particulate matter. Finally it enters the analyzer through a selector valve and flowmeter. Several different analyzers can be provided with a conditioned sample from this system, and the system is provided with a bypass flow to minimize sample transport time. MSA can provide high-reliability analyzers for continuous monitoring of SO_2, NO, CO, CO_2, total hydrocarbons and solvent vapors. The typical unit shown here uses a LIRA® Infrared Analyzer, calibrated for analysis of SO_2 in the 0-2000 ppm range. Zero and span gas test connections are provided for easy calibration check.

For heavy dust-loading applications—BOFs, cement kilns, cupolas, blast furnaces—MSA offers special heated filter systems. There are also pressure switches or gages to indicate plugged sample lines, and automatic back purge of traps, probes and sample lines is provided.

The MSA® Stack Analysis System can be interfaced with any recording, alarm or computer readout; and composition signals can be used with flow rates to calculate mass emissions in pounds per hour. Discuss your needs with an experienced MSA instrument specialist.

For details circle No. 38

Versatile infrared analyzers monitor everything from solvent vapors to carbon monoxide.

MSA introduced the LIRA Infrared Analyzer over 20 years ago, and we find new applications for it every year. One reason is the instrument's unique ability to select a specific component out of a mixture of gases (or liquids) and record its concentration quickly, accurately and dependably over a broad ambient temperature range. Another reason is the flexible design of the LIRA. We can offer a wide choice of cell lengths and materials, peripheral readout equipment and types of housings.

Among the LIRA systems we have supplied for pollution control are:

- A stack analysis system for 0-2000 ppm SO_2.
- Air monitoring network of LIRA detectors for CO.
- An automobile-emissions screening installation where LIRA analyzers are combined with instruments and readout meters for CO, HC, and NO in exhaust gases.

Some typical health-and-safety and process applications in current use include:

- A 5-point CO_2 detection system to protect brewery workers.
- An 8-point system for 0-2000 ppm acetone in air.
- A 10-point system for 0-1000 ppm methylene chloride in air.
- Multipoint halocarbon gas detection and alarm system for 0-3000 ppm $CHCl_2F$.
- A 5-point system for 0-200 ppm of trichloroethylene (in combination with an MSA Model I-500 Combustible Gas Detector).
- Multipoint CO_2 detector for process control in the 15-35% range, on a lime kiln.
- CO_2 detection at 0-100 and 0-1500 ppm range to guard LNG liquefaction equipment from plugging.

These are just a few of the thousands of LIRA analyzers in every type of industry today. There has to be a reason. Check it out for *your* OSHA, stack monitoring, process control or air monitoring problems.

Circle No. 39

Ask us for details.

Get the latest literature on the MSA monitoring instruments described here. Circle the appropriate Reader Service Number. MSA Instrument Division, 400 Penn Center Boulevard, Pittsburgh, Pa. 15235.

CURRENTS

INTERNATIONAL

Sweden has come up with projections of what some pollution control costs from 1975–1980 would be in that country. For sewage treatment, for example, an investment of $446–667 million (based on 1 Swedish Krona = $0.23) would give Sweden's entire urban population tertiary treatment. $222 million more would provide a quaternary filtration step. Municipal solid waste disposal, to give compacting, treatment, and the like, would require $56–67 million. Measures to reduce vehicle exhaust could cost $92 million; industrial pollution control measures $690–805 million, and energy conservation with air pollution control for fossil-fueled district heating and power production, $333 million. Cost figures are in 1974 constant prices.

An international effort, the Middle Atmosphere Program, is to be mounted during 1979–1984. MAP is being designed to study the atmosphere between the tropopause and 100 km that will embrace the stratosphere and mesosphere and the lowest portion of the thermosphere. The major experimental technique will be remote sensing using the U.S. Spacelab and other orbital and geostationary sensors. Sponsors include COSPAR, WMO, IAGA and URSI.

WASHINGTON

Federal, state and local government expenditures for environmental quality control totaled $7 billion in fiscal 1973–74 according to a Bureau of Census report. Of this total, $4.6 billion was spent on water quality control, $2 billion on solid waste management and $297.4 million on air quality control. In October 1974, the various governments employed the full-time equivalent of 225 562 people: 93 842 in water quality control; 124 191 in solid waste management and 7529 in air quality control. These are the latest Bureau figures available.

EPA has found asbestos fibers in the drinking water of Boston, Philadelphia, Atlanta, San Francisco and Seattle. The findings of a 10-city survey are preliminary, Andrew Briedenback, assistant administrator for water and hazardous materials, cautioned, and more sampling must be done. The level of contamination and the source(s) are unclear. Initial samples contained asbestos but subsequent samples have been asbestos-free. The EPA is testing the drinking water of some 30 cities and the results of these surveys should be available in a month or two. In another asbestos matter, a Fort Lauderdale, Fla., building wrecking firm was convicted in the U.S. District Court in New Orleans for violating EPA rules, under the Clean Air Act, for the safe removal of asbestos insulation from a building being demolished.

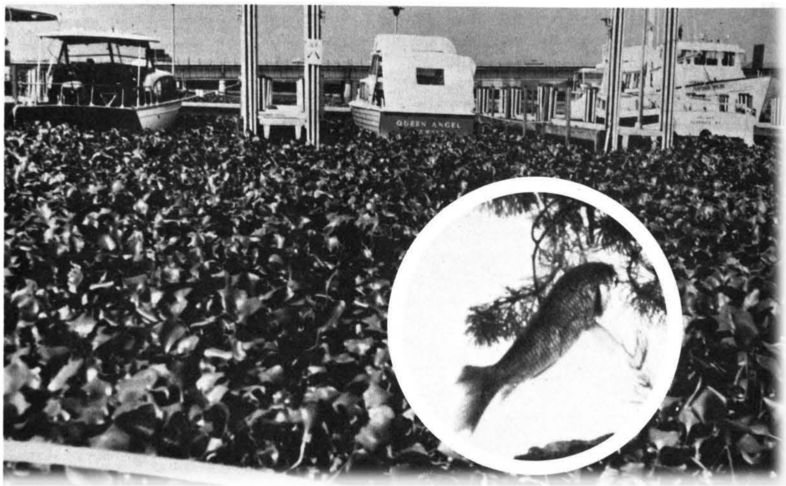
NIOSH has alerted producers of styrene-butadiene copolymer resins, latex and elastomers to potential health hazards associated with synthetic rubber production. The National Institute for Occupational Safety and Health recently held a meeting to assess the problem. Currently, 32 companies with 42 plants scattered throughout the U.S. are known to be involved in the production of synthetic rubber; not known are the numbers of workers exposed to the potential hazards. To date, four cases of leukemia have been reported in production workers in one Texas plant, and an additional three or four possible cases at another Texas plant have been reported to NIOSH. Several types of cancer, heart disease and diabetes mellitus were found in rubber workers in an Ohio plant.

The Army Corps of Engineers denied two of three filling permits for development of Marco Island, Fla. At stake were 2039 acres of mangrove wetlands that the Deltona Corp. (Miami, Fla.) had sought to fill for residential development. In his denial, a significant policy change for the Corps, the Chief of Engineers, Lt. Gen. W. C. Gribble, Jr., said the proposed filling would "constitute an unacceptable adverse impact on this aquatic resource." In another matter, the Corps is using a species of carp, the herbivorous White Amur, to control underwater plant growth. A rigidly controlled large-scale field test is being conducted in Lake Conway near Orlando, Fla. Several state agencies and the Corps will monitor the aquatic ecosystem to determine if any changes occur following the carps' introduction.

Under the Energy and Conservation Act, the Federal Energy Administration is required to set energy conservation targets for the 10 most energy intensive manufacturing industries. The date for which maximum feasible improvements attainable for each industry by January 1, 1980 must be established is December 22, 1976. The top-ranking energy-intensive two-digit SIC industry in the manufacturing category is chemical and allied products. The Manufacturing Chemists Association (MCA) has been consolidating data from chemical companies, and reporting energy conservation achievements to the FEA since 1975. In its most recent report for the calendar year 1975, the MCA declared a 4% reduction in energy consumption, over the base year 1972, for 107 reporting chemical companies.

President Ford signed into law rail legislation that, among other things, directs the Interstate Commerce Commission to investigate the rail rate

Controlling underwater plant growth



structure of recyclable or recycled materials *vis-à-vis* the competing virgin materials (see *ES&T,* May 1976, p 440). The act, P.L. 94-210, the Railroad Revitalization and Regulatory Reform Act, was signed into law in February.

In a move to minimize improprieties in the construction grant program, the EPA has published an audit guide that codifies and updates auditing practices in light of new regulations. The guide, to be used by EPA auditors and CPA firms under contract to EPA, will assist in auditing the grant funds spent in planning, design and construction of wastewater treatment facilities in the U.S. It has been estimated that by fiscal 1977, resources assigned to auditing construction grants will have increased eightfold and that the types of audits performed will be expanded to include pre-award in addition to the interim and final audits now performed.

STATES

California is taking a look at how environmental regulations effect its energy needs. Established about one year ago, California's Energy Resources Conservation and Development Commission (CERCDC) is required to submit a comprehensive report to the governor and the legislature early next year. With an operating budget of $10 million for fiscal year 75 and $23 million for fiscal year 76, and 275 staffers, CERCDC is contracting for more than 15 studies. The environmental regulations study is being performed by the Stanford Research Institute; other projects will be looking at European experiences and experiments in electric utilities' rate structures, and energy options for major industries in California whose natural gas deliveries are being curtailed.

Two thousand acres of Oregon's coast have been set aside as the nation's first estuarine sanctuary. Deeds to the acreage on the South Slough of Coos Bay were passed to The Nature Conservancy from Georgia-Pacific Corp. Oregon and the Conservancy are still negotiating with 33 other property owners to bring the total sanctuary acreage to 4000 acres. Eventually the sanctuary will revert to the Oregon State Land Board and become a mecca for saltwater and other wildlife studies.


Michigan governor Milliken

Michigan's Gov. William Milliken recently signed into law legislation banning polychlorinated biphenyls for all purposes other than electric transformers and capacitors. The act prohibits the manufacture, sale, and use of products containing more than 250 000 ppm of PCBs by July 1, 1976 and 1000 ppm by January 1, 1977. This concentration is further lowered to 100 ppm by January 1, 1978, but the director of the Dept. of Natural Resources may prescribe lower maximum concentrations if public health and safety is deemed in danger. The law also requires proper labeling of products containing PCBs and prohibits the disposal of solid or liquid waste resulting from PCB use except in conformity with rules to be established at a later date.

Implementation of Chicago, Ill.'s transportation control plan has resulted in a 14% decrease in carbon monoxide being discharged via vehicle exhausts in the city's downtown area. This decrease translates to 14 tons/day of carbon monoxide not being discharged to the air. The control plan bans on-street parking on selected streets in the downtown area.

Three southeast Texas counties are the beneficiaries of space age technological fallout. The Gulf Coast Waste Disposal Authority, responsible for sewage treatment in Harris, Galveston, and Chambers counties, is cooperating with NASA's Johnson Space Center (Houston, Tex.) and NASA's contractor, the Boeing Co. in conducting a year-long experiment that will monitor that area's treated water quality. NASA and Boeing have built a trailer-mounted automated water monitoring system whose evaluation begins this month. This system will electronically monitor dissolved oxygen, total oxygen demand, TOC, bacteria, chlorides, temperature, turbidity, hardness and pH, among other parameters, in the treated water. The system will process data from 20 commercially available water sensors and four NASA-developed sensors.

Arizona and ERDA have signed the first federal/state energy cooperative agreement. Under the Memorandum of Understanding, which remains in effect for five years, Arizona may identify regional needs, skills and resources in energy-related matters and then submit specific proposals to ERDA for funding, technical assistance or other support. The agreement provides the framework under which the development of new energy sources and the improvement in energy conservation can take place.

Washington's new computerized air monitoring and reporting system completed its first year of operation, a fact reported in the 1975 Annual Report of the state's natural resources and recreation agencies. This system continuously collects data from six primary air mass stations and sends the information to the Dept. of Ecology at Olympia. A survey undertaken during the report year, an assessment of the impact of the 1972 State Model Litter Control Act, showed a 60% reduction in litter statewide. Also during the report year, the Dept. of Ecology adopted motor vehicle noise regulations effective July 1, 1975, and environmental noise regulations effective September 1975.

MONITORING

How do you assure that the unleaded gasoline you sell meets EPA requirements? One way is with a Varian (Palo Alto, Calif.) Techtron 200 atomic absorption spectrophotometer (AAS) installed in a motor home which is also a mobile laboratory. Ron Sublett and Dan Cameron of Ashland Oil Co., Inc. (Ashland, Ky.) travel in such a motor home-cum-laboratory to Ashland's more than 1400 service stations, and use the Varian AAS to perform fast, accurate quantitative analyses of lead in "gas," in order to assure quality. "Gas" is monitored for lead contamination from refinery to pump. Sublett calls the system "expensive, but one that has produced a real savings in time and money." He has logged thousands of miles in doing field gasoline tests.

Checking lead in gasoline

TECHNOLOGY

Performance of the powerful sodium-sulfur (Na-S) battery could be enhanced by new ceramic membranes, the most promising of which seems to be a zirconium phosphosilicate, the ACS Centennial Meeting heard. H. Y.-P. Hong of the Lincoln Laboratory of Mass. Institute of Technology (Lexington, Mass.) sees this membrane as solving some of the problems hindering development of the lightweight, rapidly recharged Na-S battery, especially for use in electric automobiles. The membrane's job is to allow sodium atoms at at least 300 °C, which become positively charged, to pass through while it filters out electrons. The new membrane allows passage in all directions, improving efficiency; previous membranes cut efficiency by allowing sodium passage in only two directions.

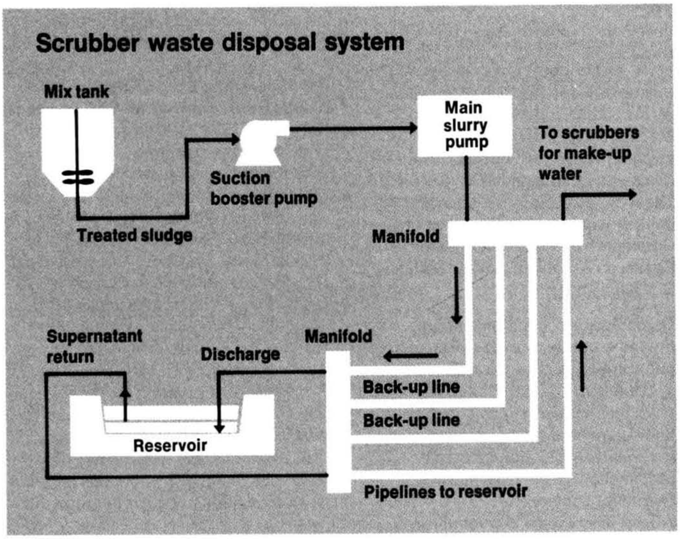
A demonstration garbage-to-fuel plant of 10 tpd, or more (eventually 30 tpd) should be on stream at Baytown, Tex., this month. Built by Wallace-Atkins Oil Corp. (*ES&T,* March 1974, p 197) for J-Mar Energy, Inc., of Baytown, the plant would start by using waste bark, and then process municipal waste from a suburb of Houston, Tex. According to Lyle Atkins of Wallace-Atkins Oil, the plant produces hydrogen by a highly proprietary catalysis-electronic method that breaks down organic waste and reforms it into desired organic fuels and char in a five-reactor system. Atkins told *ES&T* that each reactor uses 0.27 W of power, produces no air, water, or noise pollution, and yields glass and metal values.

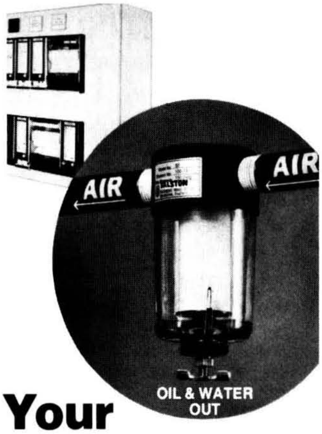
Disposal of wastes from a lime wet scrubber system on the world's largest coal-fired power plant that uses one is being accomplished by means of the Calcilox sludge stabilizer technique of Dravo Corp. (*ES&T,* July 1975, p 622). The scrubber, which started up in May, and is to remove about 99.5% of particulates and 92% of SO_2, was supplied by Chemico Air Pollution Control Co. to Pennsylvania Power Co., which will use the Dravo stabilizing technique. The scrubber and sludge stabilization systems work at Unit 1 of Penn Power's Bruce Mansfield Power Generating Station (Shippingport, Pa.). The sludge will be slurried six miles to Little Blue Run Valley, after Dravo system treatment, and form an inert, soil-like material behind the largest earth and rockfill embankment in the eastern U.S. Aged, the material could support up to 4.5 tons/ft^2.

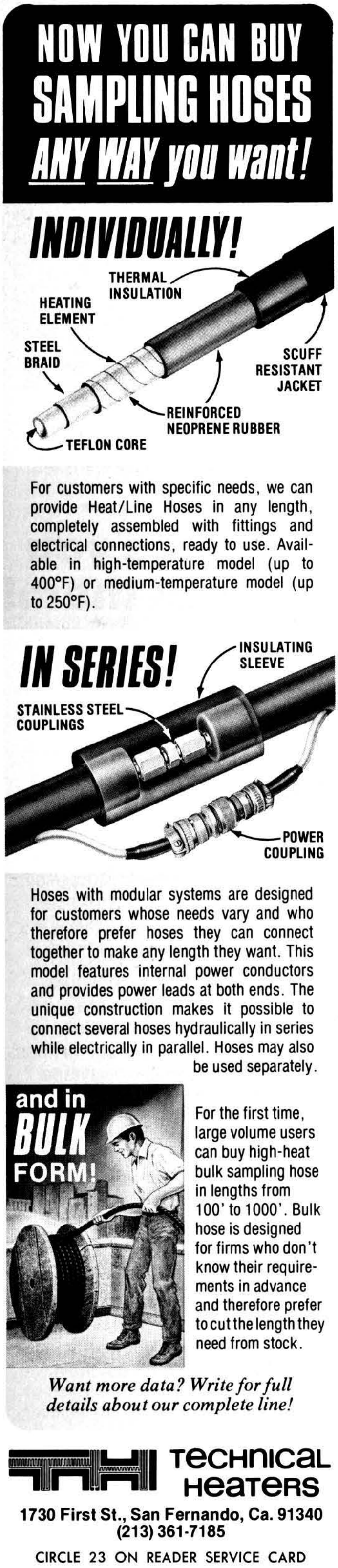
To handle hard-to-treat propylene oxide (PO) wastewaters, Malcolm Pirnie, Inc., working at the Brandenburg, Ky., plant of Olin Corp., devised a system that adjusts pH of PO wastewater with carbon dioxide and settling of limestone solids. PO wastewaters must then be cooled and equalized, as much non-PO wastewaters. The two wastewaters are then mixed and sent to activated sludge aerators, treated biologically, flocculated, and clarified; effluent can be discharged. Biological waste solids and limestone precipitate are gravity-thickened, blended with lime sludge and fly ash, dewatered by vacuum filters, and disposed to a clay-lined landfill site with a 6.5-yr life. The idea is to meet 1977 rules of average 2500 lbs/day of BOD_5 (peak, 4870 lbs/day) and 4165 lbs/day of total suspended solids (peak, 8370 lbs/day).

High-density ammonium nitrate is produced with less expensive pollution control system than prill towers require. This production is now commercial for the first time in the U.S., with a facility that Ferro-Tech, Inc.

Scrubber waste disposal system







designed and built for a diversified producer of nitrogen fertilizers in the Southwest. The plant's design rate is 400 tpd of 6 × 12 mesh granular product. Concentrated hot melt of ammonium nitrate is combined with cooled granular recycle (2:1 recycle-product ratio) in a hooded and vented inclined plane that has an oscillating scraper. Pollution control is by a system incorporating wet scrubbers. Ferro-Tech says that the plant provides higher product quality at lower capital and operating costs.

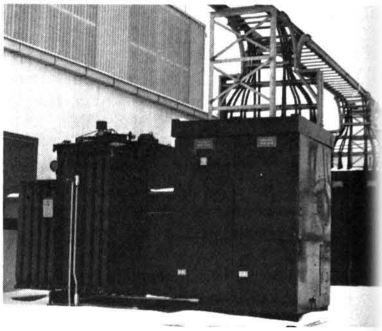
The first continuous, integrated pilot plant conversion of coal to synthetic gas in the U.S., was demonstrated at Rapid City, S.D., by Continental Oil Co. (Conoco, Stamford, Conn.). The product was pipeline-quality gas for residential and commercial use, and was made from raw lignite coal from North Dakota. The plant was developed by a Conoco subsidiary under contract with ERDA and the American Gas Association (AGA). Recently, the plant ran for more than 7 days at full design capacity of 32 tpd of lignite. Advantages are moderate pressure requirements, high thermal efficiency, production of synthesis gas amenable to methanation, and absence of phenol or tars produced. Full carbon utilization, simplified sulfur cleanup, and no need for an oxygen plant are also features of the system.

INDUSTRY

According to The Electric Utility Industry Clean Air Coordinating Committee, the Clean Air Act and amendments to it could cause sharp increases in electricity bills. "No significant deterioration" (NSD) regulations for power plants being built between 1975–1990 would add more to these bills. Moreover, a nuclear moratorium could raise bills in lower-cost areas (West and Northeast) to equal higher costs (central regions). For example, in the Northeast, the Clean Air Act could add $37/household/yr to electric bills, and NSD could add $2 more. In Texas, by contrast, Clean Air could add $1765, and NSD, $860 more. These figures, based on constant 1975 dollars, were compiled for the Committee by National Economic Research Associates (Washington, D.C.) in a study.

Osmonics, Inc. (Hopkins, Minn.), has helped a candy manufacturer reclaim sugar from his plant's wastewater, according to D. Dean Spatz, Osmonics' president. In recognition of its achievement in the application of reverse osmosis (RO) for sugar reclamation in the food industry, Osmonics received the Putnam Food Award. This award is given every 2 years to recognize innovations introduced over the previous 2 years, and is based on the innovative contribution by the manufacturer, as well as the breadth of application, and significance to the food industry. Osmonics is also in the pilot stage of using RO to recycle cooling tower and boiler blowdown, Spatz said.

Dow Corning has developed an alternative to PCB-containing transformer liquids (askarels) that will be found in a silicone liquid (*ES&T*, February 1976, p 123). This fluid is known as Dow Corning 561 transformer liquid, which the company says is an environmentally safe alternative to askarels used in power transformers where fire safety is essential, and which is being offered commercially for the first time. The liquid is chemically identical to polydimethyl siloxane liquids made for almost 30 yrs by Dow Corning. What is new are the very tight specifications for electrical use to which the liquid is compounded. The firm says that "561" ratings are good to excellent for fire/explosion hazard, and excellent for electrical performance (dielectric) and environmental safety.



Transformers: Silicones, not PCB's

Hoechst-Uhde Corp. (Englewood Cliffs, N.J.) received an EPA contract for a feasibility study for converting vinyl chloride monomer (VCM), chlorinated solvent, and other chlorination process wastes into carbon tetrachloride (CCl_4), by use of the Hoechst AG (Frankfurt, W. Ger.) "Chlorolysis" process. The study would involve a regional concept, and would allow for wastes from process plants, as well as toxic wastes containing oxygenated compounds. Also, by-product hydrochloric acid would be converted into chlorine for recycling to the Chlorolysis process. This technology is now in use by Hoechst AG, and a new plant (Frankfurt, Ger.) with a capacity of 50 000 metric tons/yr of product is to be in operation this year.

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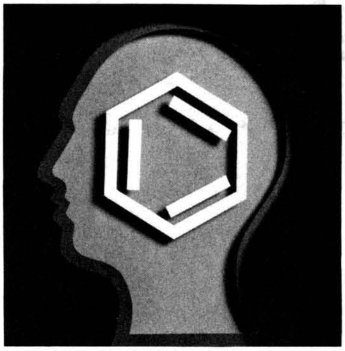

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CIRCLE 20 ON READER SERVICE CARD

OUTLOOK

The call for water reuse

Why the long face? That despondent feeling? Have the water pollution control (wpc) laws and regulations, especially P.L. 92-500, been getting to you? Well, you cannot expect to get much help with your problem from alcohol or aspirin, but Joe Moore of the University of Texas/Dallas, former program director of the National Commission on Water Quality (NCWQ), suggested a course you can take. He reminded the general session of the Water and Wastewater Equipment Manufacturers Association's (WWEMA, McLean, Va.) Fourth Industrial Pollution Conference and Exposition that if you feel that changes in P.L. 92-500—or other laws, for that matter—are in order, you should talk to your candidates for public office while they are still in candidate status, this being an election year. Candidates, Moore noted, listen to what people, especially prospective constituents, have to say. After elections, a defeated candidate would be of little help, and a successful candidate, i.e., Congressman, Senator, Governor, or what have you, becomes far more difficult to approach.

The WWEMA conference at which Moore made this cogent point was held at the end of March at Houston, Tex. Its general theme was resource recovery—case histories for the 1970's; however, many other topics concerning technology, regulations, and advances in wpc were also covered. Another important subject discussed was whether or not it is really economically feasible to try to reach 1983, or "best available" (BATEA) goals, or whether it is more advisable to hold to 1977 "best practicable" (BPCTCA) milestones, and give economics and technology a chance to catch up and move ahead. About 1300 people heard more than 50 papers presented at the generally, though not exclusively, industry-oriented conference, and had a chance to see over 70 exhibits.

Will and wealth

Converting pollutants to non-pollutants is an exercise in changing matter, which one can do, as opposed to creating or destroying matter. However, as conference chairman Allen Baker of Hercules, Inc. (Wilmington, Del.), reminded the general session, this changing of matter requires "will and wealth," with wealth being the challenging word. He observed that no responsible company throws away wastes that it can use or convert to something useful. The question that arises, he noted, is, "Have you made the product more valuable than the cost of your investment in waste collection and conversion?"

Baker characterized wpc, for example, as a "sacred domino." However, in the present industrial/economic climate, as energy is also a sacred domino (and almost never can one convert waste without using energy), so is the profit picture. He said that today's sacred domino could be tomorrow's sacrifice, and that balancing this sacredness and need to sacrifice becomes a moving target, particularly if the conversion of wastes—which takes dollars and energy—is undertaken to make useful by-products, or simply to meet environmental and social goals.

Should BATEA be delayed?

One general consensus appeared to evolve from the conference, and that is that 1983 "best available" or BATEA interim goals are unrealistic, at least when viewed from the economic vantage point of the present. Fortunately, P.L. 92-500 provided for creation of the NCWQ, which has completed a 2.5-yr, $17.2 million study aimed at developing mid-course corrections.

Conference chairman Baker
"Balancing sacred dominoes"

Joe Moore made it quite clear that *standards* for 1983 should not be rolled back. What he recommended was a rollback of the 1983 *date,* possibly for 5–10 years, provided that limitations are revised to update 1977 "best practicable" (BPCTCA) requirements. Nevertheless, compliance with 1977 standards, maybe with extensions (to 1980, for example), or even waivers on a case-by-case or category-by-category basis is called for, and industry seems to "buy" this concept, perhaps with threats of contention or expressions of fatalistic resignation from some quarters. Moreover, Moore said that toxic pollutants should be controlled by no later than 1980.

Moore's general description of P.L. 92-500, however, was somewhat less than complimentary. He complained that the statute is complicated, and poses a critical risk that the law's application will collapse "for lack of administrative ability," and especially because of difficulties brought about by decisions rendered in recent court cases. He warned that the administrative structure cannot sustain the actions that EPA has taken up to now, and continue to push ahead. He also observed that water quality improvements have stemmed principally not from P L. 92-500, but from previous laws and programs, and that no assessment of the benefits of 92-500 can be made without careful monitoring.

Voices from industry

Comparing P.L. 92-500 to the Apollo moon program, Arthur Goeschel, president of Calgon Corp. (Pittsburgh, Pa.), a major carbon systems supplier, likened striving for wpc goals to a trip to Jupiter (1977), to Pluto (1983), and to the nearest star (zero pollution discharge goal or ZPD, 1985). Citing calls for re-examination of the law, Goeschel predicted that it will be amended with BATEA requirements substantially modified or eliminated. He expects that BPCTCA will, for all practical purposes, become the standard for a considerable number of years, and that the ZPD goal will essentially be dropped as impractical.

Goeschel foresees that these changes

It was heard loudly and clearly at the WWEMA conference this year. So were recommended mid-course corrections for P.L. 92-500

"will not spell disaster for the wastewater equipment industry." He noted that whatever happens to P.L. 92-500, "there can really be no turning back the goal of creating a better environment." Goeschel said that this goal, however, would be approached from a "sounder philosophical base," and that the crux of this philosophical base is to aim for elimination of environmental health hazards, rather than for aesthetic objectives.

The equipment user's view—that of a principal chemical company—was presented by R. E. Chaddock, executive coordinator of environmental affairs for Hercules, Inc. Chaddock called upon equipment supplier to stand ready to render quick, reliable assistance when equipment goes awry. He complained of how his own company was not only embarrassed—but also fined—for noncompliance when repair help was not rapidly forthcoming, and echoed plant personnel suggestions that perhaps the supplier should share in the responsibility when equipment proves to be at fault. Chaddock recommended closer coordination between suppliers, users, and regulatory agencies to nip wpc problems in the bud before they get out of hand.

As for P.L. 92-500, Chaddock told the conference that after 1977 goals are reached, the chemical industry recommends

- reassessment of U.S. waters to determine the extent to which required water quality has been achieved
- where the necessary quality is achieved, no further wpc technology need be added, except to maintain that quality
- where the necessary quality is not achieved, wpc facilities should be installed to achieve required quality.

Chaddock said that this approach would be the most cost-effective, and called for a cooperative relationship between EPA and the chemical industry, rather than the adversary approach that results in so much court action and wastes government and industry manpower.

Resource recovery

As stated above, one main conference theme was resource recovery, and Alex Himsley, president of Himsley Engineering Ltd. (Toronto, Canada) explained how ion exchange can be made more efficient in recovering metals, recycling water, and treating turbid liquids without clarification. Himsley's approach involves a novel design of a fluidized-bed ion exchanger that ensures equal residence time in the system for all resin particles, regardless of their size or settling rate.

Resource Conservation Co. (RCC, Renton, Wash.) is marketing a vertical-tube, falling-film vapor-compression evaporator that purifies up to 98% of the water in a waste stream for recycling to an industrial process. Typical installations require less than 90 kWh/1000 gal of recovered water—an energy reduction of at least 25%—and wastes are reduced to a slurry of less than 3% of original waste stream volume, according to RCC. The company's system is in use with cooling towers, and is being tested in pulp and paper plants. Chemical recovery from dilute streams is also possible, according to the firm, which says that sales and orders for the system now exceed $13 million.

For ammonia recovery, CH2M Hill (Redding, Calif.) announced up to 99% efficiency (for 10–6000 ppm) by a closed air cycle stripping and acid absorption system with no calcium carbonate scaling, temperature, or air pollution problems. On the other hand, Houston Research, Inc. (Houston, Tex.) explained to the conference how ozone can be used to break metal cyanide complexes, and collect resultant metal oxides in a sludge with a view to metal recovery.

Monitoring and treatment

For monitoring simplification, General Automation, Inc. (Anaheim, Calif.) took the position that special minicomputers can streamline wastewater monitoring, analysis, control, and treatment applications, even to the operation of devices such as controlling values and actuators. The Sparling Division (El Monte, Calif.) of Envirotech Corp., described its new obstructionless flow meters, and Hydrolab (Austin, Tex.) told *ES&T* that it should be marketing a compact monitoring system that can handle numerous parameters, while it eliminates the need for a whole array of different monitoring instruments.

On the municipal front, Aubrey La Fargue, assistant manager of the Surface Water Section, Houston Public Works Department, told *ES&T* that the $6 million Houston Water Treatment Plant Alum Dewatering Facility (built with no federal funds) is working on doubling its present daily solids-handling capacity of 60 000 lbs/day. Also, the conference was reminded that the world's largest construction program, managed by EPA's Office of Water Program Operations, has obligated $8.4 billion as of last December 31, leaving $9.6 billion to be obligated, pursuant to P.L. 92-500.

Some commission recommendations

- **Maintain the July 1, 1977 date for compliance with uniform treatment requirements by industry and publicly-owned treatment works, but provide some flexibility to grant extensions, and even waivers, on a case-by-case and category-by-category basis.**
- **Keep the 1983 goals, but postpone requirements for uniform technology application for 5–10 yrs, pending assessment of water quality improvement progress and results by a new NCWQ by 1985.**
- **Meet 1983 goals by application of 1977 requirements to all dischargers; revisions of 1977 limitations; immediate imposition of limitations for elimination of toxic pollutants in toxic amounts; new source performance standards for all new point source discharges; upgrading of permits for discharges into waters of limited quality; and application of control measures to combined sewer overflows, urban stormwater runoff, and agricultural and non-point sources.**
- **Decentralize regulatory and administrative functions of the national program by selective certification of states, if their plans and programs for point and non-point source control are satisfactory.**
- **Assure 75% federal financing for priority treatment needs ($5–10 billion/yr) for 5–10 yrs.**
- **Redefine pollutant discharge elimination goals to stress conservation and reuse of resources.**
- **Allow flexibility in applying treatment or control measures to irrigated agriculture after an inventory of the problem, and support salinity alleviation projects to reduce salt loads from sources other than man's activities.**

It might well be that one day, municipal and industrial water treatment will provide ZPD. Such a situation would, of course, be ideal. However, this goal, now slated for 1985, will probably not be achieved until technology provides economical means of total water recycling and profitable conversion of polluting wastes to useful by-products. JJ

Green plants as solar energy converters?

Economic, technological and environmental factors make fuels and food from wastes and biomass viable alternatives to fossil and nuclear fuels

In the protoplasmic muck aeons ago, Nature learned how to tap the sun's radiant energy and re-package it into more usable energy forms—wood, coal and oil. And ever since he learned to make fire by rubbing two sticks of wood together, Man has thoughtlessly been squandering Nature's bioenergy gifts. These once-abundant carbonaceous fuels are becoming scarce, and Man must now search for renewable alternative sources to support his civilization.

At two recent meetings—one held in Florida this past January and the other in Washington, D.C. in March—the exploitation of untapped energy sources was discussed. Concepts put forward included the development of terrestrial and oceanic energy farms—the intense "harvesting" of energy through the process of photosynthesis—and the utilization of urban and industrial wastes, and agricultural and forestry residues for fuel, food and chemicals.

The bioconversion process, a two-step procedure, simply ihvolves the creation of biomass via photosynthesis, and the subsequent transformation of this matter into gaseous/liquid/solid fuels to provide heat and electricity. Enzymatic hydrolysis, anaerobic fermentation, pyrolysis (destructive distillation) and direct combustion are the basic conversion processes for which much of the technology is already known. More exotic technologies such as biophotolysis may become feasible in the future.

According to EPA estimates, solid waste alone could supply between 1–12%, depending on the economics, of the nation's energy requirements for the near- and mid-term future, and biomass (organic matter grown for energy) has an even greater potential, perhaps making the U.S. totally independent of foreign energy sources over the long term.

The potential total energy production from biomass has been variously estimated at a conservative 3 quadrillion Btu's (quads) annually by the year 2000 and 10 quads by 2020 (ERDA's Solar Energy Definition Report, 1975), to a high of 15 quads in the year 2000 (Project Independence Report, 1974). And once the production and conversion problems are ironed out, the potential for bioconversion appears to be limited only by the public's perception of future energy alternatives.

Waste-as-fuel technologies

Theoretically, bioconversion techniques can simultaneously solve, or at least minimize, waste disposal and the attendant pollution problems while providing solid supplemental fuel, or new conversion products—liquid or gaseous fuels, sugar, protein and fertilizer. These man-designed technologies may rid cities of their burgeoning solid wastes and, at the same time, open up new sources of revenue.

The magnitude of urban waste generated annually is overwhelming. An EPA estimate places the quantity at 135 million tons/year, of which approximately 80% or the equivalent of 400 000 barrels of oil is in a form suitable for energy recovery. According to Dun & Bradstreet, the recovery of energy and materials will be the nation's number one growth industry in the last quarter of this century.

Waste-as-fuel technologies are available for the prudent utilization of those commodities now thrown away. For example, waterwall incineration is being used in the Chicago Northwest Incinerator, modeled after the Martin incineration system widely used in Europe; in the Saugus, Mass., refuse-energy plant soon to be completed; and in the fully operating Nashville, Tenn., thermal transfer unit.

Another technology—prepared waste as supplementary fuel for co-firing with coal or oil—has been successfully demonstrated at the St. Louis/Union Electric plant (see *ES&T,* May 1976, p 430), a project that is soon to be expanded into a profit-making commercial venture. And this very same technology is spreading to Ames, Iowa, and Chicago, Ill. A variant method—solid waste co-combusted with sewage sludge—is being tested, under EPA funding, at the St. Paul/Seneca Treatment Plant Sludge Incinerator. And the investigation of fluidized-bed combustion, again under EPA sponsorship, is now underway.

Another physical process, pyrolysis, the destructive distillation of wastes to produce gases, oils and char for use as boiler, residential-heating and motor fuels, is being demonstrated in Baltimore, Md. (see *ES&T,* February 1975, p 98), Charleston, W.Va., and San Diego, Calif.

Slow but sure

Biological processes available to convert solid wastes to useful products include fermentation and enzymatic hydrolysis. Anaerobic digestion can transform organic solid wastes to methane-containing gases. Under an ERDA contract, design and construction plans for digesting 50–100 tons/day of municipal solid wastes are being drawn up by Waste Management, Inc. at its Pompano Beach, Fla., facility. The Institute of Gas Technology (IGT) has built a 400-liter digester at its Chicago facility that is being used to demonstrate the feasibility of accomplishing biogasification of municipal solid waste and sewage solids to a methane-rich product gas. IGT's project is at the pilot-plant stage.

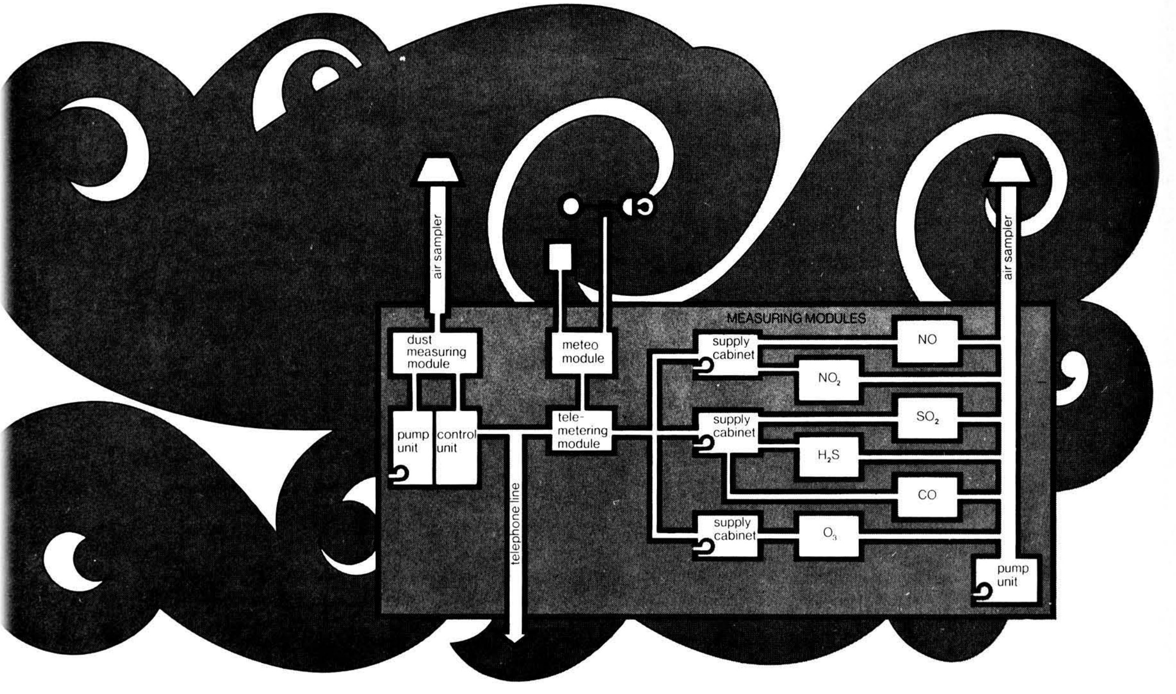
A bench-scale effort at the Dept. of the Army's Natick (Mass.) Laboratory is, with EPA support, being conducted to demonstrate the feasibility of enzymatic hydrolysis of the cellulosic materials found in the urban waste stream (see *ES&T,* November 1975, p 1011). Here, the conversion product is glucose, which can be further manipulated to a single-cell protein or ethyl alcohol.

Certain industries, sugar refining and paper products, for example, are reusing, albeit in an altered form, their formerly discarded wastes as a means of reducing both their pollution problems and their dependence on externally obtained fuels.

In pursuit of Btu's

Preliminary studies are underway to estimate the quantities of forest, field crop and animal wastes potentially available for bioconversion. Institutional, technical, economic and environmental variables associated with the large-scale conversion of these residues to fuels, fertilizers and chemicals are also being delineated.

To minimize their disposal headaches, lumber companies are using most of the slash and mill residues that they formerly discarded to heat and power their mill operations. These companies are even studying the economics and ecology of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uprooting the stumps and roots that now remain after trees are toppled; they hope to be able to use these "wastes" as fuel directly or as the feedstock for other fuels and chemicals.

The biogasification of animal wastes by using small-scale, on-site digesters to produce methane gas for cooking and lighting, and a nutrient-rich residue that can be used as a feed supplement for ruminant animals or as a fertilizer, is a technology being considered for farms in the U.S.

Elsewhere in the world, a cow-dung biogas plant, the Gobar Gas Plant, was built in India in 1939. Today, India is considering the installation of 100 000 of these farm-size digesters. China already has about 500 000 in operation, and Korea is installing 50 000.

Energy farming

One side of the bioconversion coin, the better utilization of civilization's wastes, would add only incrementally to near- and mid-term energy supplies. The flip side of the coin, energy from biomass, would offer the most significant future source of fuels. An intentional increase in the worldwide rate of carbon fixation could be achieved through the establishment of land and open-ocean farms. The intense cultivation of rapidly growing plants and trees such as canes and conifers, adjunctive to existing agricultural and forestry operations or as de novo energy-farming enterprises, could serve as energy feedstocks. Frequently harvested, this biomass could be converted to fuels, sugars and proteins.

Fresh water environments could also be used for the aquaculture of algae and the nefarious water hyacinth. NASA has shown that the hyacinth, once thought only to be a fouler of water ways, is able to "digest" sewage and can thus help clean up sewage lagoons. Harvested, dried and ground into meal, these plants can be blended into corn sillage and fed to cattle. Alternatively, the harvested hyacinths can be converted, via fermentation, to methane gas. The hyacinth, now man's bane, may yet turn into a booming industry.

Large floating artificial meshes or rafts of plastic lines have been used as the "land" on which marine life forms have been grown. The rapidly growing giant California kelp, sargassum and plankton have been shown to be suitable feedstock for the production of methane gas, fertilizers, chemicals, and food.

Although the ability to grow biomass for energy has been proven, the economics of energy farming—both the direct and indirect costs—still need to be carefully worked out. And although major environmental benefits may accrue from the use of biomass as the energy source in lieu of the traditional hydrocarbon fuels, studies are needed to assure that adverse effects are not inadvertently introduced.

Urban and industrial wastes
- **Solid wastes**
- **Sewage sludge**
- **Process discharges**

Agricultural & forestry wastes
- **Crop residues**
- **Manures**
- **Slash**
- **Mill residues**

Land & fresh water energy farming
- **Field crops**
- **Trees**
- **Pond and lake plants**

Open ocean farming
- **Seaweeds**
- **Plankton/fish**

Gaseous fuels
- **Methane**
- **Low-Btu gas**
- **CO/H_2**

Liquid fuels
- **Alcohols**
- **Oils**

Solid fuels
- **Refuse-derived fuels**
- **Plant residues**
- **Logs**
- **Char**

Associated products
- **Fertilizers**
- **Animal feeds**
- **Sugars**
- **Chemical feedstocks**
- **Minerals**

Anticipated products
- **Hydrogen**
- **Fixed nitrogen**
- **Special hydrocarbons**

The problems, benefits

Some potentially grave problems, whose resolutions may be difficult if not impossible, can even now be surmised. For example, the reflectivity over huge areas of the earth's surface may be altered by rapidly growing plants raised for biomass. To fertilize the surface-floating ocean farms, the nutrient-rich waters of the cold ocean depths could be pumped to the surface. Will world weather modifications occur as a direct result of altered temperature and reflectivity over enormous terrestrial and oceanic areas specifically dedicated to energy farming?

If large land masses are devoted to single crop horticulture, will the absorption of moisture in these areas be modified with accompanying loss of nutrient-rich soil and increased water pollution? What happens to the established ecological structure in areas whe
crop farming is introduced? If
merly used for ground cover
harvested for bioconversion,
erosion be accelerated?

To profitably establish oce
huge areas of the marine enviro
have to be utilized. Is this the b
the world's oceans? Even mo
can international cooperation
massive scale be achieved?

On the benefits side, the use
and biomass grown especially
most definitely reduces air, wate
pollution. If prime land is set as
growth of edible crops and l
shelter and other essential purp
energy crops will have to be
marginal or infertile land. The co
benefit is then reclamation of
or eroded lands. It is even pos
with prudent planning, the dev
of energy farms will have the
effect of stabilizing global we
terns.

Certainly, bioconversion tec
offer the assurance of future fuel
chemical supplies. For the U.S.
highly industrialized countries,
both the petroleum leverage
nations now enjoy, and the ha
sociated with advanced coal an
technologies—especially the d
of fissionable materials. For
World countries, bioconversi
small farms and villages self-s
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A bright sunny future

Public awareness of the
hazards inherent in nuclear en
nologies is resulting in, if not
groundswell against, at least
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production. Advanced coal tec
while they permit the expanded
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And so, with the problems att
increased utilization of coal, th
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possibility of a non-nuclear futur
may yet witness the enhanced
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its brightest, bioconversion offe
renewable and clean sources

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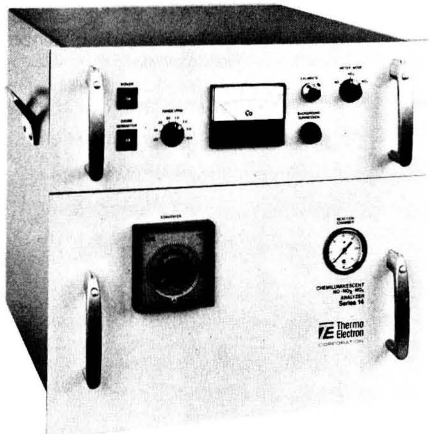


Model 14D NO_X

Love 'em

CIRCLE 17 ON READER SERVICE CARD

NOAA oceanographers are getting hard data that should help to resolve the controversy concerning what might result from . . .

. . .Dumping sewage sludge in the ocean

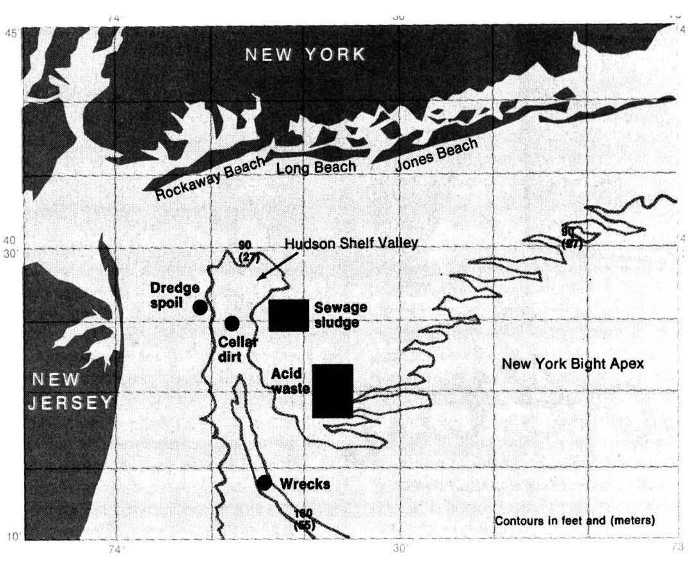
There it is—a huge blob of noxious dark sludge oozing along the bottom of the ocean toward Long Island and New Jersey beaches like the pseudopods of a monstrous, slimy amoeba. Authorities have closed the beaches indefinitely, forbidding any taking of fish or shellfish; large areas of adjacent waters are biological deserts, and—

Hold everything! As you were!

This scenario should not occur, NOAA Cdr. R. Lawrence Swanson who heads the New York Bight Project (NYBP) of the Marine EcoSystems Analysis (MESA) Program, based at Stony Brook, N.Y., told *ES&T*. Indeed, a short time after sewage sludge is dumped at the designated New York Bight site, there is very little evidence that the sludge was ever dumped there. To be sure, organic material-rich muds are detected, but they may be composed partly of dredged material (DM), or even material of natural origin, as well as sewage sludge. Most of this material is found to the north and west of the sewage sludge dump site, in a topographic depression at the head of the Hudson Shelf Valley. "Contaminating materials cannot necessarily be specified as having come from sewage sludge, or, for that matter, other waste materials," Cdr. Swanson said.

Volatile issue response

MESA became an operating entity under the National Oceanic and Atmospheric Administration (NOAA) in 1972; the MESA/NYBP started up in August 1973. One of the original MESA missions was to assess effects of marine contamination, with emphasis on ocean dumping. However, by December 1973, sewage sludge dumping (SSD) had become a very volatile issue, the response to which led to allocation of more dollars to SSD studies than were originally planned. This fiscal year 1976, \$3.4 million are earmarked for the project, of which approximately 75% was for ocean dumping-related research. All told, the project directly employes about 20 people, (both uniformed NOAA Corps and civilians). It depends heavily on scientific involvement of other NOAA laboratories on the East Coast. Close cooperation exists between NOAA and the EPA, especially EPA's Region II office (N.Y., N.J., P.R., and V.I.). The MESA/NYBP operations office is at Floyd Bennett Field (Brooklyn, N.Y.).

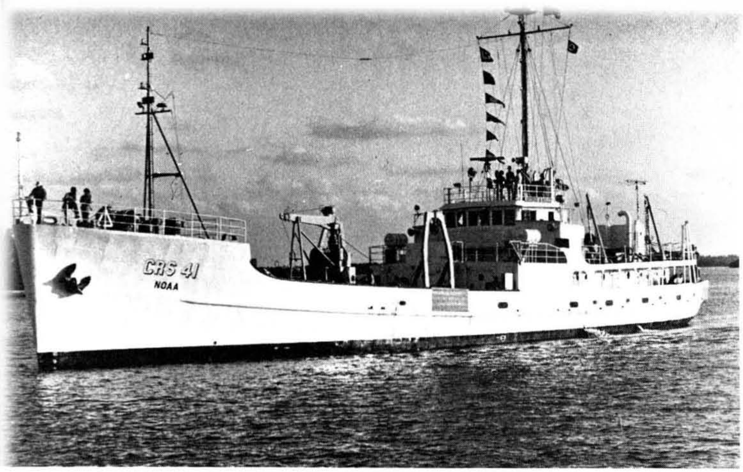


A study such as the MESA/NYBP involves intensive oceanographic surveying, and the NOAA Ship GEORGE B. KELEZ acts as the main platform for such surveying and data acquisition. From the KELEZ, up-to-date electronic instruments, built by InterOcean Systems, Inc. (San Diego, Calif.) provide conductivity (salinity), temperature, light (turbidity), depth, dissolved oxygen (DO), and pH data. Also, the ship sends down and retrieves probes with Rosette samplers made by General Oceanics (Miami, Fla.). These samplers furnish temperatures by means of reversing thermometers, and water samples collected in Niskin bottles. Data readouts are on printed paper and "mag" tape; water goes to the chemistry laboratory.

In addition to shipboard data acquisition, instruments on buoys, capable of being left unattended for as long as 90 days, acquire salinity, pressure (depth), temperature, and current velocity data that are made computer-compatible. Time is given in Greenwich Mean or "Z" Time, and positioning is by a Raydist (Hampton, Va.) four-party range-range, or circular grid system. A new type of buoy system, to gather data in real-time, with one time "flag"/h, is being built and evaluated by NOAA's Electronics Development Laboratory (Rockville, Md.), with a view to synoptic data collection that would also involve much more intensive water and sediment quality monitoring than is being done at present. Data will be made publicly available.

Why is there no dark blob?

Cdr. Swanson explained why. He told *ES&T* that the sewage sludge at the New York Bight Apex site consists of about 5% solids and 95% water. Its density is less than that of water. The material does not sink as a unit; rather, it fractionates and is distributed throughout the water column, rapidly losing its identity. For this reason alone, the dark blob will be found only in scare stories. Another reason is that the dumped sewage sludge is carried off by currents and eddied about. Thus, one can hardly identify sludge, much less look for the feared dark blob, even though in 1974, for instance, 131 million ft^3 of raw and digested sewage sludge, 138 million ft^3 of DM, clean earth, and fly ash, 80 million ft^3 of waste acid (about 5% dissolved solids), and 28 million ft^3 of



Site study. *NOAA Ship GEORGE B. KELEZ on its way to visit a dumping area*

cellar dirt and construction debris were dumped.

Nevertheless, adverse effects were noted in the New York Bight Apex. For example, fin rot on certain fish, and exoskeleton erosion and gill clogging on crabs and lobsters have been observed. The U.S. Food and Drug Administration banned the taking of inner New York Bight shellfish because of high *Escherichia coli* counts. Also, adult surf clams are no longer found near the several dumping sites; and DO is often down to about 30% of saturation, and nutrients are present in high abundance. In the topographic depression of the Hudson Shelf Valley near the sites, high concentrations (3–5%) of total organic carbon (TOC), and of heavy metals were found, and some muds with about 2% TOC have occurred within 0.5 n mi of some Long Island beaches. Pathogens were also in evidence.

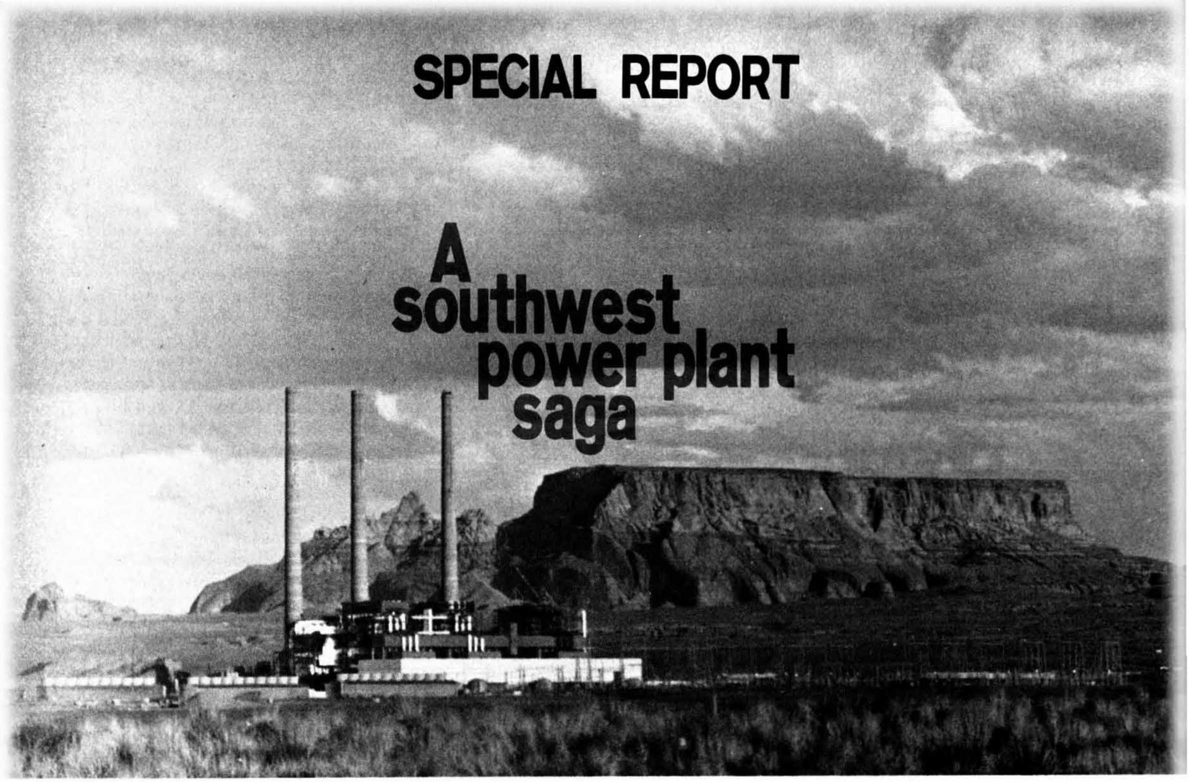
Use the same site until 1981

Since plankton in the dump site vicinity produces about 370_g of carbon/m^3/yr, the area cannot be characterized as a biological desert. To be sure, the area is contaminated; however, by no means does all of this contamination originate from SSD and DM, acid waste, and cellar dirt dumping. Much of it comes from the Hudson River, air pollution fallout such as uncaptured power plant fly ash, and waste disposal activities not associated with dumping. All these other contamination sources can and do mask those originating from sewage sludge dumping.

Naturally, the marine environment cleanup effort would be better served if SSD were phased out, as indeed it is supposed to be by 1981. However, seriously cleaning up the Hudson and East Rivers, New York Harbor, and Raritan Bay (N.J.) would probably be of equal, if not greater help, Cdr. Swanson said. However, he told *ES&T* that since dumping is to be eliminated by 1981; since there is no proof satisfactory to public health authorities that a health threat is posed to people using Long Island or New Jersey beaches; and since the feared dark blob from SSD never materialized, NOAA does not recommend relocation of dump sites to presently clean areas of the Middle Atlantic shelf. Such an action may be politically expedient, but costly ($5 million/yr) and ineffective for water-quality improvement because of large pollutant influx from shoreline outfalls, rivers, and embayments. Rather, NOAA suggests using the existing dump sites until the 1981 ocean dumping phaseout. JJ

SPECIAL REPORT

A southwest power plant saga



ES&T's Stan Miller finds that electric utilities have installed certain environmental safeguards because their officials also want clean air and clean water; however, they find uniform federal guidelines and regulations of little value to site-specific requirements

The current thrust of Federal energy policy is to increase the use of domestic fuel resources. Low-sulfur western coal is largely an untapped domestic resource and a new energy development of this type will severely impact that part of the U.S.

On one hand, utilities, in their opinion, find both justification and need for fossil-fuel development in the Southwest. The Western Energy Supply and Transmission Associates (WEST), an unincorporated organization of 22 public and investor-owned electric utilities, provide electricity in all or part of 11 western and southwestern states. They have filed with the Federal Power Commission their planned expansions for the next 10 years, as required by law.

On the other, environmentalists are concerned with threatened air quality, strip-mining effects, and decrease in visibility—from 160 miles today to perhaps 40 miles—if and when expansions occur.

A big issue, largely unresolved at this time, is whether this coal will be stripped and shipped to eastern users or stripped and burned on the spot to generate electricity for transmission across interstate boundaries to users locally and as far away as Los Angeles and San Diego.

What, of course, is badly needed for power plant development decision-making are superregional air emissions data for the entire Southwest. It is important to know not only the contribution to air quality from individual power plants but to be able to assess the overall effect that new power plants might add to an area already burdened with existing power plants.

Recently, baseline monitoring for the Southwest has been renewed; it goes by the name, Western Area Environmental Monitoring Study. The EPA Environmental Monitoring and Support Laboratory (EMSL) in Las Vegas, Nev. (*ES&T*, December 1975, p 1109) is performing a 5-year monitoring study; it involves more than 50 airborne monitoring systems.

Earlier, the Department of the Interior conducted a Southwest Energy Study in 1970, which measured total air, water, and land impacts of existing and proposed plants in the Four Corners area. Also, a joint ambient air program with eight monitoring stations was started by the utilities at the Four Corners and San Juan stations in 1972 and is still going on.

But it is likely that complete monitoring data will neither be available nor evaluated before decisions on expansions are finalized. It is also important to note that this monitoring activity will be the first time EPA has obtained its own baseline data for the superregional area of the Southwest, including many states of WEST involvement. However, monitoring activity on a more local basis has been performed for many years by local agencies and independent consultants.

This development is needed; there can be little doubt. Dr. Chauncey Starr, president of the Electric Power Research Institute (*ES&T*, January 1975, p 13), says, "Coal-derived fuels and nuclear sources must account for most of U.S. electric power production for the next quarter century." He continues, "Substantial dependence on foreign fuel sources is undesirable for reasons of national security, balance of payments, and unforeseeable costs. Therefore, electricity generation options must concentrate on indigenous fuel resources, which, between now and the year 2000, are principally coal and uranium."

Putting the clean energy potentially in perspective, Starr says, "Advanced technological concepts such as fusion and solar energy cannot play an important electricity production role before the year

2000. Although most scientists and engineers actually working on the development of these new concepts fully agree with this point, unfortunately, the lay public has been grossly misled by others to believe that such novel approaches are viable in the near term as alternatives to coal and nuclear power."

This position was reiterated recently by the Electric Edison Institute (EEI), a principal national association of investor-owned electric utility companies, and the National Coal Association (NCA), the national association of commercial coal producers and allied interests. In a joint statement EEI president W. Donham Crawford and NCA president Carl Bagge said that the demand for electricity will continue to increase, and that the utilities must meet this demand by expanded use of coal and faster growth of nuclear power.

By 1984, they said, 781 million tons of coal a year will be required for making electric power, almost twice as much as last year—and this assumes the predicted growth of nuclear power. If nuclear power is delayed, they said, the demand upon coal will be even greater. In its report, "Economic Growth in the Future," EEI describes several scenarios including high growth, moderate growth, and low growth. It is being published by McGraw-Hill, Inc.

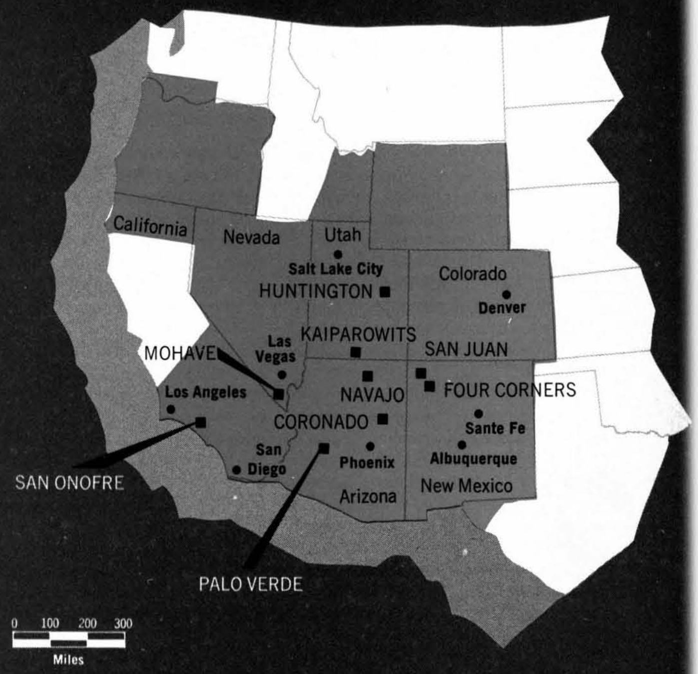
Some of the major power plants in the Southwest include Mohave, Navajo, San Juan, Cholla, Kaiparowits (whose construction was cancelled this April) and, of course, Four Corners (*ES&T*, June 1974, p 516). Their experiences in protecting the environment are noteworthy.

Mohave and Four Corners

Operated by Southern California Edison (SCE), the Mohave plant has two units of 790 megawatts each for a total plant generating capacity of 1580 megawatts —equivalent to the electricity needs of about 1.5 million people. Bechtel Corp., the major architectural-engineering (a-e) firm, started construction on the plant, which includes C-E boilers, in 1967. Unit 1 started up in the Fall of 1970, Unit 2 six months later.

Mohave is unique; it is the only power plant in the U.S. that uses slurry coal as fossil-fuel input. The slurry is about 50% finely divided coal and 50% water. The coal comes from the Black Mesa area, which has been leased by the Peabody Coal Company from local Indian tribes. It is transported by pipeline for a distance of nearly 275 miles from Black Mesa, near Kayenta, Ariz., via an 18-inch pipeline that is owned by the Black Mesa Pipeline Company, a subsidiary of the Southern Pacific Railroad. The trip takes three days; it begins at an elevation of 6500 ft and ends at an elevation of 700 ft.

On arrival at the Mohave plant, the slurry is stored in four working tanks that provide a smooth, uninterrupted flow of fuel to the boilers. From these tanks the slurry is pumped into centrifuges that



Major southwest power plants at a glance

Fossil fueled stations

MOHAVE station 2 units totaling 1580 megawatts

operated by Southern California Edison

participating companies

SCE (56%)
Los Angeles Dept. of Water & Power (20%)
Nevada Power Company (14%)
Salt River Project (10%)

NAVAJO station 3 units totaling 2250 megawatts

operated by Salt River Project

participating companies

Salt River Project (21.7%)
Los Angeles Dept. of Water & Power (21.2%)
Arizona Public Service (14.0%)
Nevada Power Co. (11.3%)
Tucson Gas & Electric Co. (7.5%)
U.S. Bureau of Reclamation (24.3%)

FOUR CORNERS station 5 units totaling 2085 megawatts

operated by Arizona Public Service

units 1, 2, & 3, wholly owned by APS, totaling 575 000 kw
units 4 & 5 participating companies

SCE (48%)
APS (15%)
Public Service Co. of New Mexico (13%)
Salt River Project (10%)
El Paso Electric Co. (7%)
Tucson Gas & Electric (7%)

SAN JUAN station 4 units totaling 1700 megawatts

operated by Public Service Co. of New Mexico

participating companies

Public Service Co. of New Mexico
Tucson Gas & Electric Co.

first unit operating, second end of 1976, three & four, late '70's early '80's

CORONADO fossil fuel generating station 3 units totaling 1050 megawatts

to be operated and wholly owned by Salt River Project

unit 1 to be operating by April 1979
unit 2 to be operating by April 1980
unit 3 not yet determined

Nuclear fueled stations

SAN ONOFRE nuclear generating station 3 units totaling 2650 megawatts

operated by SEC
unit 1 started in 1968, 2 and 3 to be operational in 1982

PALO VERDE nuclear generating station 3 units totaling 3800 megawatts

operated by Arizona Public Service

units to be operating by 1982, 1984, and 1986
participating companies

Arizona Public Service (28.1%)
Southern California Edison (15.4%)
Salt River Project (28.1%)
Public Service Co. of New Mexico (10.2%)
El Paso Electric Co. (15.8%)
Arizona Electric Power Cooperative, Inc. (2.4%)

produce a force of 1000 G's to separate the coal from the water. Approximately 75% of the water is removed, enough to permit combustion of the coal.

Geographically, the Mohave plant is about 90 miles south of Las Vegas, the point being that it is still in the state of Nevada, but more importantly in Clark County. After construction was started, Clark County imposed an SO_2 emissions regulation of 0.15 lbs of SO_2/million Btu, eight times more stringent than the EPA new source performance standards (NSPS) (1.2 lbs of SO_2/million Btu) for new electric generating plants.

In January 1973, the Mohave Generating Station was granted a variance to provide for full compliance, by December 1976, with Clark County emissions regulations (subsequently amended to July 1977). This variance provided for the installation and testing of SO_2 emission scrubbers.

The State of Nevada legislators upset the regulatory apple cart by looking into the regulations and the extremely high cost to the public implied by the regulations. When the state legislature realized that the Clark County regulations were eight times more stringent than EPA's NSPS they put a 2-yr moratorium on meeting emissions standards to allow time for thorough review of the emission standards and their relation to ambient air quality.

Meanwhile, the Mohave experience reveals that SCE made a decision in 1970 to test eight different pilot scrubbers with four different chemicals. One of those was a 1 megawatt-size scrubber which, by now, has become known as the Weir horizontal scrubber, named after Alexander Weir, Jr., the inventor, who is principal scientist for air quality at SCE.

In 1972, SCE and Salt River Project (SRP) proposed a full-scale program to test two scrubbing modules, each larger than had ever previously been built anywhere in the world. Each was to scrub one-fifth of the total air flow from one of the two units at the Mohave plant. In power plant parlance this flow is referred to as a one-fifth slip stream. Simultaneous with the Weir scrubber evaluation was an evaluation of the UOP vertical turbulent contact absorber (TCA), again on a one-fifth slip stream, equivalent to about 170 megawatts of power generation. The testing decision became known as the Mohave-Navajo test program, the Navajo plant being operated by the Salt River Project with main business offices in Tempe, Arizona, although the plant is located at Page.

SRP director of communications and public affairs, Stanley E. Hancock, says that the Mohave-Navajo test scrubber evaluation was jointly paid for by the participating companies and agencies of the two plants and was based on a kilowatt distribution—the split being 60% Navajo and 40% Mohave. He says it was a voluntary program and cost about $30 million. Testing lasted 1.5 years, and was started on the Weir horizontal scrubber on January 16, 1974 and on the UOP vertical on November 1, 1974, delayed from the spring of 1974 because of a fire during startup in January 1974. Testing was completed on the horizontal on February 9, 1975 and on the vertical on July 1, 1975.

Mohave station superintendent Greg L. Fraser, a former tank commander with service in the Italian and African campaigns during World War II, says that the plant investment is $234 million. "To put scrubbers on the entire flow stream of the Mohave plant would necessitate an additional investment of many millions of dollars," Fraser says. The plant employs about 250 people, and 80 are at the plant at all times. He indicated that putting scrubbers on the two units for full rated emissions would not only increase the capital outlay but estimates that his present maintenance staff of 150 people would have to be increased by as much as 60%.

Mohave is a base-load plant and operates routinely between 60% and 70% of rated capacity, on an annual basis. Power from this plant is transmitted via station switchyard facilities to a transmission system from which it flows into the electrical system that supplies the southwestern U.S.

SCE research scientist Dr. Dale Jones says that the cost of constructing and testing the two scrubbers ($30 million) included $1.8 million fire damage repair to the UOP vertical. He indicates that the space requirement is 15 ft by 28 ft for the horizontal and 18 ft by 40 ft for the vertical. He also says that there is a lower tonnage of steel on the horizontal system, resulting in lower capital costs.

When *ES&T* visited the Mohave plant last September, the Weir scrubber had been sold at salvage value, disassembled, and reassembled and refurbished for further evaluation on Unit 5 of the Four Corners plant, near Farmington, N. Mex., which is operated by the Arizona Public Service Co. (APS).

The five units at Four Corners are equipped with various pollution control equipment. Originally, Units 1, 2, and 3 were equipped with mechanical collectors capable of removing 77% of ash. However, with the construction of Units 4 and 5, and the advancement of control technology, APS retrofitted Units 1, 2, and 3 with wet scrubbers at an estimated cost of about $5 million. A Chemico system was added to these units at a final cost of approximately $30 million (*ES&T,* June 1974, p 516).

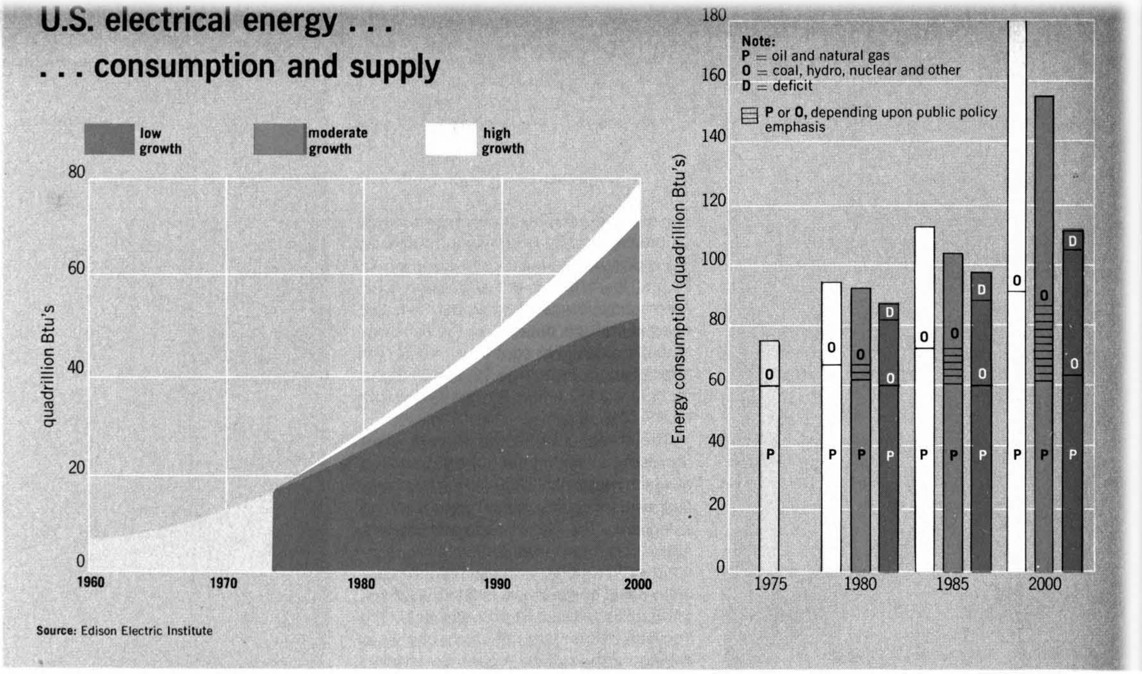
The scrubbers meet particulate removal regulation (99.2%) and inadvertently remove approximately 30% of the SO_2 because of the inherent pH control and alkalinity of the ash. The result is a relatively clean stack with a vapor plume only visible during the cold winter months.

Units 4 and 5 are currently operating with electrostatic precipitators removing 97% of the particulate matter. Additional control of both particulates and SO_2 are required by state and federal agencies. The first stage of this program is the testing of the horizontal scrubber from Mohave.

APS vice-president T. G. Woods, Jr., says that testing began this February on unit 5 operating on coal with 22% ash and 0.6–0.75% sulfur. One objective, Woods says, is to operate as continuously as possible for a minimum of 6 months testing and operational evaluation. The purpose of the testing is the determination of the commitment that will be made for SO_2 removal, and also the technical and economical feasibility. Woods also mentioned that one difference between the two scrubbers is energy use. The horizontal scrubber requires less energy in its operation than the vertical design.

But SCE is not enamored with the use of scrubbers on its plants. Nor is APS for that matter. Dr. Raymond E. Kary, manager of the environmental management department, says Arizona Public Service, which has had costly experience with scrubbers at the Four Corners Power Plant in northwestern New Mexico, takes exception to the EPA claims. He described APS' pioneering efforts to develop low-sulfur coal beds of the Southwest.

The original cost estimate for the scrubbers for the plant's three original units was $5.5 million, Kary said. But the final cost skyrocketed to $30 million, because of last minute design changes, delayed deliveries, unproductive overtime, and unavailable equipment and materials, he added. "When we add the installation cost, the cost of the money over 30 years, and the O & M costs over the same period," Dr. Kary pointed out, "the scrubbers would cost APS customers up to $546 million."



U.S. electrical energy . . .
. . . consumption and supply

Source: Edison Electric Institute

The installed value for each kilowatt at Mohave is $147/kW, including the cost of electrostatic precipitators for fly ash removal. In general, western coal is less than 1% sulfur, averaging 0.5% sulfur. The WEST consensus questions the need for scrubbers for removing SO_2 from plants utilizing low sulfur western coals. It would take an additional $50-100/kilowatt to put on scrubbers that would push the cost of power generation to $400-500/kilowatt; there would also be higher operating costs, including more maintenance to service the units.

Pullman Kellogg, formerly the M.W. Kellogg Co., one of the tall stack builders (*ES&T,* June 1975, p 522) has an exclusive license to build the Weir scrubber in the U.S., West Germany, and Japan. At press time, only one order had been placed. At the same time, all participants in the Mohave-Navajo test program could obtain a royalty-free license on the scrubber, meaning that the operators and owners of these plants can contract for the equipment with any other a-e firms.

Navajo

Operated by the Salt River Project, the Navajo plant is newer than the Mohave plant; its environmental safeguards are also noteworthy. There are three units at the Navajo plant; unit 1 started operation on May 30, 1974, the second nearly a year later—specifically on April 3, 1975—and the third unit started this April. Again, the a-e firm is Bechtel. Construction began in 1970 and each unit has a 775 ft stack built by the tall stack builder Pullman Kellogg.

Navajo, the largest electric generating plant in the state of Arizona, where only 15% of the land is privately held, is classed as an existing source rather than a new source and hence not regulated by EPA new source performance standards.

Navajo station superintendent is Dean Johnson, but Navajo plant environmental supervisor, Mike Webb, a chemist from Arizona State University, was *ES&T's* guide. Like Mohave, the Navajo plant gets its coal from the Black Mesa, which is only 75 miles from the plant; the coal is transported by the BM&LP (Black Mesa & Lake Powell) railway. The trains are electrified; they travel 24 hours/day. The BM&LP railroad cost nearly $75 million, and was constructed by Morrison-Knudsen Co., (Boise, Idaho).

The coal that is delivered is about 0.5% sulfur and 8.0% ash. It is ground to the consistency of flour before burning in the C-E (Combustion Engineering) boilers. With the Navajo plant being 4360 ft above sea level and tall stacks dispersing its emissions at an elevation of 5135 ft, one might still ask what the emissions will be.

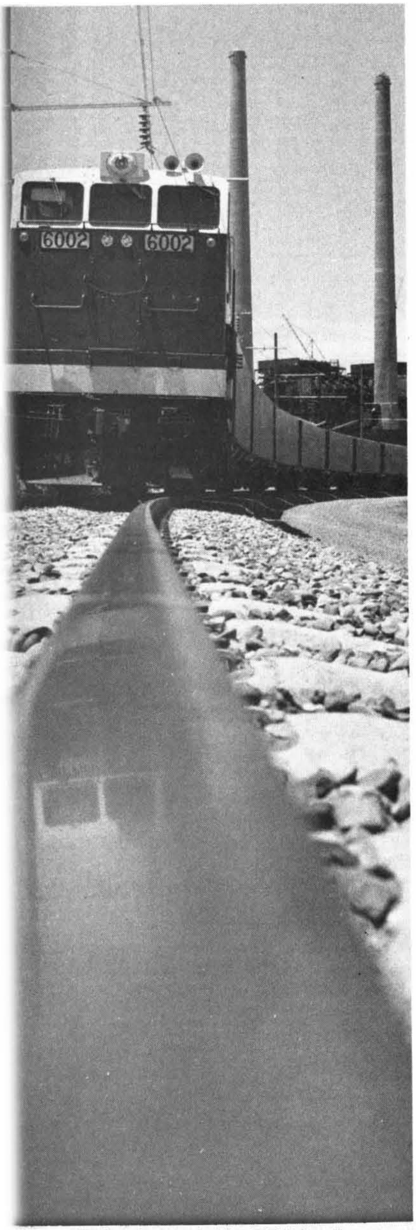
The EPA, based on the application of a NOAA model, promulgated regulations required 70% SO_2 removal. SRP challenged the regulations in Federal Court since SRP recognized that such models were subject to potential inaccuracies in modeling and input data. As a result of litigation and discussions with the federal agencies involved, an agreement was reached that the degree of SO_2 removal required at Navajo should be established by a scientific method of testing. Accordingly, SRP initiated an SO_2 monitoring program to provide actual field data and to develop analytical procedures to determine SO_2 ambient concentrations impacts.

In September 1974, Rockwell Science Center and their subcontractors, Meteorology Research Inc. and Systems Applications Inc., began monitoring SO_2 emission and ambient concentrations at Navajo and in the surrounding area. The field program, which was conducted from September 1974-February 1975, was comprehensive and included not only SO_2 measurement noted above, but plume tracking by aircraft and collection of detailed meteorological data.

The reductions and processing of all data were monitored by EPA-RTP as well as an independent consultant. Also, EPA was involved in the establishment of analytical procedures as were SRP and Bechtel Power program manager for Navajo. The cost for this study was $2 million. The principal conclusion of this monitoring program is that no SO_2 removal is needed to meet federal ambient SO_2 standards. Resolution of program results are now registered with the EPA regional administrator.

Hancock explains that NSPS requirements are not applicable to the Navajo plant. Ground breaking for construction of this plant was in April 1970, prior to promulgation of federal NSPS regulations of August 31, 1971. On the other hand, Hancock says that the state of Arizona differentiates between existing and new generating stations. The state also required annual testing of emissions control devices. The state of Arizona views the three units at Navajo as one stationary source and the state has a sliding scale for particulate emissions based on unit size.

According to the calculations of Richard F. Durning, a professional engineer and staff consultant of the Salt River Project, there are 7000 × 10^6 Btu/h/unit.



Delivering coal. *The BM&LP railway runs 24 h/day bringing coal from the Black Mesa to the Navajo plant, a distance of 75 miles*

The heat input for the three units would be on the order of 21 000 million Btu/h and the allowable particulate emissions would be 0.60 lbs/h/million Btu, based on a 24-h arithmetic average. Durning also says the needed controls depend on the ash content of the coal. For coal with 8% ash the needed control would be 99.1% whereas for coal with 13% ash the removal would be 99.46%.

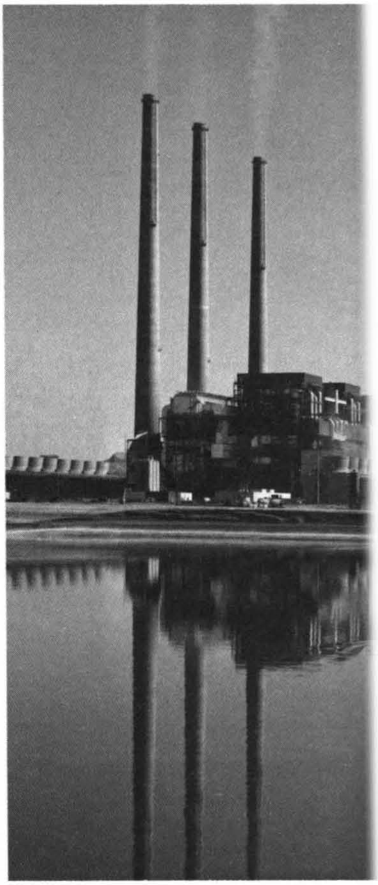
The three units at the Navajo plant represent an investment of $659 million of which more than $200 million has been budgeted for environmental protection and safeguards. The electrostatic precipitators alone cost more than $40 million. Conventional scrubbers on the Navajo plant units could come to an additional cost of $100 million, if installed. Southwest utility decision-makers are not unreasonable in asking for the rationale behind spending such large sums of money to provide protection to the ambient air for periods of concern that amount to only a few days per year. They make their point, but will it be heeded?

For cooling purposes, the plant may use up to 34 000 acre ft of water each year and takes that water from Lake Powell. The efficiency of a fossil-fuel power-generating plant is 38%, because of the limitations of Carnot cycle efficiency. The remaining 62% of the energy is not available for electric power generation, and is rejected to the ambient air via cooling towers and the stacks. Each unit has a bank of two cooling towers. Built by the Marley Co. (Mission, Kansas), these plant towers cost nearly $9 million.

Also in Page, Arizona, is the Glen Canyon hydroelectric plant. Its generating capacity is 980 megawatts. The Glen Canyon Dam blocks up the water of the Colorado River for as far as 186 miles upstream; in essence, it filled in the canyon. The Glen Canyon Dam was started in 1956 during the Eisenhower administration, and the last bucket of concrete was poured in 1963. It started producing electricity in 1964.

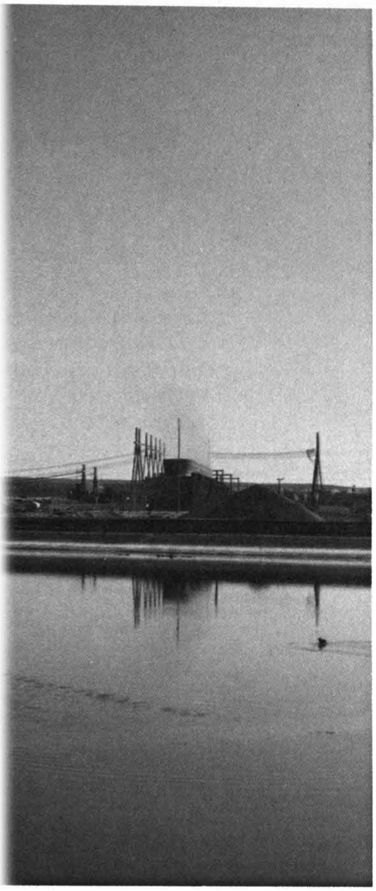
But the Navajo plant will be generating 2.5 times the electricity of its hydroelectric neighbor. One of the big users of the Navajo electricity is the federal government. Its Bureau of Reclamation gets 24% of the power and plans to use it for the Central Arizona Project. Some of this electricity will be used to pump water to Phoenix and Tucson, the latter being one of the largest cities in the U.S. that has no natural flow of water!

The Navajo plant is located on 1021 acres of land leased from the Navajo tribe. Peter MacDonald is chief of the tribal council, which meets at Window Rock, Arizona. Although the water for the plant is taken from Lake Powell, it is important to note that there is no discharge to the lake. The cooling water is softened before use and after use is placed in holding ponds that cover 125 acres. The evaporation rate in that part of the U.S. is on the average 8 ft/year. Also, there is an ash disposal area of 765 acres.



Starting last September, the ash collected by the electrostatic precipitators is hauled away from the plant by Cement Transporters, Inc. (Phoenix). Then, The Tanner Co. of Phoenix incorporates the material in their concrete formulations, similar in concept to the process of IU Conversions Systems, Inc. (*ES&T*, October 1972, p 874).

The plant uses approximately 24 000 tons of domestic coal each day when all three units are operating at full load. On a Btu basis, this is equivalent to 90 000 barrels of imported oil. Webb says that the Black Mesa coal costs about $3/ton. Assuming that oil costs $15/barrel, its cost would be $1.35 million/day, but the cost of the coal would only be $0.072 million each day. In other words, based on those costs, the Navajo fossil-fuel generating station could save $1.278 million each day on fuel costs alone, and also produce



Cooling water. *At the Navajo plant such water, taken from Lake Powell, is placed after use in holding ponds that cover 125 acres*

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San Juan & Cholla

Located in northwestern New Mexico, the San Juan project involves four coal-fired units totaling 1700 MW. Operated by the Public Service of New Mexico, in conjunction with Tucson Gas & Electric Co., Unit 1 is now in operation, and Unit 2 is under construction. The third and fourth units, each 500 MW, are scheduled for completion in 1980.

The units have Foster Wheeler boilers, provide 99.8% removal of fly ash by electrostatic precipitators, and will remove 90% of the SO_2 from stack gases. The coal is 18% ash, 0.8% sulfur, and 10% moisture. Unit 1 cost more than $107 million, and unit 2 cost $80 million. The SO_2 removal systems will add $40 million to the final cost of each unit. Arizona Public Service Co. is expanding its Cholla Power Plant in northern Arizona, with two 250 MW units to be completed in 1978 and 1979. A fourth unit (350 MW) is slated for operation in 1980.

Kaiparowits

Without any question, the most controversial development in the Southwest was the planned Kaiparowits power plant on federal land in southern Utah. With 4 units totaling a 3000 megawatt generating capacity, it would have been the largest coal-fired power plant in the world. This April, utility companies withdrew their backing for the plant. Originally, the first unit was planned for 1980, a second for 1981, and the full plant by 1982.

William R. Gould, executive vice president of Southern California Edison—the project director for Kaiparowits—said, "It didn't die slowly; it was beaten to death by the environmentalists." (The battle lasted 13 years.)

The plant would have been located in an otherwise inaccessible area of southern Utah. WEST utility men go to remote places to build their generating stations because the areas have underground coal supplies. It is more economical for the customers using electric power in the Southwest to receive that power from mine-mouth, coal-fired power plants.

Recoverable coal reserves in the Kaiparowits Plateau are 15.2 billion tons. About 1.8 billion tons of coal reserve lie within the lease holding of the project participants. The plant would take about 12 million tons annually of raw coal from four underground mines.

Utah governor Calvin L. Rampton called the project's demise, "A serious blow at the attempts of the U.S. to secure energy independence."

Environmentalists warned that the plant would be located within a 100–200 mile radius of the Golden Circle of National Parks and monuments. This impact area includes eight national parks, 26 national monuments, three national recreation areas, and two historic sites, in addition to numerous primitive areas, de facto wilderness areas, Indian sacred grounds, and state parks, according to one environmentalist's tabulation. This scenic area is under the jurisdiction of the Bureau of Land Management or the Navajo Tribal Council. Visibility is usually very high and noise levels are minimal.

What about nuclear?

One of the largest nuclear power plants in the U.S. will be the San Onofre plant (near San Clemente, Calif.) of Southern California Edison and San Diego Gas and Electric Co. Construction of the second and third units began last year; nuclear fuel is to be loaded in 1980, and the second of three units is scheduled to begin operation in 1982. The first 450 MW unit was initially operated in 1968. Each of the units is rated at 1100 megawatts for a total generating capacity of 2650 MW. Palo Verde is 3810 MW.

APS is also project manager and operating agent for the proposed 3810 megawatt Palo Verde Nuclear Generating Station to be built 50 miles west of Phoenix. Completion dates of the three 1270-MW nuclear units are 1982, 1984, and 1986. Other participants include: Salt River Project, Southern California Edison, Public Service Co. of New Mexico, El Paso Electric Co. and Arizona Electric Power Cooperative, Inc. Favorable action on APS' application for a construction permit, may see the project get underway this spring.

The only other non-nuclear planned project is that of the Coronado generating station. Wholly owned by SRP there will be three 350 megawatt units. Construction began in August 1975. It will be located on private land in northeastern Arizona.

Looking ahead

Fifteen years ago, a fossil-fuel power plant could be built for about $100–150/kilowatt of generating capacity. At that time, the argument against nuclear energy was that it was too expensive, on the order of $1000/kilowatt of generating capacity.

But what has happened since then is that the cost of a fossil-fuel power plant, what with all the environmental safeguards, has escalated to the comparable cost of a nuclear plant. The remaining difference is that a nuclear plant takes a longer lead time from ground breaking to operation than a fossil-fuel plant.

But recent development in the Southwest can be put into the perspective of economics. The Mohave station represents an investment of $147/kilowatt of generating capacity, The Navajo plant, constructed somewhat later, represents about $300/kilowatt of capacity. The Kaiparowits plant is in the $900–1000/kilowatt range. The proposed Coronado plant will cost $1000/kilowatt.

Key utility officials fail to see the need to remove SO_2 from the burning of western low-sulfur coal, and why controls need be the same for this coal and high-sulfur eastern coal. What is the rationale for transporting low-sulfur western coal to eastern utilities? Transportation costs only add to the price of this coal and might jump the price to about $20–25 per ton. $20/ton of coal is equal to $6/bbl of oil on the same heating value basis.

On the record, utility officials also allege that eastern utilities justify the purchase of the low-sulfur western coal on the assumption that no SO_2 removal is needed. Again, where is the logic in requiring western utilties to scrub?

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Factors influencing plume opacity

Previously unrecognized uncontrollable variables such as the angle of the sun, the time of day and the geographic location of the power plant greatly influence smoke plume opacity

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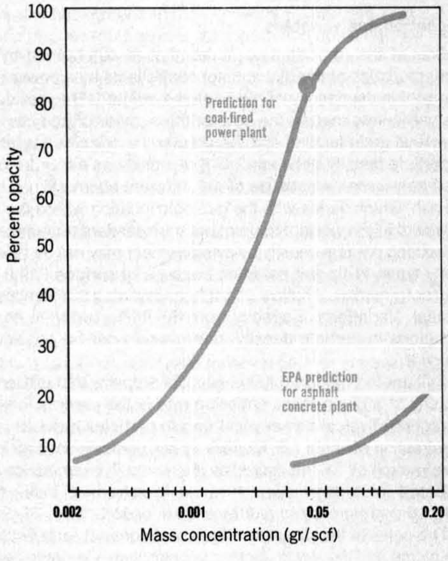
Southern California Edison Company
Rosemead, Calif. 91770

Seymour Calvert and Shiu Chow Yung
Air Pollution Technology, Inc.
San Diego, Calif. 92117

Numerous experiments on the removal of particulate matter with electrostatic precipitators and wet scrubbers have been conducted at the 1580 MW coal-fired Mohave Generating Station at South Point, Nev. It was established that opacity is not a function of particulate grain loading alone, but is influenced by a number of other independent variables, some of which are beyond the control of the operator of the stationary source. Thus, mass emissions cannot be determined by opacity measurements alone.

The experimental data, including plume opacity observations by trained smoke observers, were obtained in conjunction with 11-ft and 32.5-ft diameter stacks and fly ash particles of similar shape having 0.95 and 2.5 μ mean diameters. Mass emissions of particulate matter ranged from 0.004–0.40 gr/scf. The data indicate that it is possible for opacity to vary from 14–87% with a 32.5-ft diameter stack at a constant mean particle diameter of 2.5 μ and a constant mass emission rate of 0.05 gr/scf.

FIGURE 1
Effect of mass concentration on opacity



This paper presents the quantitative effect of a number of independent variables on opacity. It also shows that the use of opacity measurements by regulatory agencies to determine the degree of particulate emissions is contrary to the laws of nature, regardless of the laws of man.

Variables affecting opacity

There are a number of variables that affect opacity other than the mass emissions of particulate matter. These variables can be divided into two categories: Those variables that are a function of the control equipment and can be "controlled" by the operator or the designer; and those variables beyond the control of the operator (see box).

Control equipment could be installed to influence plume opacity as a result of controllable variables, but opacity standards would still reflect the influence of five other "controllable" variables in addition to mass emissions.

Light-scattering theory (see Reference 1 Additional reading) predicts opacity values within a reasonable degree of accuracy over a range of mass emissions (from 0.004–0.4 gr/scf) and large variations in mean particle sizes compared with the observations of trained observers.

In this paper the theory is used to quantitatively determine the effects of changes in a single parameter on opacity, while all other factors are held constant. Several arbitrarily selected conditions were used as a basis for conducting this parametric study. In the figures that follow, the opacity that corresponds to this nominal set of conditions is indicated as a black dot on a curve generated by variations in a single parameter. By using the Halow-Zeek equation and making certain assumptions, the opacity corresponding to the arbitrarily selected conditions (see Table 2 for "black dot" values) is 85%.

Controllable variables

Mass concentration of particulate emissions was the first parameter considered. A Functional Opacity-Mass Relationship for an Asphalt Concrete Plant was recently reported by the EPA in the *Federal Register*. These EPA data have been replotted in Figure 1, which also shows the predicted opacity-mass relationship beginning with the "black dot" conditions typical at the Mohave Generating Station. Note that for the coal-fired power plant, as the grain loading approaches a large value, the opacity

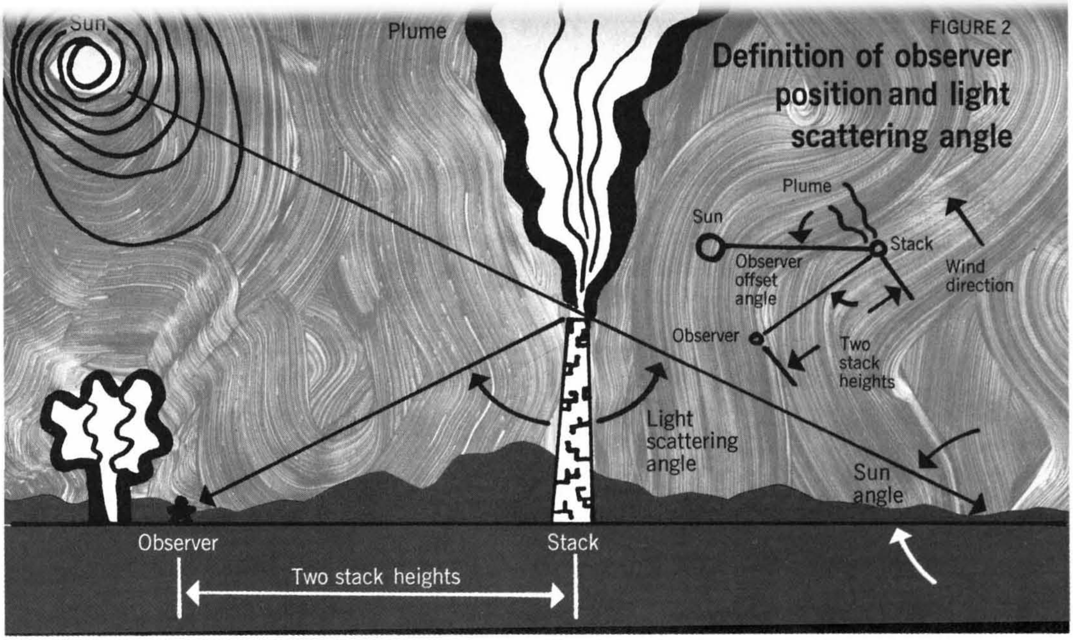


FIGURE 2
Definition of observer position and light scattering angle

asymptotically approaches 100%. Conversely, as the grain loading approaches zero, the opacity asymptotically approaches zero. In coal-fired power plants, opacity is thus not a simple linear function of mass emissions as EPA published for asphalt-concrete plants.

Figure 1 indicates that at a grain loading of 0.05 gr/scf, the EPA data suggest an opacity of 6%, while at the same grain loading the opacity at the coal-fired power plant would be 85%, as indicated by the black dot. This large difference is accounted for by the influence of variables other than the concentration of mass emissions.

One important independent variable is the diameter of the stack, which fixes the path length that light traverses during penetration of a smoke plume. The larger the diameter, the greater the path length over which light is scattered by smoke particles, and the greater the apparent plume opacity.

The size of the particulate matter in the smoke plume is another variable that has a pronounced effect on opacity. If 50% of the particles by weight are larger than a given size (and the remaining 50% by weight smaller than a given size), then the characteristic size is called the mean particle size. At a given grain loading, the smaller the mean particle size, the greater the number of particles in a given volume of gas and the greater the degree of light scattering and resultant opacity.

Deviation from the mean size is another important variable. Particle size distribution can be measured with a sampling device called a cascade impactor that separates the particles into different sizes. By weighing the amount of particles collected for each size range, the weight fraction of particles can be determined as a function of particle size. Most particle size distributions for coal-fired power plants can be plotted as a straight line on log probability paper, corresponding to a gaussian distribution of the ratio of particle diameter to the mean particle diameter. Thus, the geometric standard deviation from the mean particle size can be defined as the ratio of the particle size at 84 wt % to the mean size, or also the ratio of the mean size to the particle size at 16 wt %. If all the particles are the same size, the geometric standard deviation is one, but increases as more particles are found in size categories different from the mean size.

For mean particle diameters of 2.5 μ and larger, the smoke plume opacity is minimum at a geometric standard deviation of one, and increases as the deviation increases. This is because of a larger percentage of small particles fall between 0.2–2.0 μ (the most effective size range for light scattering). For a mean particle diameter of about one micron, the converse is true. The opacity is a maximum at a geometric standard deviation of one since all the particles are within the optimum light-scattering size range. As the deviation increases, an increasing fraction of particles fall outside the optimum light-scattering size range, and the opacity decreases. Therefore, for the small particles (0.95 μ) opacity *decreases* as the deviation from the mean particle size is *increased,* while for large particles (2.6 μ) the converse is true.

Stack gas temperature is also an important factor. One convenient measure for mass emissions of particulate matter, which is reported in the literature and frequently used for comparisons between different coal-fired power plants, is grain loading, or grains of particulate matter per standard cubic foot. If such a measure is used, then variations in the temperature of the stack gas will influence the relationship between standard cubic feet and actual cubic feet of stack gas. The higher the stack gas temperature, the higher the ratio of actual to standard cubic feet, and the lower the particle concentration per cubic foot, thus decreasing the opacity.

Uncontrollable variables

One of the important variables that is determined by the characteristics of the fuel and not controllable by a power plant operator is the density of the particles emitted. The less dense the particulate matter, the greater the number of particles at a specified grain loading and the greater the opacity. Variations in particle density between 2.0–4.0 g/cm^3 can occur for coal-fired power plants because of the different chemical nature of the ash, which varies with the geologic location where the coal is mined. It is important to point out that standard techniques of measuring particle density by displacement may not be valid for many types of fly ash particles because of surface inclusions and/or formation of hollow ash spheroids during the combustion of coal. Variations in opacity from 60–90%, owing to normal variations in particle density alone, would not be considered unusual.

Still another uncontrollable particle property that influences opacity at a given mass emission rate is the particle index of refraction. Typical power plant fly ash particles have an index of refraction of about 1.5. Mohave fly ash particles have an index of refraction of 1.6 (measured by microscopic examination with selected immersion oils). A range in refractive index from 1.4–1.6 corresponds to a difference in opacity from 77–95%.

The color of the plume and the color contrast ratio between the plume and the sky is another uncontrollable variable related

TABLE 1

Effects of geographic location and calendar date on opacity

	Kauna Point, Hawaii	Key West, Florida	Grantley Harbor, Alaska
Latitude	19° 02′N	24° 33′N	65° 16′N
Angle of Sun at time of maximum opacity			
June 21	85.5°	89.0°	48.0°
Dec. 21	47.5°	42.0°	1.0°
Percent opacity under "black dot" conditions at maximum opacity			
June 21	86.4%	86.8%	68.5%
Dec. 21	67.5%	64.5%	14.5%

Note: The opacity at sunrise or sunset is 14.0% at all three locations.

Variables influencing plume opacity

Controllable factors

- Mass emission of particulate matter
- Mean particle size
- Deviation from the mean size
- Stack diameter
- Stack gas temperature
- Stack velocity and other factors influencing plume dispersion

Uncontrollable factors

(Related to type of fuel burned or process involved)

- Particle density
- Particle index of refraction
- Water vapor
- "Color" of the plume

(Related to human observer, ambient weather conditions and movement of earth about the sun)

- Wind speed
- Wind direction
- Wind turbulence
- Ambient air temperature and humidity
- "Color" of the sky
- Distance of observer from stack
- Non-level terrain
- Observer offset angle
- Time of day
- Day of year
- Longitude of stack
- Latitude of stack
- "EPA allowable" human error
- Sun angle

to the type of fuel burned. Even if all factors such as mass emissions and particle size are the same, the opacity of a "black" plume against an overcast background will be different from the opacity of a "white" plume against an overcast background. If the overcast is white, the "black" plume will have a higher apparent opacity than the "white" plume. If the overcast is black or dark grey, the opposite situation will prevail.

Plume color is caused by the nature of the particulate matter in the plume. Silica or glass-like particles produce "white" plumes while carbon or light-absorbing particles produce "black" plumes. Because of combustion temperatures achieved in coal-fired power plant boilers, the particles in the plume are generally glass-like in nature, and the plume is generally "white" in color.

Data have been obtained for a white plume viewed against a blue sky background. If the sky were a white overcast color, a white plume would tend to disappear and could only be seen by a brightness difference between the plume and the overcast. There are no data upon which to base a prediction of the opacity of a white plume on an overcast day. Similarly, a white plume on a clear day viewed against a dark background (such as a forest-covered mountain) will produce a different opacity than the same white plume viewed against a blue sky. The color of the background thus has a significant effect on the opacity of a white plume.

Seasonal variations in ambient airborne particulate matter (caused by wind or other factors) tend to change the color of the sky. Daily variations in sky color resulting from sunrise/sunset effects, photochemical smog or changes in weather conditions all influence the opacity of a white plume without any change in the mass emissions of the plume itself. Such factors are difficult to quantify since no data for white plumes are available for correlating Ringelmann number to color contrast ratio as a function of background color.

Another uncontrollable factor related to the type of fuel burned is the water vapor content of the flue gas. While it is generally recognized that water is one of the products of combustion emitted by oil-fired power plants, it is not always recognized that large quantities of water also result from the combustion of coal. Specifically, the combustion of a coal containing 10% ash would result in over five times (by weight) as much water as ash being formed. If a wet scrubber were used to remove the ash, additional water would be introduced in the gas so that the gas would be saturated with water vapor at 120–130 °F leaving the scrubber. While not adding water, an electrostatic precipitator will not remove any water vapor from the gas.

Ambient temperature and humidity conditions can result in the condensation of some of this water vapor and there are no presently available scientific methods with which an observer can distinguish between the degree of opacity caused by the presence of the condensed water vapor and the opacity caused by the presence of fly ash. This factor is interrelated with the variables of wind direction, velocity, and turbulence and no attempt has been made to quantify it in this report.

Unlike previously discussed variables that were quantitatively related to opacity, variables such as stack and wind velocity are more difficult to quantify. Although it is not difficult to measure either stack or wind velocity or wind direction, plume opacity is measured by a human observer, and the appearance of the plume in the atmosphere is subject to atmospheric conditions such as turbulence and velocity. Haythorne and Rankin, describing the effects of these variables, said: "The velocity of the exhaust gas and the external wind conditions also will have obvious effects. In a still atmosphere the particulates may build up increasing opacity. In a high wind particles may be dispersed so that there may be no opacity at all even though the same volume of particulates is emitted." It is also obvious that the wind direction will have an influence on the opacity with observations parallel with the flow of the plume giving higher values than observations made perpendicular to the flow. This "path length effect" is similar to the effect of stack diameter presented previously.

Because of the many combinations of stack velocity, wind velocity, wind direction, and atmospheric turbulence that exist, no attempt has been made to quantify these interrelated variables.

The position of the sun

An important category of uncontrollable factors that influences plume opacity is the position of the sun and the observer with respect to the plume.

The degree of plume opacity seen by an observer depends critically on the scattering angle through which incident light is reflected and refracted from the particles in the smoke plume. This "scattering angle" and other geometric relationships are presented in Figure 2. The maximum opacity would be seen when looking at the sun through the plume and the minimum opacity would be seen when the plume is observed with the sun directly behind the observer. The closer to the stack that the observer stands, the more he must tilt his head upward toward the sky and the greater the opacity (because of the decreased light-scattering angle). A remote observation, on the other hand, gives a low reading and is another reason why an opacity measurement is not a reliable indicator of mass emissions.

Another variable affecting plume opacity is non-level terrain. Occasionally, the sun is in such a position relative to the stack that power plant equipment obscures a view of the plume at a distance of two stack heights from the base of the stack. Alternatively, coal-fired power plants are sometimes located near the edge of a cliff or near elevated terrain. In these cases, an observer must usually make an observation at a location elevated or depressed with respect to the base of the stack. This influence on the light-scattering angle has been calculated for an observer at two stack heights from the base of the stack.

The variation in opacity with changes in the elevation of the observer are more pronounced at low sun angles in the winter than at high sun angles in the summer. Also, the opacity increases as the observer position is depressed with respect to the base of the stack. Depending on sun angle, aircraft observations would normally indicate a lower opacity than would be seen on the ground. The effects of distance from the stack would be a severe problem, however, in making airborne observations.

If opacity changes when an observer moves closer to the stack at a fixed sun angle, then the opacity obviously must also change when the sun angle changes as the sun moves across the sky relative to a fixed observer position. If all opacity readings are made with the sun directly behind an observer who is two stack heights from the stack, then on June 21st at latitude 35°, the sun angle varies between 0° at sunrise or sunset and 79° at the time of maximum opacity. The opacity correspondingly varies between 18% at sunrise or sunset and 85% at the maximum sun angle when all other variables are held constant.

This sun angle effect is illustrated in greater detail in Figure 3, where the variation in opacity, as seen by a perfect observer, is plotted as a function of the time of day. Figure 3 is computed from data presented in the Nautical Almanac and Sight Reduction Tables for Air Navigation to obtain the angle of the sun as a function of the time of day. Knowledge of the latitude, longitude, and time zone in which the power plant is located was also required to obtain the sun angle data. Figure 3 is plotted for the location of the Mohave Generating Station at South Point, Nev.

Since a perfect observer always has the sun directly behind him, he would thus begin the day east of the stack and traverse a circular path at two stack heights from the stack before ending his day west of the stack. Note that this assumes no obstructions within the circular path around the stack, which probably never occurs at an actual power plant.

If the perfect observer returned to the Mohave site every day of the year, and only made an observation at the time of maximum opacity (the highest sun angle), and if all other variables were held constant for the entire year, the records of the perfect observer would be such that the opacity would vary between 54% on December 21st and 85% on June 21st. Naturally, the daily variations in opacity between sunrise and sunset would occur throughout the year, with the opacity at sunrise/sunset being 14%. The wintertime daily variation in opacity would be less than the summertime daily variation.

Obstructions between the observer and the stack (for example, the power plant boilers) might require that observations be made when the sun is not directly behind the observer (see Figure 2). By using solid geometry to calculate the scattering angle when the sun angle and observer offset angles are known, the effects of making an observation when the sun is not directly behind the observer can be calculated.

The lower the sun angle, the more pronounced the effects of observer offset angle. If an observer looks at the smoke plume when he is in the wrong position with respect to the stack and the sun, the impression received would always indicate an opacity that is greater than the correct value. This is especially pronounced when the sun angle is low and is more likely to occur in the winter than in the summer.

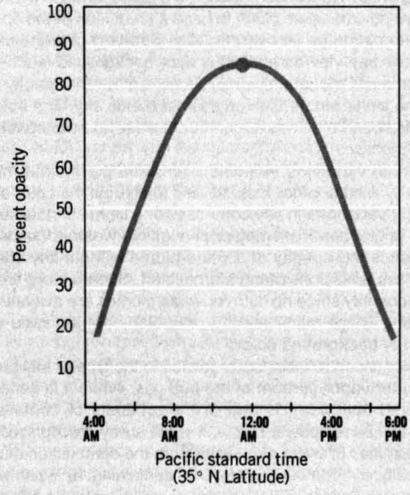
It was previously indicated that observations should be made with the wind at right angles to the direction of observation, since the EPA has established that the observation point should be "perpendicular to the plume." However, it also should be noted that this set of circumstances—wind at right angles, sun at observer's back—will only occur under certain specific conditions.

A smoke inspector who wished to make visual measurements when the opacity of the plume was at its maximum value would chose the time when the angle of the sun was at its maximum value for that day. This time occurs when the sun crosses the meridian of longitude of the observer and is referred to as "Local Apparent Noon" by navigators and astronomers. However, the time of "Local Apparent Noon" seldom coincides with twelve o'clock on the observer's watch. For an observer who is located in the exact center of the time zone, this coincidence only occurs four times a year (on April 15, June 15, September 1, and Christmas Day). On the other 361 days of the year, maximum opacity occurs either before or after twelve noon "Local Standard Time" on the observer's watch.

This irregular variation of the time of occurrence of maximum opacity throughout the year at any given location is caused by differences in the speed of rotation of the earth around the sun, tidal action and other factors. However, the time of maximum opacity occurrence can be calculated for any given day by use of information presented in the Nautical Almanac and knowledge of the local longitude.

FIGURE 3

Effect of time of day on opacity



The effects of latitude

The angle of the sun at the time of maximum opacity is a function of the latitude of the power plant or other source of smoke plume, with greater angles (and greater opacity) occurring at the lower latitudes.

If a power plant is located at different areas within the continental U.S.—all other factors remaining constant—the opacity values for a power plant in the south will always be higher than those seen by the same observer under identical conditions and at an identical power plant in the north. This effect is the result of higher sun angles in the southern latitudes. If national opacity standards were applicable, a power plant in Alaska would obviously have less difficulty meeting the regulations than an identical power plant in Florida.

Figure 4 indicates quite clearly that visual opacity is not an indication of the amount of pollutants being emitted from a stationary source. With all other variables being constant (grain loading, particle size and density, and stack diameter) opacity can vary from 14–87% depending on the geographic location and time of day. If power plants located in Hawaii and Alaska are considered, these effects are even greater.

Table 1 presents the opacities that would exist if power plants were located at Kauna Point, Hawaii; Key West, Fla.; and Grantley Harbor, Alaska. The opacity at the time of maximum opacity on June 21st in Alaska is almost the same as the opacity on December 21st in Hawaii (68.5% vs. 67.5%). However, the opacity in Hawaii increases to a maximum of 86.4% in the summer, while in Alaska the opacity decreases to 14.5% in the winter. The winter opacity in Alaska, even at the maximum daily opacity, is just slightly greater (14.5% to 14.0%) than the opacity at sunrise or sunset.

The opacity in summer at Key West would be slightly greater (86.8–86.4%) than in Hawaii even though the latitude is greater. This is because the maximum sun angle in summertime occurs when the latitude is equal to the declination of the sun (23° 26.5′N in 1975). The latitude of Key West (24° 33′N) is closer to this value than the latitude of Kauna Point (19° 02′N).

FIGURE 4

Effect of geographic location and time of day on opacity

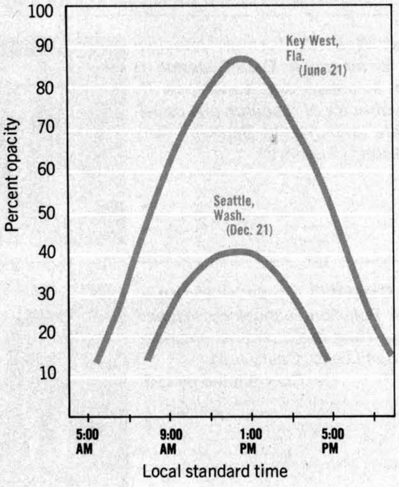


TABLE 2

Relative effects of variables on opacity

Independent variable	"Black dot" value	Typical range of variation	Resultant change in opacity with all other variables held constant
Particulate grain loading	0.05 gr/scf	0.01–0.20 gr/scf	25–98%
Stack diameter	32.5 ft	10–35 ft	37–87%
Mean particle size	2.6 μ	0.9–10 μ	96–34%
Deviation from the mean size	3.0	1.5–5.0	70–80%
Particle index of refraction	1.5	1.4–1.6	77–95%
Particle density	2.2 g/cc	1.5–5.0 g/cc	93–51%
Stack gas temperature	270 °F	130 °–350 °F	91–82%
Stack velocity	90 ft/s	70–130 ft/s	—
Water vapor content of stack gas	10%	6–14%	—
Color of the plume	White	White to black	—
Wind speed	Zero	Zero to 70 mph	—
Wind direction	Perpendicular to observation direction	±180°	—
Wind turbulence	Zero	Zero to ±30%	—
Ambient air temperature and humidity	70 °F, 15% R.H.	−10 °F to 130 °F 0–100% R.H.	—
Color of the sky	Blue	Blue to overcast	—
Distance of observer from stack	2 H_s	0.5–50 H_s	92–74%
Effect of nonlevel terrain	Level	±20% H_s	84–86%
Sun angle	79°	0–90°	18–87%
Time of day	11:30 AM (PST)	4 AM to 7 PM	18–85%
Day of year	June 21 at maximum sun angle	January 1 to December 1 at maximum sun angle	55–85%
Geographic location—longitude	114° W. Long. time of max. sun angle	±15° of Lat.. time of maximum sun angle	83–85%
Observer offset angle	0°	0–60°	85–88%
Geographic location—latitude	35° N. Lat. at max. sun angle	25° N. Lat. to 48% N. Lat. max sun angle	79–88%
Allowable human error	Zero	Zero to ±15% opacity	70–100%

Summing up

The prediction of plume opacity by using light-scattering theory and measurements in the stack gas at Mohave were in agreement with the observations made by trained observers. A parametric study of the effects of independent variables on plume opacity by using the same light-scattering theory has shown that plume opacity can vary from 14–87% depending only on the geographic location of the source and the time of day, with all other factors such as particulate matter emissions remaining the same. This implies that the EPA New Source Performance Standard for plume opacity (20%) is not consistent with the particulate matter emissions standard (0.1 lb/10^6 Btu) for all power plant locations or times of day and days of the year.

The relative effects of the 24 variables are tabulated in Table 2. As can be seen, there is an extremely wide variation in possible values of opacity, even when the mass emission of particulate matter remains unchanged. It is concluded that opacity measurements are not indicative of the mass emissions of particulate matter, and that mass emissions cannot be accurately determined from opacity observations. The use of an opacity standard to enforce a mass emission limitation is therefore difficult to justify on a technical basis.

Additional reading

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Alexander Weir, Jr. (center) *principal scientist for air quality;* **Dale G. Jones** (r) *research scientist; and* **Lawrence T. Papay** (l) *director of research and development are employed by Southern California Edison Company.*

Seymour Calvert (l) *is founder and president of Air Pollution Technology, Inc. and* **Shiu Chow Yung** *is a chemical engineer with this San Diego, Calif., firm.*

Coordinated by LRE

Control systems on municipal incinerators

Federal and state particulate matter emissions standards dictate the use of electrostatic precipitators, fabric filters, or scrubbers

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Even a modern well-designed and operated municipal incinerator cannot meet federal and state regulations for particulate matter emissions without an air pollution control system. Federal emission standards in effect require a control efficiency of at least 93% on a weight basis, but design bases are normally higher because of uncertainties and opacity requirements. To achieve the necessary efficiency, all particles larger than 1–3 μ must be removed, effectively eliminating the simple air pollution control systems traditionally used on incinerators.

Electrostatic precipitators, fabric filters, and certain types of scrubbers appear to be the only commercially available devices that have the capability to meet current emission standards for incinerators. Newer forms of these devices, including charged droplet scrubbers and high-velocity wet precipitators, may have advantages over more conventional devices, but these have not yet been commercially demonstrated for municipal incinerator applications.

Electrostatic precipitators

Not until 1969 were electrostatic precipitators applied to municipal incinerators in the U.S., although they had previously been used in Europe and Japan. Almost all new thermal processing facilities built since 1969, however, have used electrostatic precipitators for particulate emission control (Table 1). Although the design efficiencies for incinerators shown in the table are less than normally required for coal-fired steam boilers, extraordinary attention to all design and construction details is still required to ensure continuing high-efficiency performance. Mechanical and electrical designs are as important to adequate electrostatic precipitator performance as the basic size parameters. With careful design and operation, efficiency requirements for "dry catch" particles (filterable at 121 °C) can be met.

Corrosion resulting from acidic gases can be a problem in precipitator operation. The gas temperature must be maintained high enough to avoid acid condensation on cold surfaces. Hot air purging and preheat burners to minimize acid-gas contact with cold surfaces during shutdown and startup, and sufficient insulation of metal surfaces exposed to outdoor conditions are especially important in corrosion prevention. Hopper heaters are useful in avoiding corrosion and bridging problems resulting from moisture deposition in flyash.

Scrubbers

Simple devices such as baffled-water-spray chambers traditionally used to protect duct, stack, and fan materials, are inadequate as scrubbers to meet modern particulate emission control requirements, but they can still be useful for flue gas cooling. Much more sophisticated devices are needed to efficiently remove particles in the important 1–5 μ size range.

Various techniques are used in scrubbing, but all rely on "wetting" the particle with water to increase its size and permit

TABLE 1. Some ESP installations at thermal processing facilities in the U.S. and Canada

Plant	Capacity, TPD	Furnace type[a]	Gas flow, ACFM	Gas temp, °F	Gas velocity, FPS	Residence time, s	Plate area, ACFM/ft^2	Input, KVA	Pressure drop in. H_2O gage	Efficiency, wt %
Montreal	4 × 300	WW	112 000	536	5.5	3.3	6.2	35	0.5	95.0
Stamford	1 × 220	Special R	160 000	600	6.0	3.3	6.6	57	0.5	95.0
Stamford	1 × 360	R	225 000	600	3.6	5.0	4.5	225	0.5	95.0
Stamford	1 × 150	R	76 000	600	3.8	4.9	4.6	75	0.5	95.0
SW Brooklyn	1 × 250	R	131 000	550	4.4	3.2	6.7	47	2.5	94.3
So. Shore, N.Y.	1 × 250	R	136 000	600	5.6	3.3	6.8	33	0.5	95.0
Dade City, Fla.	1 × 300	R	286 000	570	3.9	4.0	5.7	48	0.4	95.6
Chicago, NW	4 × 400	WW	110 000	450	2.9	4.6	5.5	40	0.2	96.9
Braintree, Mass.	2 × 120	WW	32 000	600	3.1	4.5	5.5	19	0.4	93.0
Hamilton, Ont.	2 × 300	WW	81 000	585	3.5	5.4	3.9	70	0.5	98.5
Washington, D.C.	6 × 250	R	130 800	550	4.1	3.9	4.9	77	0.4	95.0
Eastman Kodak	1 × 300	WW	101 500	625	3.4	5.5	3.8	106	—	97.5
Harrisburg, Pa.	2 × 360	WW	100 000	410	3.5	5.1	5.0	40	0.2	96.8
Saugus, Mass.	2 × 750	WW	240 000	428	—	—	—	—	—	97.5

[a] R = refractory-lined; WW = waterwall.
Note: Except for capacity, data refer to design parameters for one precipitator; several may exist

ier removal from the gas stream. The efficiency of a par-ılar type of scrubber on a given particle size can be related ıe energy used to force the gas through the collector and to ıerate the water sprays. This energy usually is supplied by s supplying pressure to the gas stream (gas motivated) in turi or orifice scrubbers; or by pumps supplying pressure to water stream (liquid motivated) in jet ejector or impact ıbbers. The energy required in either case represents a very ıificant incinerator operating cost.

ince scrubber water requirements are high, recirculation ısually practiced, both to minimize makeup water and the ount of wastewater to be treated. The ratio of recycle to ‹eup water is determined by the quantity of particles to be ıoved; by the tolerance of the scrubber design to the con-ıtration of both soluble and insoluble materials in the water, ch tend to buildup with increased recycling; and by the ount of water evaporated or otherwise lost.

ncinerator stack gases contain gases that dissolve during ubbing and cause the water to become acidic. As a result, n stainless-steel scrubbers have been known to corrode. refore, pH control by the addition of alkali must be practiced. s has two other important effects: First, undesirable acidic es such as hydrogen chloride, hydrogen fluoride, and sulfur les are removed to some degree; and second, some carbon ‹ide (CO_2) is removed, which increases alkali consumption. removal of CO_2 may also have an important regulatory ef-t. Since emission standards are based on a 12% CO_2 con-, the lower CO_2 content exiting from a scrubber may require even lower actual particulate emissions rate. The regulations not clear on this matter.

everal venturi scrubbers have been applied to incinerators operating data see Figure 1). It would appear that a pressure p of at least 22–32 mm Hg (12–17 in. H_2O) is required to ıieve the Federal standard. A "clear stack" (0.07 g/scm or 3 gr/scf) may require more than 37 mm Hg (20 in. H_2O), al-ugh the scrubber water vapor plume tends to reduce this uirement by masking the opacity. The visible water vapor ıe is exempt from opacity regulations.

Vastewater from the scrubbers can be used to quench the ıace residue prior to treatment or disposal, thereby reducing h water and treatment costs.

ric filters

aghouses are widely used in industrial applications, but only w have been built for refuse incineration in the U.S. and ope. In this device, the particle-bearing gas stream is passed ugh a fabric-filter medium of woven or felted cloth that traps particles and allows the gas to pass through the pores of the ric. Although the pores are as large as 100 μ, sub-micron ticles are captured because particles collect on the cloth to n a fragile porous layer that effectively decreases the pore . For various economic and practical reasons, fabric filters usually constructed in tubular form (bags) and several bags housed together in a steel vessel, the baghouse.

he design of fabric filter baghouses depends on several ameters:

- choice of fabric (based on gas temperature, humidity, and ticle characteristics)
- size-length, diameter, and number of bags (based on an oirically obtained air flow-to-cloth area ratio, and mechanical ısiderations)
- method of cleaning (based on particle characteristics and ıdor preferences)
- method of precooling the gases to the operating temper-e.

operate continuously, the filter must be intermittently cleaned manual or mechanical means or pneumatic shaking. The odged particles fall to a hopper where they are removed by ew or other types of conveyors.

or dry catch particles, there is no apparent reason why fabric rs will not easily meet any existing particulate matter stan-d. The lack of significant use in incinerators may be due to the filters' dramatic sensitivity to high and low temperature; large space requirements; difficult maintenance; and significant operating costs.

A pilot baghouse was operated with some success around 1959, and a recent commercial installation on a municipal incinerator has apparently been operating reasonably successfully (Table 2).

Selection of control systems

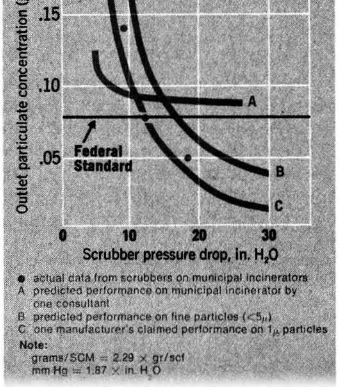
To choose among electrostatic precipitator, scrubber, and fabric filter systems for particulate removal from incinerator gases, several factors need to be considered. The first factor is initial cost, including those for the cooling systems, fans, stack, waste disposal, and other items dependent on the method of particulate matter control. Second, operating costs, including power, water, maintenance, labor, and waste disposal costs. A third consideration is reliability, which must take into account the best possible estimates for downtime, the effect of downtime on other operations, sensitivity to upsets and ranges of operating conditions, possible degradation of performance with age, and problems induced in associated equipment.

Finally, environmental and other considerations, including the ability to meet and exceed emissions standards; removal of non-particulate matter pollutants; the effect on the air quality of surrounding areas; the possibility of undesirable plumes; and the availability of facilities for waste disposal need to be assessed.

The initial cost for particulate matter control systems tends to be comparable when the complete system is considered, including startup heaters, insulation, gas coolers, hoppers, and conveyors for precipitators; alloy metal construction, alkali addition, water supply, wastewater disposal, water vapor plume control for scrubbers; and startup heaters, gas coolers, hoppers, conveyors, and pulse air supply for baghouses. However, definitive capital cost estimates are advised for system selection.

Energy requirements probably represent the single most important difference among systems. Because of low-pressure drop through an electrostatic precipitator, total energy requirement is low, even though power is required for the corona discharge and the rappers and heaters. Fabric-filter-pressure drops are higher, requiring more energy, but the energy requirement for scrubbers is by far the greatest of the three systems (Table 3).

Since all of these systems are highly automated, operating labor requirements are essentially comparable and low when the systems are operating properly. Maintenance material and labor requirements for particulate matter control systems may be very significant when design and preventive maintenance are



● actual data from scrubbers on municipal incinerators
A predicted performance on municipal incinerator by one consultant
B predicted performance on fine particles (<5μ)
C one manufacturer's claimed performance on 1μ particles

Note:
grams/SCM = 2.29 × gr/scf
mm Hg ≒ 1.87 × in. H_2O

FIGURE 1
Performance of venturi scrubbers on incinerators

TABLE 2. Operating and design parameters for a baghouse on municipal incinerator

Air flow, m^3/min (CFM)	5090 (180 000)
Air temperature, °C (°F)	260 (500)
Fabric	glass fiber
Air/cloth ratio, $m^3/min/m^2$ (CFM/ft^2)	0.61 (2/1)
Bag size,	
diameter, m (in.)	0.14 (5.5)
length, m (ft)	4.27 (14)
Number of bags (approx.)	4350
Method of cleaning	reverse air
Design pressure drop, mm Hg (in. H_2O)	3.7–5.6 (2–3)

TABLE 3. Comparison of energy requirements for control systems[a]

System	Gas motivated scrubber	Fabric filter	Electrostatic precipitator
Gas pressure drop mm Hg (in. H_2O)	28.0 (15.0)	9.3 (5.0)	1.9 (1.0)
	kW per 1000 m^3/min (hp/1000 CFM)		
Fan power	103.2 (3.92)	34.5 (1.31)	6.8 (0.26)
Pump power	2.1 (0.08)	— —	— —
Electrostatic power	— —	— —	15.8 (0.6)
Total power	**105.3 (4.00)**	**34.5 (1.31)**	**22.6 (0.86)**

[a] This table is based on a hypothetical calculation for approximately equivalent particulate matter removal efficiency. It does not necessarily include sufficient fan power for all furnace and duct pressure drops. Fan efficiency is approximately 60%. Power for heating hoppers (electrostatic precipitators, baghouses) or for tracing water lines (scrubbers) is not included.

inadequate. Thus, differences among systems may be less important than the care that is tendered to adequate design and operation.

Acid-dew-point corrosion of metal surfaces can be a problem in all systems, but is more likely to occur when gases are cooled with spray water rather than with steam boilers. Cooling with spray water is sometimes done ahead of either precipitators of baghouses, and is always an integral part of a scrubber operation. Increased pressure drop and plugging can be serious problems with scrubbers or baghouses, but seldom occur with precipitators. Problems of hopper operation, which can occur with baghouses and precipitators, are obviously not a part of scrubber operations. Moderate excursions of temperature may have relatively minor effects on precipitator and scrubber operations, but can have drastic effects on filter bags so that frequent changes involving significant labor and downtime may result.

The performance of all particulate matter control systems can deteriorate. Dust buildup on either discharge or collection electrodes will cause diminished precipitator performance. Discharge electrodes in precipitators are subject to deterioration and breakage, sometimes shorting out a section of the precipitator and reducing its effectiveness. Hopper bridging can cause problems in both precipitators and baghouses. Tears in filter bags can have drastic effects on baghouse performance. Deterioration in scrubbers can be caused by failure of spray nozzles, mist eliminators, and poor pump performance.

Dry flyash disposal, as usually practiced with electrostatic precipitators and baghouses, is considered advantageous; but, unless the flyash is carefully handled, a considerable amount of fugitive emissions can occur. The removal of solids in a slurry from scrubbers is less objectionable with incinerators than in other applications because this system can be integrated with the residue system for common water recycle and residue disposal facilities.

Scrubbers (or wet precipitators) have at least one major advantage over dry methods of particulate matter removal: The ability to simultaneously remove a significant portion of gaseous emissions. However, present regulations do not require this control; efficient, low-energy, second-stage, gas scrubbers can be added to dry systems at a later date, if extra space and static pressure allowance in the fans are provided.

The major disadvantage of scrubbers, in addition to the high-energy requirement, is the formation of visible moisture plumes and the possibility of icing and condensation problems in the surrounding area.

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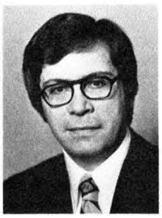

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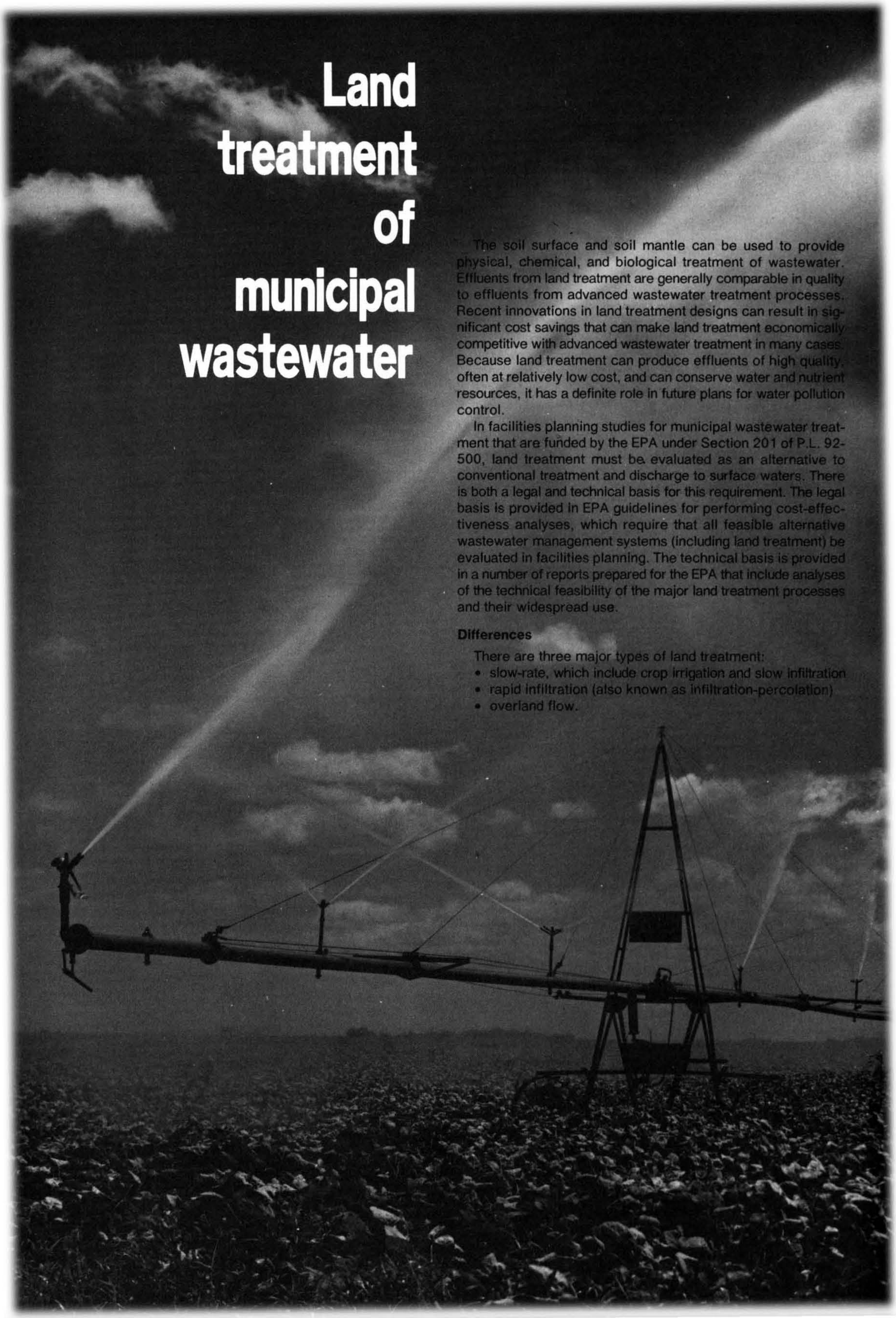

Land treatment of municipal wastewater

The soil surface and soil mantle can be used to provide physical, chemical, and biological treatment of wastewater. Effluents from land treatment are generally comparable in quality to effluents from advanced wastewater treatment processes. Recent innovations in land treatment designs can result in significant cost savings that can make land treatment economically competitive with advanced wastewater treatment in many cases. Because land treatment can produce effluents of high quality, often at relatively low cost, and can conserve water and nutrient resources, it has a definite role in future plans for water pollution control.

In facilities planning studies for municipal wastewater treatment that are funded by the EPA under Section 201 of P.L. 92-500, land treatment must be evaluated as an alternative to conventional treatment and discharge to surface waters. There is both a legal and technical basis for this requirement. The legal basis is provided in EPA guidelines for performing cost-effectiveness analyses, which require that all feasible alternative wastewater management systems (including land treatment) be evaluated in facilities planning. The technical basis is provided in a number of reports prepared for the EPA that include analyses of the technical feasibility of the major land treatment processes and their widespread use.

Differences

There are three major types of land treatment:

- slow-rate, which include crop irrigation and slow infiltration
- rapid infiltration (also known as infiltration-percolation)
- overland flow.

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Future water pollution control plans will reflect the competitiveness of this technique with advanced wastewater treatment schemes in terms of cost, efficiency, and management

The main differences in these types of land treatment are in the ways that the wastewater interacts with the vegetation and soil and in the application rates and land area requirements. A comparison of important characteristics is presented in Table 1.

Slow-rate land treatment includes crop irrigation and slow infiltration—two approaches with similar loadings rates and treatment performances but with different objectives. In crop irrigation, the objective is to maximize crop yield; the application rate is based on crop requirements. In slow infiltrating, the objective is to maximize the application rate without sacrificing effluent quality. The application rate is based on the hydraulic and renovative capacity of the soil and crop.

Crop irrigation encompasses the irrigation of forest, landscape, and turf areas as well as food and forage crops. Generally, the application rates are 1–3 inches per week. Nearly all of the applied wastewater is lost to evapotranspiration. In slow infiltration land treatment, grass crops are used because they can take up nitrogen and tolerate application rates ranging from 2–5 inches per week or more. Usually, the critical factor in determining the maximum application rate is either soil drainability or nitrogen loading.

In rapid infiltration (infiltration-percolation) land treatment, most of the applied wastewater percolates through the soil and the treated effluent eventually reaches the groundwater. The wastewater is applied to rapidly permeable soils, such as sands and sandy loams, by spreading in basins or by spraying and is treated as it travels through the soil matrix. Vegetation is not usually used, but there are exceptions in some cases.

Application rates can vary widely—from 5–120 inches per week—depending on soil permeability. The more permeable the soil, the greater the distance of travel must be for full treatment. This distance can be vertical, horizontal, or both.

In overland flow land treatment, wastewater is applied over the upper reaches of sloped terraces and allowed to flow across the vegetated surface to runoff collection ditches. The wastewater is renovated by physical, chemical, and biological processes as it flows in a thin sheet down the relatively impermeable slope. Ideally, slopes have a 2–4% grade and are 100–200 ft long to provide adequate treatment and to prevent ponding or erosion. Application rates range from 2–10 inches per week, depending on the organic loading and the runoff quality required. Slowly permeable soils, such as clays or clay loams, are required. Wastewater is applied near the top of the slope either by spraying or surface techniques. Water-tolerant grasses provide slope protection, media for soil bacteria, and nutrient removal by plant uptake.

Soil treatment mechanisms

The soil surface and profile can provide physical and chemical treatment of wastewater and a habitat for microorganisms that can provide biological treatment. The capability of land treatment systems to remove organics, nitrogen, phosphorus, exchangeable cations, and trace elements from applied wastewater depends on a variety of factors.

For organics, the soil is a highly efficient biological treatment system. Therefore, liquid loading rates for land treatment operations are normally governed by the hydraulic capacity of the soil rather than by the organic loading rate. This operational independence from BOD loading is a distinct advantage of land treatment over conventional in-plant processes, especially in treating high-strength wastewaters and industrial wastes.

TABLE 1
Comparison of land treatment types

Characteristic	Slow-rate	Rapid infiltration	Overland flow
Soil permeability	moderately slow to moderately rapid	rapid (sands and sandy loams)	slow (clays and clay loams)
Wastewater lost to:	evapotranspiration and percolation	mainly percolation	surface runoff and evapotranspiration with some percolation
Vegetation required	yes	no	yes
Weekly application rate, in./wk	1–5	5–120	2–10
Annual application rate, ft./yr	2–20	20–500	10–50
Land required, acres/mgd[a]	56–560	2–56	22–110
Application techniques	spray or surface	usually surface	spray or surface

[a] Field area only. Does not include buffer area, roads, or ditches

There are limits, of course, to the organic loading that can be placed on the land without stressing the ecosystem in the soil, but they are unlikely to be reached with the application of municipal wastewater. The effects of organic overloads on the soil include damage to vegetation, severe clogging of the soil surface, and leaching of undegraded organic material into the groundwater.

The limiting organic loading rate must be defined for each land treatment process on an individual basis, but rule-of-thumb rates have been developed on the basis of experience. For example, Richard E. Thomas of the EPA cites 25 pounds per acre per day as a loading rate at which decomposition will approximately balance organic matter accumulation. This represents a typical BOD loading rate for rapid infiltration operations. Substantially higher loading rates (over 600 pounds per acre per day) are used on a short seasonal basis for rapid infiltration of industrial wastewater. Moderately higher rates (40–100 pounds per acre per day) have been used successfully for overland flow.

Nitrogen can be removed in land treatment by crop uptake and harvest and by denitrification. In slow-rate land treatment, crop uptake is the main technique, and the quantities of uptake vary by crop. For example, corn can account for 150 pounds per acre per year, while coastal bermuda grass can account for 600 pounds per acre per year. In overland flow denitrification is mainly used, but crop uptake is also significant. In rapid infiltration, the only significant removal process is denitrification, which must be managed by using relatively long flooding cycles to create anaerobic conditions in the soil profile.

Although plants take up some **phosphorus,** the major removal processes in all land treatment systems are chemical precipitation and sorption. In overland flow, only partial removal of phosphorus is achieved because not all of the applied wastewater comes into contact with the soil matrix for chemical fixation.

Exchangeable cations, particularly sodium, calcium, and magnesium ions, deserve special consideration because high sodium concentrations in clay-bearing soils disperse soil particles and decrease soil permeability. To determine the sodium hazard, the sodium adsorption ratio (SAR) may be used. The SAR was developed by the U.S. Department of Agriculture Salinity Laboratory, and is defined as follows:

$$\mathrm{SAR} = \frac{\mathrm{Na}}{\sqrt{\dfrac{\mathrm{Ca} + \mathrm{Mg}}{2}}}$$

where Na, Ca, and Mg are concentrations of the respective ions in milliequivalents per liter of water. High SAR values (>9) may adversely affect the permeability of fine-textured soils. Other exchangeable cations, such as ammonium and potassium, may also react with soils. Occasionally, high sodium concentrations in soil can be toxic to plants, although the effects on permeability will generally occur first.

TABLE 2

Expected quality of renovated water

Constituent	Slow-rate, mg/l^a	Rapid infiltration, mg/l^b	Overland flow, mg/l^c
BOD	1–2	2–5	5–10
Suspended solids	1–2	1–2	8–10
Ammonia nitrogen as N	0.5–1	0.5–1	0.5–1
Total nitrogen as N	2–4	10–15	2–5
Phosphorus as P	0.1–0.5	1–3	3–5

^{a} after percolation through about 5 ft of soil
^{b} after percolation through about 15 ft of soil
^{c} after about 150 ft of runoff

Although many **trace elements** are essential for plant growth, some become toxic at higher levels to both plant life and microorganisms. Retention of trace elements, such as heavy metals, in the soil matrix occurs mainly through sorption and ion exchange. Retention capabilities are generally good for most metals in most soils, especially for pH values above 7. Under low pH conditions, some metals can be leached out of soils.

Need for preapplication treatment

There are a number of sound engineering reasons for treating municipal wastewater prior to land application, including the following:

- to settle and screen out large materials
- to allow the storage of wastewater without nuisance conditions
- to allow application of wastewater to food crops or to areas with public access. Secondary treatment prior to land application, however, is not always necessary, and in some cases, not even desirable.

For irrigation of food crops or landscape areas, the bacteriological quality of municipal wastewater must be very high to protect public health. For irrigation of forage crops, however, a lower bacteriological quality may be acceptable. In either case, it is the level of bacteriological quality that should be specified rather than a BOD or suspended solids concentration.

For overland flow or rapid infiltration in which nitrogen removal is an objective, a relatively high BOD (possibly 50 mg/l or more) may be desirable to promote denitrification. Wastewater that has received prior treatment only by sedimentation, oxidation ponds, or aerated lagoons has been applied successfully in many cases. The need for preapplication treatment should be determined on a case-by-case basis.

Renovated water quality

Most existing land treatment systems have not been adequately monitored with respect to the quality of renovated water. On the basis of the relatively sparse data available, the expected water quality that can be produced by the three types of land treatment is given in Table 2. For a given type of land treatment, the quality of the effluent that can be attained, as shown by Sherwood C. Reed of the Corps of Engineers, is nearly the same whether untreated, primary, or secondary wastewater is applied. This same quality is achieved because the conventional treatment processes of sedimentation and biological oxidation are duplicated in land treatment.

There are numerous variations in land treatment systems used today. Examples of different successful approaches used in the U.S., and one used in Australia, are described.

Slow-rate examples

The slow-rate land treatment operation in **Bakersfield, Calif.,** represents an example of surface irrigation of cropland. The city owns 2400 acres, which it leases to a grower for agricultural reuse of 13 mgd of wastewater that has received primary treatment. Field corn, barley, alfalfa, cotton, and pasture grass are grown. This system has been operating successfully for more than 40 years, and the return to the city represents 20% of the annual operation and maintenance costs for wastewater treatment. Current plans are to add aerated lagoons to the preapplication treatment and to expand the system to 4300 acres.

The city of **Tallahassee, Fla.,** has experimented with spray irrigation of forest and cropland since 1966. Current plans are to spray irrigate 850 acres at an application rate of about 3 inches per week. The selected crops are coastal bermuda grass, which is overseeded with a winter rye grass in November. The expected nitrogen uptake of this combination of grasses is 600 pounds per acre per year.

Irrigation. *After primary treatment, wastewater effluent is used to grow crops for cattle*

In **west central Texas,** the city of San Angelo owns and operates a 5-mgd, 640-acre irrigation system. A hay crop is grown, which is baled and sold, and an average of 500 cattle are grazed on the pasture land. Primary treatment of the wastewater precedes surface irrigation, and about 1 week of storage capacity is available when irrigation is not needed. Because the system has operated successfully since 1933, the EPA is currently studying the effects on crops, soils, and groundwater of this operation.

Rapid infiltration examples

At **Lake George N.Y.,** a rapid infiltration system has been in operation since 1936. Wastewater that has received secondary treatment is spread at a summer rate of about 30 inches per week. In the winter the application rate is reduced to 7 inches per week because of reduced flows (the city's population fluctuates seasonally). Spreading of the wastewater is continuous, and when ice forms on the surface it is not removed but merely floated by the next application.

At **Phoenix, Ariz.,** a 15-mgd rapid infiltration system has been constructed with pumped withdrawal. Wastewater that has received secondary treatment is spread according to the design criteria determined from a 5-year experimental study in which the loading rate was 84 inches per week. The high quality of renovated water collected through a series of wells is discharged to an irrigation canal for agricultural reuse.

Overland flow examples

An experimental overland flow treatment system using settled municipal wastewater has been operated by the EPA since 1972 at **Ada, Oklahoma.** Using a low-pressure rotating-boom applicator, the wastewater is applied at a rate of about 4 inches per week. After a runoff distance of 110 feet, the effluent was sparkling clear, with 8 mg/l of BOD and suspended solids, and less than 3 mg/l of total nitrogen. Full-scale operation with these design criteria has begun in an 8-acre system at nearby Pauls Valley, Oklahoma.

At **Melbourne, Australia,** overland flow is used to treat 70 mgd of wastewater that has received primary treatment. The wastewater is applied by surface flooding at a rate of 5.2 inches per week. Application is continued throughout the winter season. The system has been operated in this manner for several decades.

The economics

The costs of land treatment can compare favorably with conventional treatment and discharge systems, depending on the choice of design approach and criteria, the land price, and the transmission distance to the site. A fixed, buried sprinkler system is generally the most expensive method of application. Considerable cost savings can be realized if moving sprinkler systems (such as center pivot) or surface application can be used. For example, the use of surface application for overland flow can result in cost savings in the distribution system and in capital and power cost savings in the pumping station.

Looking ahead

In the future it is expected that there will be increased use of forests, marshes, and wetlands for land treatment, as well as further investigation and use of overland flow. Wastewater applied to forests is being studied in the Pack Forest in Washington and near Lake Arrowhead in Southern California. Both the EPA and the Corps of Engineers are conducting significant research projects in several climatic regions on the use of overland flow for wastewater that has received either primary sedimentation or oxidation pond treatment prior to application.

The renovation capacity and ultimate use of land treatment is not yet fully understood. The implementation of land treatment systems has been slowed by the need for research and monitoring of recently developed variations of land treatment processes and by the need for answers to questions concerning the long-term effects on the environment.

Both proper management and monitoring are required for successful and ecologically sound land treatment systems. When these requirements are met, land treatment can compete with advanced wastewater treatment in many locations not only in terms of costs, but also in the quality of the renovated water, and in water and nutrient resource management. Thus, land treatment can be an effective tool in water pollution control, whether it is used in place of, in addition to, or in conjunction with conventional treatment processes.

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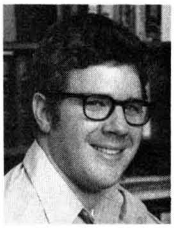

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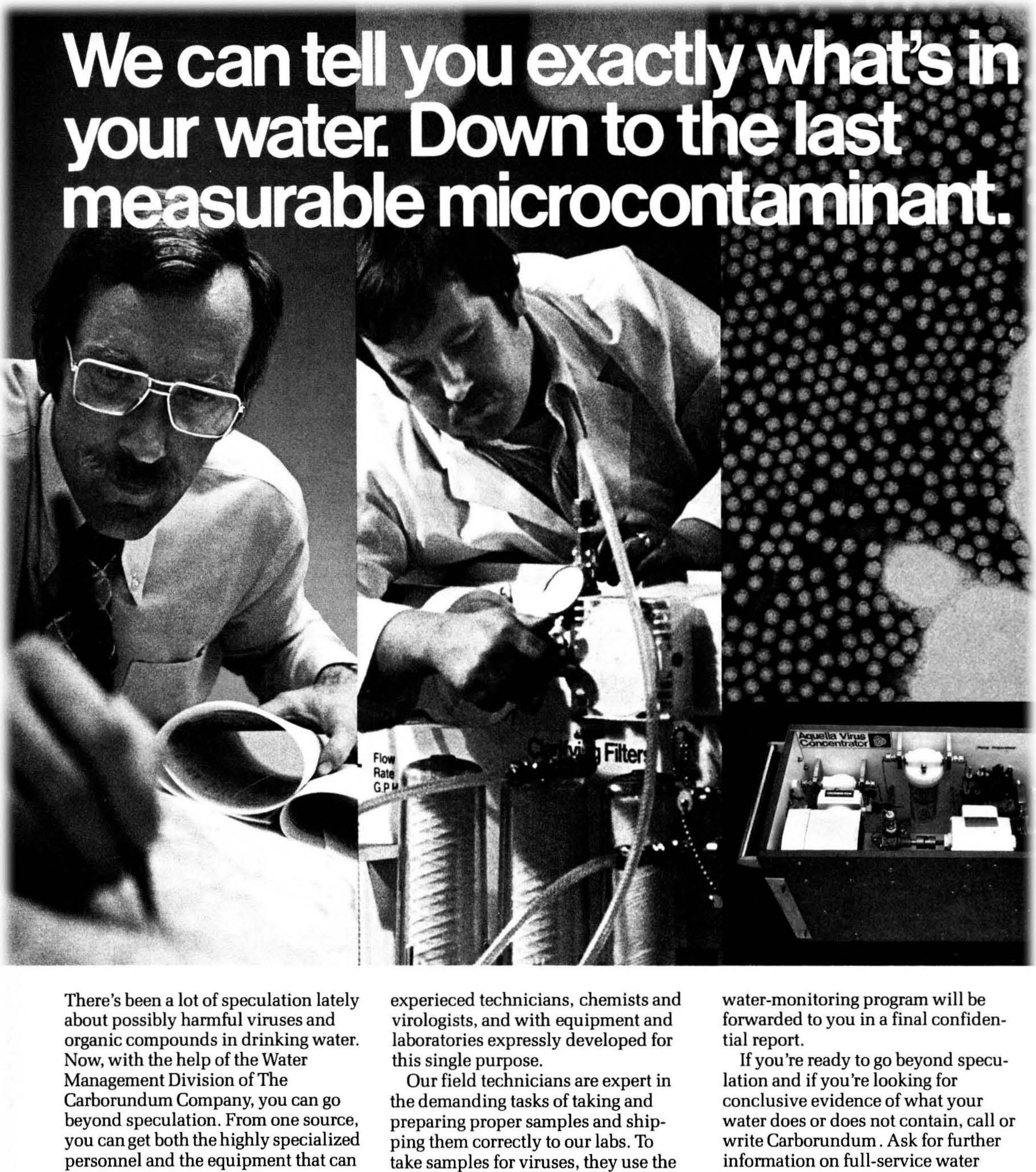

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Experimental. Apparatus: List devices only if of specialized nature. Reagents: List and describe preparation of special reagents only. Procedure: Omit details of procedures which are common knowledge to those in the field. Brief highlights of published procedures may be included, but details must be left to literature cited. Describe pertinent and critical factors involved in reactions so the method can be reproduced, but avoid excessive description. Results and discussion: Be complete but concise. Avoid nonpertinent comparisons or contrasts.

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Three complete, legible copies of the manuscript are required. They should be typed double- or triple-spaced on 8½ × 11 in. paper, with text, tables, and illustrations of a size that can be mailed to reviewers under one cover. Duplicated copies will be accepted only if very clear.

If pertinent references are unpublished, furnish copies of the work or sufficient information to enable reviewers to evaluate the manuscript.

In general, graphs are preferable to tables, if precise data are not required. When tables are submitted, however, they should be furnished with appropriate titles and should be numbered consecutively in Roman numeral style in order of reference in the text. Double space with wide margins, and prepare tables in a consistent form, each on a separate 8½ × 11 in. sized sheet.

Submit original drawings (or sharp glossy prints) of graphs, charts, and diagrams prepared on high-quality inking paper. All lines, lettering, and numbering should be sharp and unbroken. If coordinate paper is used, use blue cross-hatch lines as no other color will "screen out."

Typed lettering does not reproduce well: use black India Ink and a lettering set for all letters, numbers, and symbols. On 8 × 10 in. copy, lettering should be at least ½ in. high and 0.017 in. thick—for example, with a Leroy lettering set, use template 120C and pen No. 0. Lettering on copy of other sizes should be in proportion. Label ordinates and abscissas of graphs along the axes and outside the graph proper. Do not use pressed wax for numbering or lettering; it rubs off in all the mailings and handlings necessary before receipt by printer.

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Number all illustrations consecutively using Arabic numerals in the order of reference in the text. Include a typed list of captions and legends for all illustrations on a separate sheet.

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Use consistent units of measure (preferably metric).

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Acknowledgment

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Identification of Organic Compounds in Unbleached Treated Kraft Paper Mill Wastewaters

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■ Wastewaters from two kraft paper mills in Georgia were sampled at various points in the waste treatment systems. Gas chromatography of the organic extracts and identification of many of the specific chemical components by gas chromatography–mass spectrometry provided a "chemical profile" of the effluents. The mills, in different geographical locations, have very similar raw wastewater compositions but different wastewater treatments. In spite of these differences, the treated effluents are qualitatively similar in composition although the quantities of the various components differ. After two years the raw and treated effluents of both mills were resampled. Analyses showed that although concentrations of the organics varied, the same compounds are still present.

"The need to know what chemicals may escape into the environment and at what levels they may be harmful leads rather quickly to a realization that until one can identify these compounds with certainty and measure their presence in selected compartments of the environment, effective control of these chemicals is essentially impossible" (*1*). Knowledge of the specific chemical composition of treated wastewaters is basic to the evaluation of the environmental impact of these wastewaters and to the problem of analyzing and controlling their discharge. By tracing the chemicals through the treatment system one can identify which compounds are being effectively removed and which are resistant to the treatment in use. Any new chemicals produced during treatment are readily apparent. Once identifications are made, the approximate concentration of each compound can be calculated at each stage of the treatment. To our knowledge this study represents the first attempt to characterize a wastewater chemically, trace the dissolved volatile organics through a treatment system, and correlate this information with the traditional collective pollution prarameter measurements (BOD, TOC). The results detailed in this paper were gathered over a six-year period and portions of them have been presented previously (*2–4*).

Paper Mill Treatment Facilities

Two mills, having similar processes but different waste treatments, were used in this study. The first, Paper Mill "A", daily produced about 1400 tons of containerboard in March 1972 when the samples were taken. Approximately 13 million gal of water passed through the treatment system daily. The treatment system is diagrammed in Figure 1. The total BOD reduction through the whole system is reported to be in excess of 70%.

The second mill, Interstate Paper Corp., Riceboro, Ga., daily produced about 540 tons of containerboard in March 1972 when the samples were taken. Approximately 5.5 million gal of water passed through the treatment system daily. The treatment system is diagrammed in Figure 2. In the 650-acre stabilization lagoon, the highly alkaline effluent (pH 12) first undergoes partial neutralization to pH 10 by surface absorption of atmospheric carbon dioxide, causing precipitation of nearly all the remaining calcium salts in the inlet section of the stabilization basin. Lime treatment removes about 90% of the color from the effluent. Overall BOD reduction is reported to be 93%, with a concentration of about 6 mg/l. in the lagoon effluent (*5, 6*).

Experimental

Sampling and Materials. Burdick and Jackson "distilled in glass" solvents were used for all extractions. Effluent samples were placed in polyethylene plastic containers and

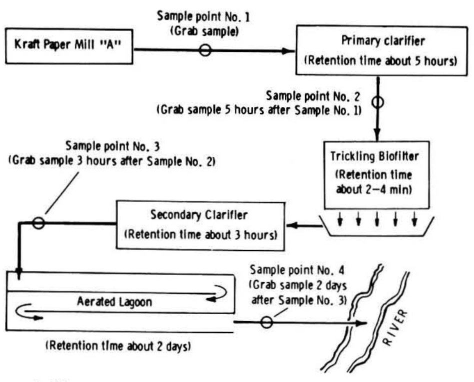


Figure 1. Waste treatment system diagram of Mill "A"

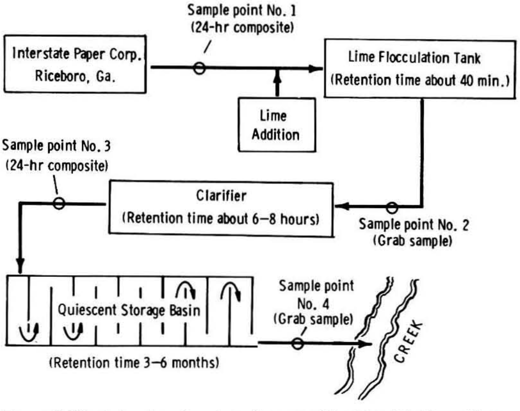


Figure 2. Waste treatment system diagram of the Interstate Paper Corp. mill at Riceboro, Ga.

immediately frozen. They were stored at −10 °C and thawed for use as necessary.

Both mills were sampled twice. In 1972, grab samples for chemical characterization were taken at various stages of the treatment systems and time delays were programmed so that a "slug" of the effluent could be followed through the treatment facilities. However, quantitative analysis indicated that the slug was missed at the outfall of Mill "A". During the second sampling period, in January 1974, three-day composites were collected from the raw effluent and the outfalls of both mills by automatic sampling devices. Samples were not taken at intermediate points.

A three-day composite composed of equal volumes from the Monday, Tuesday, and Wednesday raw wastewater samples of Mill "A" was prepared. A second three-day composite was composed of equal volumes from the Wednesday, Thursday, and Friday treated wastewater samples of Mill "A". Three-day compositles of equal volumes from the Monday, Tuesday, and Wednesday raw wastewater and of the treated wastewater samples of the Interstate Mill at Riceboro were prepared. Because the stabilization pond retention time is at least three months, no attempt was made to obtain samples of the same slug of this wastewater. The concentrations in the 1972 grab samples (Table II) cannot be considered "typical" because the concentrations of the individual components vary significantly with time. Comparison of these values with those obtained in the 1974 sampling period (which *are* more "typical" because they represent three-day composites) shows that while some compounds varied almost by an order of magnitude, others had very similar values.

Instrumentation

Both Varian 1400 and Perkin-Elmer 900 gas chromatographs (GC) equipped with flame ionization detectors (FID) were used. Generally, a commercially prepared (Perkin-Elmer) 50-ft support coated open tubular (SCOT) capillary column coated with Carbowax 20M/terephthalic acid (K 20 M/TPA) was used for separation. The optimum carrier gas flow for our GC–MS systems operating under a vacuum and using a Gohlke jet separator (16–18 ml/min) is twice the amount necessary for optimizing conditions with an auxiliary GC (operating under atmospheric pressure). From 1968 to 1971, a Perkin-Elmer/Hitachi RMU-7 double focusing mass spectrometer (MS) connected to a Perkin-Elmer 900 GC through a Watson-Bieman separator was used. Now a computerized Finnigan 1015 quadrupole MS connected to an all-glass, single-stage Gohlke jet separator is used. Complete descriptions of the instrumentation and our techniques for computer matching the mass spectral data are described elsewhere (*7, 8*).

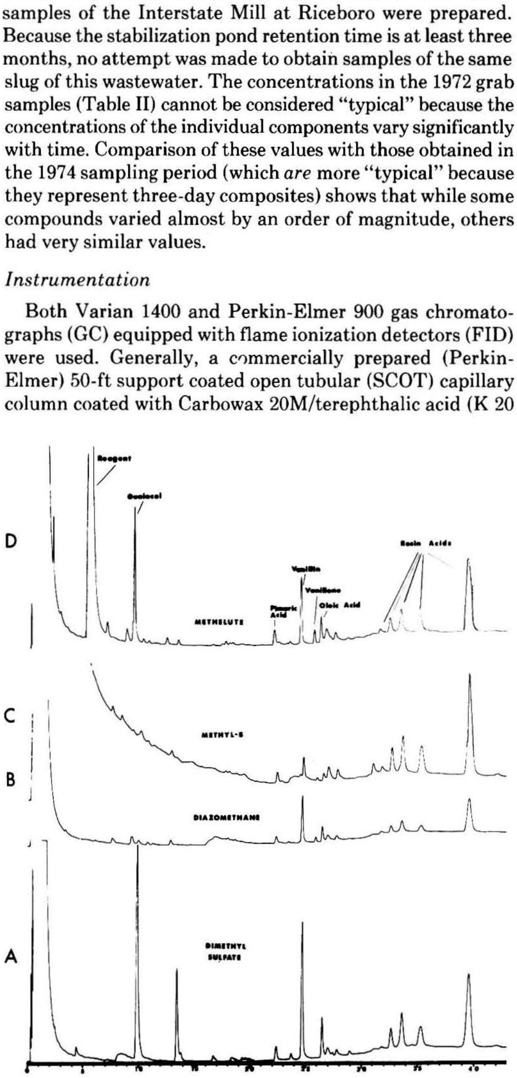


Figure 3. Gas chromatograms of the methyl derivatives from Mill "A" wastewater using (A) dimethyl sulfate, (B) diazomethane, (C) Methyl-8, and (D) MethElute as methylating reagents

Analytical Procedures

Methylation Techniques. Paper mill wastewater extracts contain two types of extractable volatile compounds: neutrals (predominately terpenes and their derivatives), and acidic compounds converted to their methyl derivatives to facilitate GC separation. The aqueous solution can be methylated directly with dimethyl sulfate and sodium hydroxide, followed by extraction of the methyl derivatives with chloroform, or methyl derivatives of the acid extracts can be made in a separate step using diazomethane, on-column GC methylation techniques, or several other common methylation procedures. Several methods were evaluated—each has its advantages and disadvantages, but their overall effectiveness is best illustrated by Figure 3.

A 500-ml portion of the Mill "A" wastewater from sample point 2 (primary clarifier effluent) was made alkaline to pH 11 with sodium hydroxide and extracted with chloroform to remove the neutral compounds. Methylation of the aqueous layer with dimethyl sulfate was followed by re-extraction with chloroform to remove the methylated organics. The procedure we use (*9*) is a variation of that described by Bicho et al. (*10, 11*). After concentration in a Kuderna-Danish apparatus to 0.5 ml, 1.2 µl of the extract was chromatographed on a 50-ft SCOT column coated with Carbowax 20 M/TPA and programmed from 100–200 °C at 4°/min with an initial 2-min hold at 100°. The chromatogram is shown in Figure 3-A.

A 1-l. portion of the same wastewater was extracted with chloroform at pH 11 to remove neutral compounds and then made acidic to pH <2 with concentrated hydrochloric acid. The aqueous layer was re-extracted with four 200-ml portions of chloroform to remove the acids and phenols. The extracts were combined and divided into two equal portions, each representing 500 ml of the wastewater extract.

One portion was concentrated to near dryness in a Kuderna-Danish apparatus and methylated with diazomethane; the final volume was adjusted to 0.5 ml. The chromatogram of 1.2 µl of this sample under conditions identical to those of the previous sample is shown in Figure 3-B.

The second portion of the chloroform extract was concentrated in a Kuderna-Danish apparatus to near dryness and MethElute (trimethylanilinum hydroxide in methanol, Pierce Chemical Co.), which methylates the sample on-column, was added to bring the volume to 0.5 ml. The chromatogram of 1.2 µl of this sample under conditions identical to those of the previous two samples is shown in Figure 3-D.

Another 500-ml portion of the wastewater, after extraction of neutral compounds at pH 11, was made acidic and extracted with four 100-ml portions of chloroform. The extracts were combined, dried, and concentrated to near dryness as before in a Kuderna-Danish apparatus. Enough Methyl-8 (DMF dimethyl acetal in pyridene, Pierce Chemical Co.) was added to bring the volume to 0.5 ml, and the solution was heated at 60 °C for 15 min in a reacti-vial. The chromatogram of 1.2 µl of this sample, under conditions identical to those of the other three, is shown in Figure 3-C.

Comparison of the chromatograms in Figure 3 shows that dimethyl sulfate and MethElute are better reagents for methylating the paper mill samples than diazomethane or Methyl-8. Phenols, especially guaiacol, were not methylated well with diazomethane or Methyl-8. Although extraction of guaiacol and other phenols with chloroform is not 100%, incomplete extraction can be eliminated as a major contributor to the smallness of the methylated guaiacol peak (veratrole) in the diazomethane sample because the samples for diazomethane and MethElute treatment came from the same extract, divided into two portions; the MethElute sample shows a large veratrole peak. The dimethyl sulfate appears to be equivalent to MethElute with respect to methylation of the resin and fatty acids. However, the larger phenolic peaks in the dimethyl sulfate sample and the absence of the MethElute reagent peak made us decide to use dimethyl sulfate for the remaining methylations.

GC–MS Techniques. After a sample is injected into the computer–GC–MS system, the mass spectrometer automatically scans its preset mass range every 4–5 s. When each run is complete, the computer plots a reconstructed gas chromatogram (RGC). To minimize the time spent identifying the hundreds of spectra resulting from the GC–MS data output from complex mixtures such as these extracts, we first executed computer matching of the spectra. This was followed by a manual comparison of the computer-matched spectra with the reference mass spectra. Widespread use of GC–MS spectral matching in pollutant identification requires easy access to a central spectra library (7), rapid matching, and an indication of the similarity of the unknown spectrum to the reference spectrum for each match. An EPA program that provides such information was developed using the algorithm of a matching program described in the literature (*12*). This rapid-matching program was developed jointly by Battelle and the Environmental Research Laboratory-Athens and utilized a CDC 6400 time-shared computer (*13*).

Results

Identification of Terpenes. Table I lists the individual compounds found in the neutral fraction of the wastewater extracts. Most of these are terpenes. The corresponding gas chromatograms of Mill "A" extract are shown in Figure 4 with peak numbers that correspond to the compounds in Table I. Vertical displays of gas chromatograms of extracts taken at consecutive points in a waste treatment system, with the compounds identified by name or code, are called "chemical profiles". The compounds present and their relative concentrations are shown as a function of the treatment. Such a display allows one to see at a glance the effectiveness (or lack of it) of each step in the treatment process with respect to an individual compound, to a class of compounds, or to all chromatographable compounds in the wastewater, whether they are identified or not. This information in conjunction with the traditional collective pollution parameters (e.g., BOD and TOC) provides a much better understanding and evaluation of the effluent composition and its possible environmental effects than the chemical profiles or collective parameters alone.

Two of the neutral extracts from Mill "A" were analyzed by a Digilab Fourier Transform infrared spectrophotometer

Table I. Neutral Volatiles Identified in Both Kraft Paper Mill Effluents with Approximate Concentrations (1972)

Peak no.	Compound identified	Confirmed by	Approximate concn. in mg/l., Mill "A" sample points				Approximate concn. in mg/l., Interstate sample points			
			1	2	3	4	1	2	3	4
4	Methyl trisulfide		0.003	0.004	0.008	0.001	—	—	—	—
62	Fenchone	MS, GC	0.007	0.007	0.015	0.015	0.015	0.002	0.001	<0.001
63	Hexachloroethane		—	—	—	—	—	—	—	<0.001
64	Sabinene		—	—	—	—	—	—	—	0.003
65	Unidentified terpene ketone		0.055	0.050	0.055	0.045	0.040	0.010	0.015	0.004
66	Camphor	MS, GC, IR	0.045	0.045	0.060	0.090	0.090	0.015	0.020	0.035
67	Unidentified terpene ketone		0.045	0.040	0.050	0.045	0.045	0.006	0.020	0.008
68	Unidentified terpene ketone		0.020	0.020	0.025	0.020	0.020	0.003	0.008	0.002
69	Fenchyl alcohol	GC	0.065	0.065	0.035	0.010	0.105	0.040	0.060	—
70	Unidentified terpene ketone		0.025	0.025	0.020	0.004	0.015	0.005	0.009	—
71	Terpene-4-ol	MS, GC	0.050	0.045	0.040	0.010	0.030	0.010	0.015	<0.001
72	2-Formylthiophene		0.010	—	—	—	—	—	—	—
73	Methyl chavicol	MS, GC	0.045	0.040	0.030	—	0.030	0.010	0.020	—
9	Borneol	MS, GC, IR	0.275	0.200	0.155	0.090	0.470	0.200	0.260	—
10	α-Terpineol	MS, GC	0.645	0.700	0.625	—	0.490	0.215	0.280	0.080
11	Veratrole	MS, GC	0.020	0.015	0.015	0.008	0.015	0.004	0.008	—
74	2-Acetylthiophene	GC, IR	0.025	0.025	0.030	0.025	0.012	0.002	0.004	<0.001
75	Myrtenol		0.010	0.010	0.008	—	0.008	—	—	—
76	2-Propionylthiophene	GC, IR	0.025	0.025	0.025	0.010	0.020	0.005	0.010	<0.001
77	Anethole		0.007	—	—	—	—	—	—	—
78	Benzyl alcohol		0.013	0.012	0.008	—	0.025	0.004	0.007	—
79	Methyl eugenol	GC	0.002	0.001	—	—	—	—	—	—
80	Unidentified terpene alcohol		0.006	0.007	0.010	—	0.030	0.015	0.015	0.008
81	Unidentified aromatic similar to methyl isoeugenol (MW = 178)		0.006	0.008	0.009	—	0.009	0.006	0.008	—
30	Ethyl palmitate	MS,GC	0.006	—	—	—	—	—	—	—
82	Unidentified monounsaturated C_{19} fatty acid methyl ester		0.038	—	—	—	—	—	—	—
83	Unidentified diunsaturated C_{19} fatty acid methyl ester		0.016	—	—	—	—	—	—	—
84	Unidentified phthalate diester		—	—	—	—	—	—	—	—
Total			1.464	1.344	1.223	0.711	1.469	0.552	0.760	0.145

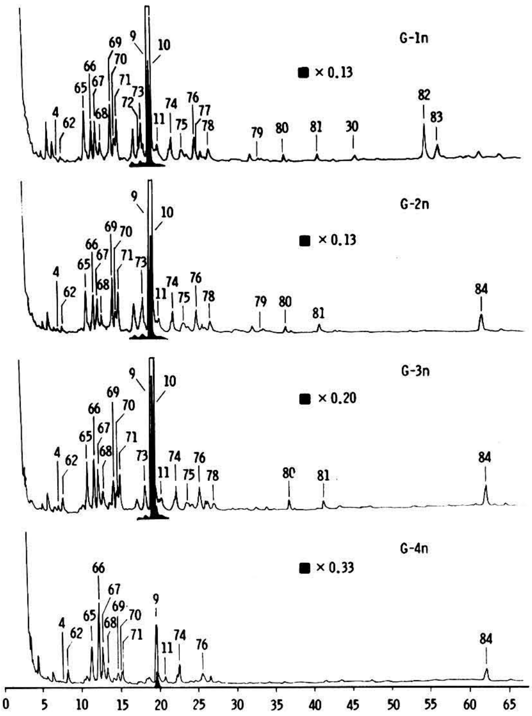


Figure 4. Chemical profile of neutral volatile compounds from Mill "A" extracts of sample points 1–4 (top to bottom)

interfaced with a gas chromatograph (GC–IR). Spectra of the eluting compounds are obtained "on the fly" as they are with the GC–MS system. These analyses were helpful in confirming the functional groups of several unidentified compounds. For example, compounds 67, 68, and 70 were all shown to be ketones. Computer matching of the mass spectra of these same peaks had led to tentative identifications of 1-cyclohexenyl methyl ketone, 4-nonyne, and 3-cyclohexen-1-yl methyl ketone, respectively. Obviously the match for 4-nonyne was wrong.

In low concentrations these neutral compounds are probably not significant pollutants. The chemical profile, supported by Table I, shows that the treatment systems are able to reduce the concentration of most of these chemicals by large factors. An exception may be the terpene ketones. Several ketones either are not reduced in concentration or are increased in concentration in short term biological oxidation systems. Ketones 65, 67, and 68 were not significantly reduced in concentration in the Mill "A" wastewater and two (camphor and fenchone) were increased. An increase in the concentrations of camphor and fenchone in similar instances has been verified in an independent report (*14*).

Identification of Fatty Acids. A total of 17 different fatty acids were found in the wastewaters of both mills, 15 were identified, and two unsaturated acids remain unidentified (Table II). The fatty acid contents of both raw wastewaters (sample point 1) were qualitatively similar. Seven of the eight fatty acids present in the raw wastewaters were found at both mills (palmitic, anteisomargaric, stearic, oleic, linoleic, arachidic, and unidentified unsaturated acid #54).

More dissimilarity existed in the fatty acid content of the two lagoon effluents (sample point 4). Ten acids were found in both effluents (isomyristic, myristic, anteisopentadecanoic,

Table II. Acids and Phenols Identified in Both Kraft Paper Mill Effluents with Approximate Concentrations (1972)

Peak no.	Compound identified as methyl derivative (parent compound)	Confirmed by	Approximate concn in mg/l., Mill "A" sample points				Approximate concn in mg/l., Interstate sample points			
			1	2	3	4	1	2	3	4
1	Furfuryl methyl ether (furfuryl)	GC	0.010	0.005	—	—	0.010	—	—	—
2	Anisole (Phenol)		0.008	—	—	—	0.005	0.005	—	—
3	1,3-Dimethoxy-2-propanol		—	—	—	—	—	0.010	—	—
4	Methyl trisulfide		—	0.005	—	—	—	—	—	—
5	Unidentified—apparent MW = 103		0.035	0.035	0.040	0.035	0.025	0.055	0.020	0.015
6	Benzaldehyde	GC	0.002	—	—	—	0.005	—	—	—
7	Dimethylsulfoxide	GC	—	—	0.055	—	0.010	0.080	0.020	0.020
8	Ethyl carbamate	GC	0.010	0.015	0.025	0.020	—	0.080	0.020	0.010
9	Borneol	MS, GC	—	—	—	—	0.010	0.020	0.060	—
10	α-Terpineol	MS, GC	0.020	0.002	0.001	—	0.005	0.020	0.115	0.002
11	Veratrole (guaiacol)	MS, GC	2.700	2.400	0.360	0.170	2.200	3.200	3.700	0.035
12	*o*-Nitrotoluene	MS, GC	—	—	—	0.015	—	—	—	—
13	Methyl *o*-hydroxybenzoate (*o*-hydroxybenzoic acid)		0.010	0.005	—	—	—	—	—	—
14	Methyl mandelate (mandelic acid)		—	—	—	0.025	—	—	—	—
15	Dimethylsulfone	GC	0.240	0.400	0.400	0.055	0.240	0.540	0.400	0.130
16	Unidentified aromatic MW = 166		0.130	0.090	0.050	0.005	0.050	0.030	0.160	—
17	Methyl isomyristate (C_{14} fatty acid)	GC	—	—	—	0.003	—	—	—	0.001
18	*p*-Methoxybenzaldehyde (*p*-hydroxybenzaldehyde)		0.055	0.050	0.020	0.025	0.090	0.240	0.190	0.005
19	Eugenol		0.025	0.025	0.025	—	—	—	—	—
20	Methyl myristate (C_{14} fatty acid)	MS, GC	—	—	—	0.020	—	—	—	0.010
21	Unidentified aromatic, MW = 196		—	—	0.045	0.035	—	—	—	—
22	Unidentified nonaromatic, MW = 196		—	—	—	—	0.170	0.175	0.245	0.065
23	Methyl anteisopentadecanoate (C_{15} fatty acid)	MS, GC	—	—	0.010	0.020	—	—	—	0.005
24	Methyl 10-methyltetradecanoate (C_{15} fatty acid)		—	—	—	0.030	—	—	—	0.002
25	*p*-Methoxyacetophenone (*p*-hydroxyacetophenone)	GC	0.020	0.025	0.030	—	0.060	0.130	0.080	0.010

Table II. (Continued)

Peak no.	Compound identified as methyl derivative (parent compound)	Confirmed by	Approximate concn in mg/l., Mill "A" sample points				Approximate concn in mg/l., Interstate sample points			
			1	2	3	4	1	2	3	4
26	Methyl pentadecanoate (C_{15} fatty acid)	MS, GC	—	—	—	0.020	—	—	—	0.010
27	Methyl isopalmitate (C_{16} fatty acid)	MS, GC	—	—	0.015	0.030	—	—	—	0.003
28	Methyl palmitate (C_{16} fatty acid)	MS, GC	0.070	0.190	0.180	0.430	0.140	0.160	0.035	0.017
29	Methyl palmitelaidate (C_{16} *trans*-9-unsaturated fatty acid)	MS, GC	0.005	0.020	0.025	0.125	—	—	—	0.010
30	Ethyl palmitate (C_{16} fatty acid)	MS, GC	—	—	—	0.030	—	—	—	—
31	Methyl anteisomargarate (C_{17} fatty acid)	MS, GC	0.020	0.025	0.040	0.050	0.030	0.120	0.040	0.001
32	Methyl 3,4-dimethoxyphenylacetate (Homovanillic acid)		0.050	0.075	0.090	0.080	0.090	0.365	0.150	0.003
33	Veratraldehyde (vanillin)	MS, GC	1.500	1.700	0.450	0.410	2.100	4.400	2.600	0.070
34	2-Methylthiobenzothiazole (2-Mercaptobenzothiazole)	GC	0.035	0.025	0.030	0.025	—	—	—	—
35	Methyl vanillate (vanillic acid)	GC	—	—	0.005	0.005	—	—	—	—
36	Acetoveratrone (acetovanillone)	GC	0.420	0.490	0.450	0.370	0.820	1.600	0.860	0.120
37	Methyl stearate (C_{18} fatty acid)	MS, GC	0.025	0.065	0.045	0.110	0.100	0.100	0.020	—
38	Methyl oleate (C_{18} *cis*-9-unsaturated fatty acid)	MS, GC	0.470	0.600	0.430	0.400	0.570	0.510	0.120	0.080
39	3,4,5-Trimethoxybenzaldehyde (syringaldehyde)	MS, GC	0.070	0.070	0.070	0.040	0.070	0.100	0.070	0.020
40	Methyl linoleate (C_{18} *cis,cis*-9, 12-diunsaturated fatty acid)	MS, GC	0.350	0.470	0.230	0.100	0.450	0.920	0.160	—
41	3,4-Dimethoxypropiophenone (3-Methoxy-4-hydroxy-propiophenone)	GC	0.060	0.080	0.025	—	—	—	—	—
42	3,4,5-Trimethoxyacetophenone (acetosyringone)	GC	0.055	0.060	0.050	0.050	0.090	0.200	0.130	0.005
43	Methyl arachidate		0.030	0.035	0.030	0.025	0.035	0.025	—	—
44	Dihexyl phthalate		—	—	—	—	—	—	—	—
45	Unidentified resin acid "A" methyl ester		—	—	—	—	0.070	0.075	0.130	0.020
46	Unidentified resin acid "B" methyl ester		0.030	0.055	0.095	0.100	—	—	—	—
47	Unidentified resin acid "C" methyl ester		0.100	0.055	0.010	—	—	—	—	—
48	Unidentified resin acid "D" methyl ester		—	—	—	—	—	—	—	0.145
49	Unidentified unsaturated fatty acid methyl ester		—	—	0.005	0.035	—	—	—	—
50	Methyl pimerate (resin acid)	MS, GC	0.245	0.475	0.570	0.800	1.270	0.825	0.610	0.500
51	Methyl sandaracopimerate (resin acid)	MS, GC	0.050	0.060	0.125	0.045	0.340	0.245	0.275	0.110
52	Unidentified resin acid "E" methyl ester		0.025	—	—	—	—	—	—	—
53	Methyl-13-abieten-18-oate (resin acid)	MS, GC	—	0.430	0.800	1.400	0.100	0.035	0.050	1.050
54	Unidentified unsaturated fatty acid methyl ester similar to araconidate		0.035	—	—	—	0.075	—	—	—
55	Methyl isopimerate (resin acid)	MS, GC	0.430	0.660	0.770	0.780	4.400	1.700	1.200	0.800
56	Methyl abietate (resin acid)	GC	0.370	0.430	0.420	0.050	3.300	1.500	1.900	—
57	Methyl dehydroabietate (resin acid)	MS, GC	1.500	1.300	4.000	1.000	3.300	2.700	3.600	3.900
58	Methyl 6,8,11,13-abietatetraen-18-oate (resin acid)	MS, GC	0.065	0.070	0.170	0.095	0.160	0.115	0.280	0.180
59	Methyl neoabietate (resin acid)	MS, GC	0.105	0.125	—	—	1.300	1.200	0.450	—
60	Methyl lignocerate (C_{24} fatty acid)	MS, GC	—	—	0.055	0.030	—	—	—	—
61	Dioctyl phthalate		—	—	—	—	—	—	—	—
Totals			9.380	10.692	10.246	7.123	21.690	21.480	17.700	7.243

10-methyltetradecanoic, pentadecanoic, isopalmitic, palmitic, palmitelaidic, anteisomargaric, and oleic). Six others were found in the lagoon effluent of one mill but not the other [ethyl palmitate (as the ester), stearic, linoleic, lignoceric, arachidic, and unidentified unsaturated acid #54]. In both mill wastewaters a greater number of fatty acids were found in the lagoon effluent than in the influent. The majority of the new compounds are saturated low-molecular-weight (C-14, C-15, C-16) branched and straight-chain fatty acids and are probably metabolites of the lagoon biota. The only fatty acid identification not verified by comparison of GC retention time with a standard is the methyl ester of 10-methyltetradecanoate. Its identification rests solely on interpretation of its mass spectrum (*9*).

Little or no work has been reported on the analyses of fatty acids in treated paper mill effluents. We have found no previous report of odd-numbered carbon and branched fatty acids in treated wastewaters. The presence of 10-methyltetradecanoic acid and ethyl palmitate, although in small amounts, was unexpected.

Identification of Resin Acids. A total of 13 different resin acids (Table II) was found in the wastewaters of both mills in the 1972 samples; eight were identified and confirmed and five were not identified. The resin acid contents of the finished wastewaters were qualitatively similar for the two mills. Seven resin acids were common to the raw wastewater extracts of both mills and six of these were found in both finished wastewater extracts. Differences were primarily found among the small, unidentified resin acid GC peaks.

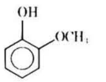
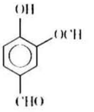
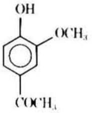
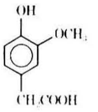
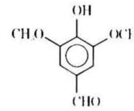
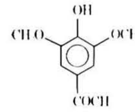
In addition to the isopimaric, abietic, dehydroabietic, and sandaracopimaric acids found in a recent study by Leach and Thakore (*15*), we identified pimaric, 6,8,11,13-abietatetraen-18-oic, neoabietic, 13-abieten-18-oic, and several unidentified resin acids. To our knowledge, neoabietic, 13-abieten-18-oic, and 6,8,11,13-abietatetraen-18-oic acids have not been reported before in kraft pulp mill wastewaters. All of these resin acids (as their methyl esters) were initially identified by comparison of their mass spectra with published mass spectra (*16*). They were all confirmed by comparison of GC retention times and GC–MS from our instrument with standards obtained from Dr. Duane F. Zinkel, USDA Forest Products Laboratory, Madison, Wis.

In general, most compounds decreased significantly in concentration as the wastewater passed through the treatment system. One exception appeared to be the resin acid content. Some of the peaks appeared to increase in concentration. We believe this to be the result of large variances in the concentration of the organics in the mill wastewaters with time and failure to have precisely sampled the "slug" of effluent we tried to follow through the treatment systems.

Identification of Phenols. Eleven different phenols were identified in the kraft mill wastewaters (Table II). Based upon the data obtained in 1974, some correlation can be made between the percent removal of the phenols in the two waste treatment systems and the complexity or degree of substitution of the phenol molecules. Table III lists the percent removal of these phenols and shows their structures. The analytical data for the calculations were obtained from 3-day composite samples quantitated with the aid of the Perkin-Elmer PEP-1 computer system. The phenols are generally more resistant to treatment as the complexity of the molecule increases. This is especially true with Mill "A", which has only biological treatment, with the single exception of *p*-hydroxybenzaldehyde, which might be produced in the aerated lagoons by biological degradation of lignin or vanillin. The chemical profiles of the acids and phenols from both mills are shown in Figures 5 and 6. The peak numbers correspond to the compounds listed in Table II. The compositions of the raw effluents from the two mills were similar, but the treated effluent samples from the two mills exhibited more differences.

Computer-Assisted Gas Chromatographic Analyses. Based on the compound identifications from the 1972 analyses, a computer-assisted GC analysis was used to analyze the 1974 wastewater samples. GC–MS was used to verify com-

Table III. Percent Removal of Phenols vs. Their Structural Complexity (1974)

Parent compound	Identified as	Structure	% removed Mill "A"	% removed Interstate
Guaiacol	Veratrole		96	98
p-Hydroxybenzaldehyde	*p*-Methoxybenzaldehyde		21	75
Vanillin	Veratraldehyde		65	93
Acetovanillone	Acetoveratrone		77	90
Homovanillic Acid	Methyl homovanillate		50	?
Syringaldehyde	3,4,5-Trimethoxybenzaldehyde		62	—
Acetosyringone	3,4,5-Trimethoxyacetophenone		57	67

pound identifications. Once compounds were identified, computer-assisted GC analysis was sufficient for subsequent qualitative and quantitative analyses. Chloroform extracts of 1 l. of each sample were concentrated to 1.0 ml. A 300-μl aliquot of each extract was spiked with 30 μl of a standard solution (11 mg/ml) of acenaphthene, the internal standard, bringing its concentration in the extract to 1.0 mg/ml. A standard solution of acenaphthene, veratrole, methyl palmitate, and methyl dehydroabietate was prepared and chromatographed using the PEP-1 computer system. From the known concentrations and the measured peak areas, response factors were calculated for each compound relative to that of acenaphthene (veratrole, 1.49; methyl palmitate, 2.05; methyl dehydroabietate, 2.32). Concentrations of the various phenols and fatty and resin acid methyl esters in the samples were then calculated by computer; we assumed that all compounds in a given chemical class have similar response factors.

Computer analyses of the three-day composite extracts from Mill "A" and from the Interstate mill are shown in Figures 7 and 8, respectively. Peak number designations, notation of the presence or absence of the compound in the corresponding 1972 sample, and the sum of all the concentration values were manually added to the data printed out by the computer.

Collective Pollution Parameters. Comparison of collective pollution parameters (Table IV) indicates that BOD removal is about 70–90% in both mill wastewaters during treatment. TOC reduction in the treated wastewaters of both mills probably varies between 60–90%. Because of large amounts of suspended solids in the raw effluent of Mill "A", the TOC values may be erroneous. Reduction in total chromatographable acidic materials is about 65–80% in both mills. The decrease of only 24% in the acidic material for the 1972 sampling of Mill "A" is probably not representative.

If treatment effectiveness is considered with respect to classes of compounds, the phenols appear to be the most susceptible to treatment. Reduction in the chromatographable phenolic content of each mill was very consistent, ranging in Mill "A" wastewaters from a 73–77% reduction. Chromatographable phenols were reduced in the Interstate wastewaters by 94–95%.

Resin acid reductions in the treated wastewaters ranged from about 50–90%. The apparent increase in resin acid content of Mill "A" in 1972 is probably due to a nonrepresentative grab sample.

Fatty acid content of the Interstate wastewaters was decreased by about 85–90%, but the overall fatty acid concentrations increased in both the 1972 and the 1974 samples of Mill "A" treated wastewaters. This is probably due to the production of fatty acids by the microbiota in the aerated lagoons. An increase in number of branched and odd-carbon fatty acids was also noted.

To maintain the proper perspective with respect to a mass balance, the total volatile acidic material as well as the three major classes of compounds comprising it is presented as a percentage of the TOC in Table V. The total of all the volatile acidic components in the wastewater extracts was less than 10% of the total organic carbon content of the wastewaters. The neutral components were less than 1% of the TOC. The sum of all the volatile components therefore is still less than 10% of the TOC. Yet this relatively small amount of dissolved organic material probably represents the bulk of problem-causing compounds—both toxic and taste- and odor-causing compounds. The dark brown color of kraft pulp mill waste-

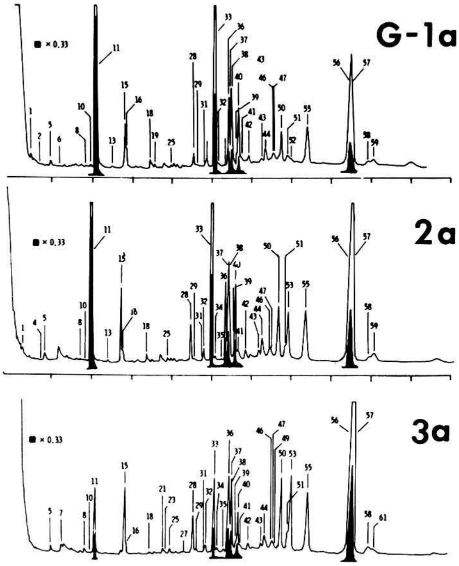


Figure 5. Chemical profile of acids and phenols from Mill "A" extracts of sample points 1–4 (top to bottom)

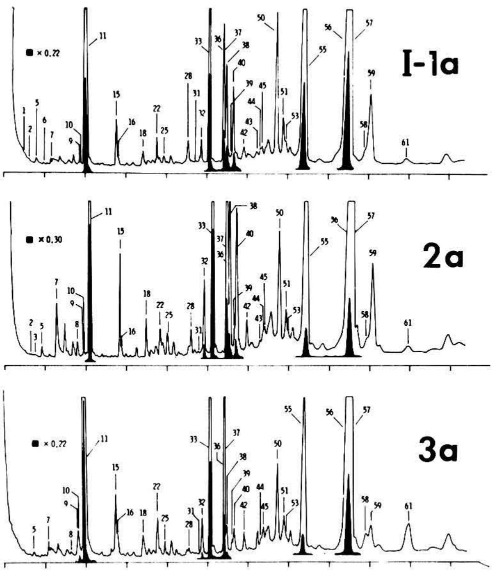


Figure 6. Chemical profile of acids and phenols from Interstate Mill extracts of sample points 1–4 (top to bottom)

Figure 7. Computer analysis of Mill "A" acids and phenols from (top) raw wastewater and (bottom) fully treated effluent (1974)

```
RUN          1   MILL A RAW EFFLUENT-ACIDS AND PHENØLS

INST   4    , METHØD   50   , FILE    37    3:

  TIME        AREA       RRT       RF              C         NAME                        PEAK     IN '72
  10.14      3.1384    1.000,   1.4900,        .5051, VERATRØLE:                     11        YES
  13.66      1.7237    1.347,   2.0500,        .3817, DIMETHYLSULFØNE:               15        YES
  16.70       .2877    1.646,   1.4900,        .0463, METHØXYBENZALDEHYDE:           18        YES
  18.48       .4908    1.822,   1.0000,        .0530, :                              --        --
  19.10      9.2566    1.883,   1.0000,       1.0000, ACENAPHTHENE:                  A         --
  20.08       .3537    1.980,   1.0000,        .0382, :                              --        --
  22.10      1.3317    2.184,   2.0500,        .2949, PALMITATE:                      28        YES
                       2.220,   2.0500,              PALMITELAIDATE:                 29        YES
  23.75       .4753    2.350,   1.4900,        .0765, ME HØMØVANILLATE:              32        YES
  24.73      5.2457    2.450,   1.4900,        .8443, VERATRALDEHYDE:                33        YES
  26.51      3.0875    2.629,   1.4900,        .4969, VERATRØNE:                     36        YES
  26.82      3.5064    2.661,   2.0500,        .7765, STEARATE AND ØLEATE:           37,38     YES,YES
  27.47       .9110    2.726,   1.4900,        .1466, ME SYRINGALDEHYDE:             39        YES
  27.66       .7588    2.746,   2.0500,        .1680, LINØLEATE:                     40        YES
  27.94       .2840    2.774,   1.4900,        .0457, 3,4-DMP:                       41        YES
  28.98       .9289    2.879,   1.4900,        .1495, 3,4,5-TMA:                     42        YES
  30.59       .5729    3.037,   1.0000,        .0618,                                --        --
  31.13       .5133    3.087,   2.3200,        .1286, ME RESIN ACID:                 --        NØ
  31.82       .4960    3.152,   2.3200,        .1243, ME RESIN ACIDS B,C:            46,47     YES,YES
  32.86      4.0798    3.250,   2.3200,       1.0225, PIMERATE:                      50        YES
  34.10      6.7065    3.366,   2.3200,       1.6808, SAND-P AND 13-AB-18-:          51,53     YES,NØ
  36.20      3.8577    3.563,   2.3200,        .9668, ISØPIMERATE:                   55        YES
  41.92     26.4614    4.100,   2.3200,       6.6320, AB- AND DEHYDRØAB-:            56,57     YES,YES
  44.11       .3482    4.305,   2.3200,        .0872, 6,8,11,13-AB-:                 58        YES
  44.59       .5035    4.350,   2.3200,        .1262, NEØABIETATE:                   59        YES
  45.81       .4653    4.464,   2.0500,        .1030, LIGNØCERATE:                   60        NØ
:
                                     TØTAL:   14.9834 MG/L
RUN             MILL A TREATED EFFLUENT-ACIDS AND PHENØLS

INST   4    , METHØD   50   , FILE    36    3:

  TIME        AREA       RRT       RF              C         NAME                        PEAK     IN '72
  10.12       .1291    1.000,   1.4900,        .0193, VERATRØLE:                     11        YES
  13.64       .1732    1.347,   2.0500,        .0356, DIMETHYLSULFØNE:               15        YES
  16.70       .2452    1.650,   1.4900,        .0366, METHØXYBENZALDEHYDE:           18        YES
  17.42       .1129    1.721,   2.0500,        .0232, MYRISTATE:                     20        YES
  18.39       .1112    1.817,   1.4900,        .0166, ARØMATIC  M W 168:             --        --
  18.71       .2002    1.848,   2.0500,        .0412, ANTEISØ C-15 :                 23        YES
  19.11      9.9590    1.888,   1.0000,       1.0000, ACENAPHTHENE:                  A         --
  19.79       .1403    1.955,   2.0500,        .0288, PENTADECANØATE:                26        YES
  20.12       .1804    1.988,   1.0000,        .0181, :                              --        --
  21.03       .1711    2.079,   2.0500,        .0352, ISØPALMITATE:                  27        YES
  22.11      1.8876    2.187,   2.0500,        .3885, PALMITATE:                     28        YES
  22.57      1.1136    2.234,   2.0500,        .2292, PALMITELAIDATE:                29        YES
  23.66       .2549    2.343,   1.4900,        .0381, ME HØMØVANILLATE:              32        YES
  24.44       .2631    2.421,   2.0500,        .0541, MARGARATE:                     M         NØ
  24.72      1.9480    2.450,   1.4900,        .2914, VERATRALDEHYDE:                33        YES
  26.48       .7781    2.626,   1.4900,        .1164, VERATRØNE:                     36        YES
  26.93      2.2860    2.671,   2.0500,        .4705, STEARATE AND ØLEATE:           37,38     YES
  27.44       .3729    2.723,   1.4900,        .0558, ME SYRINGALDEHYDE:             39        YES
  27.64       .1832    2.743,   2.0500,        .0377, LINØLEATE:                     40        YES
  27.92       .1779    2.771,   1.4900,        .0266, PHTHALATE:                     --        --
  28.55       .3314    2.834,   1.0000,        .0332, :                              --        --
  28.98       .4289    2.877,   1.4900,        .0641, 3,4,5-TMA:                     42        YES
  29.54       .2222    2.934,   1.0000,        .0223, :                              --        --
  30.53       .6486    3.031,   2.0500,        .1335, ARACHIDATE:                    43        YES
  31.04       .4631    3.081,   1.4900,        .0692, DIHEXYLPHTHALATE:              44        YES
  31.78       .2201    3.154,   2.3200,        .0512, RESIN AND FATTY ACID:          46,49     YES
  32.78       .8428    3.252,   2.3200,        .1963, PIMERATE:                      50        YES
  33.96      1.4073    3.368,   2.3200,        .3278, SAND-P AND 13-AB-18-:          51,53     YES
  35.48       .2199    3.516,   2.0500,        .0452, UNSAT FATTY ACID:              54        NØ
  36.06       .7912    3.573,   2.3200,        .1843, ISØPIMERATE:                   55        YES
  41.43      2.5728    4.100,   2.3200,        .5993, AB- AND DEHYDRØAB-:            56,57     YES
  44.17       .2192    4.368,   2.3200,        .0510, NEØABIETATE:                   59        NØ
  45.48       .2818    4.496,   2.0500,        .0580, LIGNØCERATE:                   60        YES
  49.59       .1314   *******,   1.0000,       .0131, !
:
                                     TØTAL:    3.8114 MG/L
NØTE:   10-METHYLTETRADECANØATE UNDER ACENAPHTHENE IS ESTIMATED AT
         A CØNCENTRATIØN ØF 0.03 MG/L.

        FATTY ACID METHYL ESTER AT 31.78 MIN. IS UNSATURATED.
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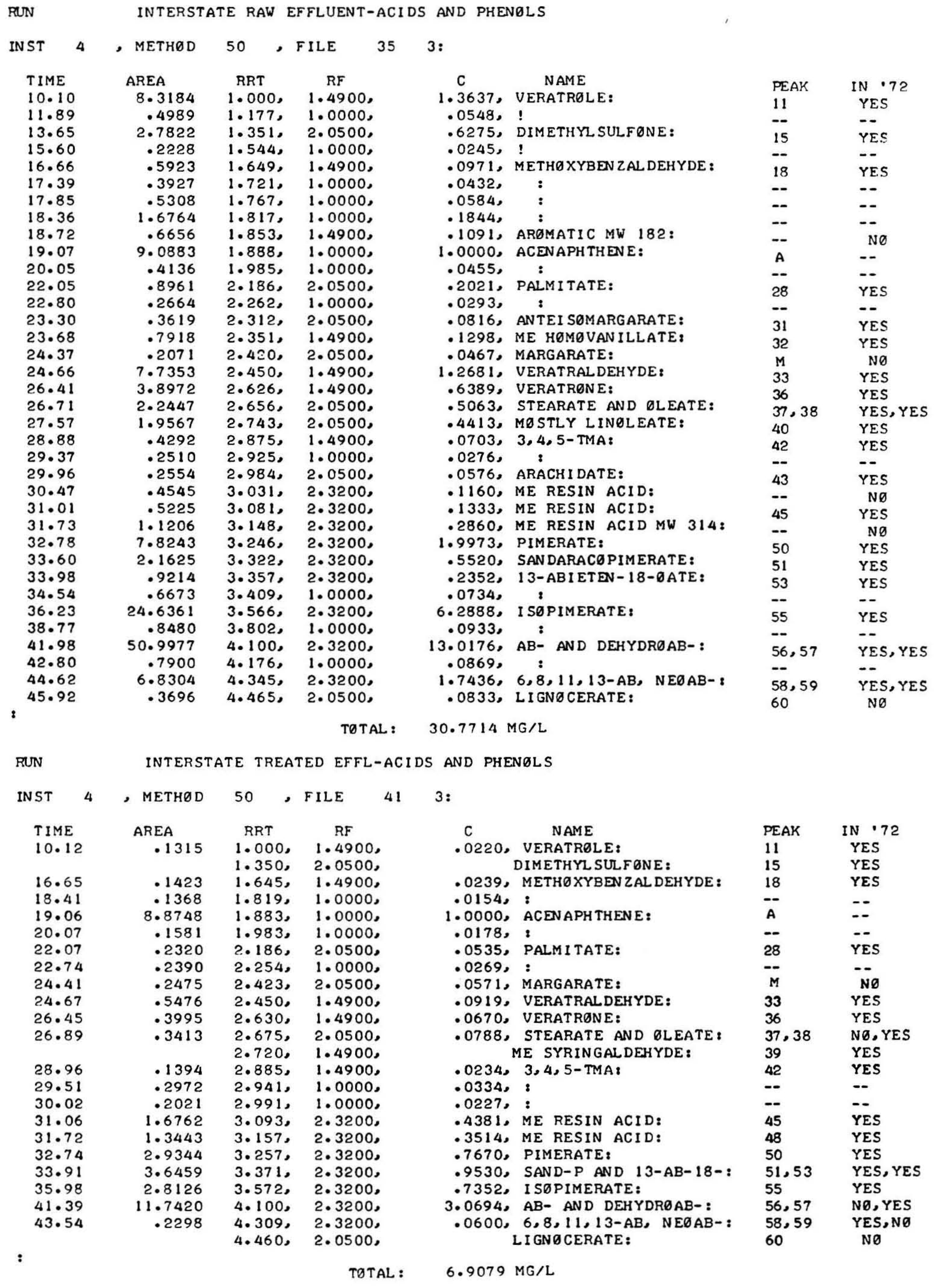
Figure 8. Computer analysis of Interstate Mill acids and phenols from (top) raw wastewater and (bottom) fully treated effluent (1974)



```
RUN            INTERSTATE RAW EFFLUENT-ACIDS AND PHEN0LS

INST   4   , METH0D    50   , FILE    35    3:

  TIME        AREA      RRT      RF           C         NAME                          PEAK    IN '72
  10.10     8.3184   1.000,  1.4900,     1.3637, VERATR0LE:                        11        YES
  11.89      .4989   1.177,  1.0000,      .0548, !                                 --        --
  13.65     2.7822   1.351,  2.0500,      .6275, DIMETHYLSULF0NE:                  15        YES
  15.60      .2228   1.544,  1.0000,      .0245, !                                 --        --
  16.66      .5923   1.649,  1.4900,      .0971, METH0XYBENZALDEHYDE:              18        YES
  17.39      .3927   1.721,  1.0000,      .0432,   :                               --        --
  17.85      .5308   1.767,  1.0000,      .0584,   :                               --        --
  18.36     1.6764   1.817,  1.0000,      .1844,   :                               --        --
  18.72      .6656   1.853,  1.4900,      .1091, AR0MATIC MW 182:                  --        N0
  19.07     9.0883   1.888,  1.0000,     1.0000, ACENAPHTHENE:                     A         --
  20.05      .4136   1.985,  1.0000,      .0455,   :                               --        --
  22.05      .8961   2.186,  2.0500,      .2021, PALMITATE:                        28        YES
  22.80      .2664   2.262,  1.0000,      .0293,   :                               --        --
  23.30      .3619   2.312,  2.0500,      .0816, ANTEIS0MARGARATE:                 31        YES
  23.68      .7918   2.351,  1.4900,      .1298, ME H0M0VANILLATE:                 32        YES
  24.37      .2071   2.420,  2.0500,      .0467, MARGARATE:                        M         N0
  24.66     7.7353   2.450,  1.4900,     1.2681, VERATRALDEHYDE:                   33        YES
  26.41     3.8972   2.626,  1.4900,      .6389, VERATR0NE:                        36        YES
  26.71     2.2447   2.656,  2.0500,      .5063, STEARATE AND 0LEATE:              37,38     YES,YES
  27.57     1.9567   2.743,  2.0500,      .4413, M0STLY LIN0LEATE:                 40        YES
  28.88      .4292   2.875,  1.4900,      .0703, 3,4,5-TMA:                        42        YES
  29.37      .2510   2.925,  1.0000,      .0276,   :                               --        --
  29.96      .2554   2.984,  2.0500,      .0576, ARACHIDATE:                       43        YES
  30.47      .4545   3.031,  2.3200,      .1160, ME RESIN ACID:                    --        N0
  31.01      .5225   3.081,  2.3200,      .1333, ME RESIN ACID:                    45        YES
  31.73     1.1206   3.148,  2.3200,      .2860, ME RESIN ACID MW 314:             --        N0
  32.78     7.8243   3.246,  2.3200,     1.9973, PIMERATE:                         50        YES
  33.60     2.1625   3.322,  2.3200,      .5520, SANDARAC0PIMERATE:                51        YES
  33.98      .9214   3.357,  2.3200,      .2352, 13-ABIETEN-18-0ATE:               53        YES
  34.54      .6673   3.409,  1.0000,      .0734,   :                               --        --
  36.23    24.6361   3.566,  2.3200,     6.2888, IS0PIMERATE:                      55        YES
  38.77      .8480   3.802,  1.0000,      .0933,   :                               --        --
  41.98    50.9977   4.100,  2.3200,    13.0176, AB- AND DEHYDR0AB-:               56,57     YES,YES
  42.80      .7900   4.176,  1.0000,      .0869,   :                               --        --
  44.62     6.8304   4.345,  2.3200,     1.7436, 6,8,11,13-AB, NE0AB-:             58,59     YES,YES
  45.92      .3696   4.465,  2.0500,      .0833, LIGN0CERATE:                      60        N0
:
                                  T0TAL:    30.7714 MG/L
```

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RUN             INTERSTATE TREATED EFFL-ACIDS AND PHEN0LS

INST    4    , METH0D    50    , FILE    41    3:

  TIME        AREA      RRT      RF           C         NAME                      PEAK    IN '72
  10.12      .1315   1.000,  1.4900,      .0220, VERATR0LE:                    11      YES
                     1.350,  2.0500,            DIMETHYLSULF0NE:               15      YES
  16.65      .1423   1.645,  1.4900,      .0239, METH0XYBENZALDEHYDE:          18      YES
  18.41      .1368   1.819,  1.0000,      .0154, :                             --      --
  19.06     8.8748   1.883,  1.0000,     1.0000, ACENAPHTHENE:                 A       --
  20.07      .1581   1.983,  1.0000,      .0178, :                             --      --
  22.07      .2320   2.186,  2.0500,      .0535, PALMITATE:                    28      YES
  22.74      .2390   2.254,  1.0000,      .0269, :                             --      --
  24.41      .2475   2.423,  2.0500,      .0571, MARGARATE:                    M       N0
  24.67      .5476   2.450,  1.4900,      .0919, VERATRALDEHYDE:               33      YES
  26.45      .3995   2.630,  1.4900,      .0670, VERATR0NE:                    36      YES
  26.89      .3413   2.675,  2.0500,      .0788, STEARATE AND 0LEATE:          37,38   N0,YES
                     2.720,  1.4900,            ME SYRINGALDEHYDE:             39      YES
  28.96      .1394   2.885,  1.4900,      .0234, 3,4,5-TMA:                    42      YES
  29.51      .2972   2.941,  1.0000,      .0334, :                             --      --
  30.02      .2021   2.991,  1.0000,      .0227, :                             --      --
  31.06     1.6762   3.093,  2.3200,      .4381, ME RESIN ACID:                45      YES
  31.72     1.3443   3.157,  2.3200,      .3514, ME RESIN ACID:                48      YES
  32.74     2.9344   3.257,  2.3200,      .7670, PIMERATE:                     50      YES
  33.91     3.6459   3.371,  2.3200,      .9530, SAND-P AND 13-AB-18-:         51,53   YES,YES
  35.98     2.8126   3.572,  2.3200,      .7352, IS0PIMERATE:                  55      YES
  41.39    11.7420   4.100,  2.3200,     3.0694, AB- AND DEHYDR0AB-:           56,57   N0,YES
  43.54      .2298   4.309,  2.3200,      .0600, 6,8,11,13-AB, NE0AB-:         58,59   YES,N0
                     4.460,  2.0500,            LIGN0CERATE:                   60      N0
:
                                  T0TAL:    6.9079 MG/L
```

Table IV. Collective Pollution Parameter Measurements and Total Concentrations of Volatile Components in Acid–Phenol Extracts

	Concentrations, mg/l.											
	Mill "A"						Interstate Paper at Riceboro, Ga.					
	1972			1974			1972			1974		
	Raw	Outfall	% Change	Raw	Outfall	% Change	Raw	Outfall	% Change	Raw	Outfall	% Change
BOD_5	323	88	−73	320	45	−86	438	70	−84	440	52	−88
TOC	240	230	−4	350	350	0	470	200	−57	490	85	−83
Total GC organics[a]	9.38	7.12	−24	14.98	3.81	−75	21.69	7.24	−67	30.77	6.91	−78
Total phenols	4.96	1.15	−77	2.31	0.62	−73	5.53	0.27	−95	3.57	0.23	−94
Total fatty acids	1.01	1.46	+45	1.36	1.59	+17	1.40	0.14	−90	1.34	0.19	−86
Total resin acids	2.04	4.27	+109	10.77	1.39	−87	14.24	6.71	−53	24.37	6.37	−74

[a] Related to concentrations of total gas chromatographable organic material.

waters is believed to be due to partially degraded lignin molecules. These high-molecular-weight nonvolatile compounds form a significant portion of the balance of the TOC. Other contributors to the TOC are the carbohydrates and, to a lesser extent, tannins and various other highly polar or nonvolatile compounds.

The increase in the proportion of the TOC represented by total volatiles in the Interstate wastewaters is a reflection of the greater decrease in the nonvolatile portion of the organic content as compared to the volatile content. Lime flocculation probably removed a large amount of the nonvolatile organics.

In summary, the major difference in the volatile organic content of wastewaters from the two mills was the fatty acid content. Whereas the fatty acids decreased significantly during the Interstate traatment, they increased during treatment in Mill "A". Reductions in BOD, TOC, total GC peak areas, and phenolic and resin acid content were similar in the wastewaters from the two mills.

Table V. Volatile Acidic Components as Percentages of TOC

	Percentage of TOC			
	Mill A—1974		Interstate—1974	
Component	Raw effluent	Outfall	Raw effluent	Outfall
Total acidic volatiles	4.28	1.09	6.28	8.13
Total phenols	0.66	0.18	0.73	0.27
Total fatty acids	0.39	0.45	0.27	0.22
Total resin acids	3.08	0.40	4.97	7.49

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Duane F. Zinkel (USDA Forest Products Laboratory, Madison, Wis.) kindly supplied us with reference standards of the resin acids.

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Acute and Chronic Toxicity of Hydrogen Sulfide to the Fathead Minnow, *Pimephales promelas*

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■ Toxic effects of molecular hydrogen sulfide to eggs, fry, and juveniles of the fathead minnow, *Pimephales promelas* Rafinesque, were determined in flow-through bioassays. The 96-h LC50 of laboratory-cultured juveniles at 20 °C was 0.0243 mg/l. H_2S. Fry were approximately twice as sensitive. Response with temperature in wild stock juveniles varied from a 96-h LC50 of 0.7754 mg/l. at 6.5 °C to 0.0423 mg/l. H_2S at 25 °C. In chronic exposure to H_2S from egg through two generations of laboratory-cultured stock in flow-through bioassays, adverse effects on growth, survival, and fecundity occurred above 0.004 mg/l. H_2S. Chronic exposure of wild stock up to 346 days caused adverse effects on growth and survival above 0.008 mg/l. H_2S. At comparable temperatures apparent safe levels with long exposure were five- to sevenfold lower than the 96-h LC50 for both stocks.

Hydrogen sulfide is highly toxic to fish and invertebrates and occurs naturally at levels that can be inimical to survival of eggs and fry (*1, 2*) and thereby reduce fish production. Smith and Oseid (*3*) reported that concentrations within a range commonly occurring in nature could be lethal to eggs and fry of several freshwater fish species. Adelman and Smith (*4*), working with northern pike (*Esox lucius* Linnaeus), showed that egg survival and fry development were limited by concentrations of H_2S as low as 0.0060 mg/l. and Adelman and Smith (*5*) found that its toxicity to goldfish (*Carassius auratus* Linnaeus) was affected by temperature and oxygen concentrations.

Smith et al. (*6*) showed that reproduction of bluegills (*Lepomis macrochirus*) was adversely affected by H_2S concentrations of 0.001 mg/l. Field observations indicate that the fathead minnow (*Pimephales promelas* Rafinesque) survived over winter under very adverse conditions where H_2S was known to be present. The study reported here on this minnow was designed to determine the effects of H_2S on growth, survival, and reproduction at subacute levels in the laboratory and to describe acute toxicity at different life history stages and temperatures. Molecular H_2S has generally been considered the toxic species of sulfide and work in our laboratory not reported here has confirmed this assumption. At any concentration of dissolved sulfide, the proportion of H_2S is highly dependent on the pH of the water. The present work has not encompassed a wide spectrum of natural waters but rather is based on a constant laboratory source.

Table I. Analysis of Laboratory Well Water[a]

Item	Concentration, mg/l.
Total hardness as $CaCO_3$	220
Calcium as $CaCO_3$	140
Iron	0.02
Chloride	<1
Sulfate	<5
Sulfide	0.0
Fluoride	0.22
Total phosphates	0.03
Sodium	6
Potassium	2
Copper	0.0004
Manganese	0.0287
Zinc	0.0044
Cobalt, nickel	<0.0005
Cadmium, mercury	<0.0001
Ammonia nitrogen	0.20
Organic nitrogen	0.20

[a] Water taken from well head before aeration and heating, pH 7.5.

Materials and Methods

Fish used in acute and chronic tests were collected from ponds in the St. Paul, Minn., area or reared in the laboratory from eggs obtained from the National Water Quality Laboratory in Duluth, Minn. Although no diseases were noted in wild juvenile fish, prophylactic treatment on arrival at the laboratory was adopted as standard practice. The treatment consisted of neomycin or tetracycline (20 mg/l.) for 3 days followed by methylene blue (2.0 mg/l.) for 3 days. Test water for all bioassays was highly alkaline water from the laboratory well (Table I).

For the acute tests, water for the controls and various solutions of H_2S was supplied with an apparatus described by Colby and Smith (*1*) and later modified and described by Adelman and Smith (*4*). Hydrogen sulfide gas was mixed with oxygen-free water, and the mixture was then combined with oxygenated water to achieve desired H_2S and O_2 levels in acute tests. Flow-through rate was 300 ml/min. Egg and fry tests were conducted in 10 × 16 × 20 cm glass chambers immersed in the 50 × 25 × 20 cm glass tanks used for later juvenile tests. Eggs rested on the chamber bottom near the inflow tube until hatched. Acute tests consisted of one control and five H_2S treatments.

Chronic tests using wild stock (chronic 1 and 2) were conducted in glass aquaria divided in the middle to form two chambers (*a* and *b*) 15 × 40 × 31 cm and filled to 12.6 l. Sodium sulfide solution and water were dispensed to each chamber through apparatus described by Mount and Brungs (*7*) and Brungs and Mount (*8*). Toxicant and water from the diluters entered the first chamber and overflowed into the second chamber. Duluth stock in chronic tests 3 and 4 were tested in 20-l. glass tanks each with separate inflow. Flow-through rate was 250 ml/min. Eggs in chronic tests were deposited by spawning fish on concrete-asbestos half-tiles. They were subsequently removed and incubated on Nitex screen attached to a vertically oscillating cylinder moving 1.5 cm in 10 s. This procedure permitted incubation of eggs from multiple spawnings in the same test solution. Photoperiod was that of Evansville, Ind. [As recommended by the National Water Quality Laboratory (Duluth): "Fathead minnow full chronic test" (revised interim procedure 1-20-71) (mimeo)]. Chronic tests 1 and 2 consisted of one control and five treatments. Each treatment was replicated as described above. Chronic tests 3 and 4 had one control and four treatments replicated three times (*a*, *b*, *c*). A fourth replication (3*d*) was run for 80 days to determine egg survival and to hatch eggs and rear fry from the control and each treatment to start chronic test 4. The fourth replication of chronic test 4 (4*d*) was run for 80 days to hatch eggs deposited during the tests. Chronic tests 1, 2, and 3 were started with 10 fish per chamber and chronic test 4 was started with 20 fish but thinned to 10 before spawning. After fish attained a total length of 20 mm, they were weighed at 4-week intervals.

All H_2S calculations were made from samples taken directly from each test chamber and analyzed for total dissolved sulfides by colorimetric analysis in accordance with "Standard Methods for the Examination of Water and Waste Water" (*9*), section 228C. Calculation of molecular H_2S was based on pH and temperature of test water and ionization constants of Broderius and Smith (10). LC50's were determined graphically.

Results

Acute Toxicity of H_2S. Six bioassays were conducted with fathead minnow eggs (Table II) at temperatures from 23.8–24.2 °C, oxygen from 5.6–6.0 mg/l., and pH of 7.9. The 96-h LC50 varied between tests from 0.0291–0.0933 mg/l., with a mean of 0.0536 mg/l. H_2S. The LC50 for the incubation period which ranged from 5–8 days had a mean of 0.0258 mg/l. H_2S.

Three tests on fry started within 24 h of hatching were run at 24 °C and 5.4–6.2 mg/l. O_2. The mean LC50 varied from 0.0208 mg/l. at 24 h to 0.0107 mg/l. H_2S at 96 h. Mean LTC at six days was 0.0093 mg/l. H_2S. LC50 at 96 h varied from 0.0100–0.0115 mg/l. H_2S and LTC from 0.0087–0.0101 mg/l. H_2S.

Bioassays were performed on juveniles at six temperatures: 6.5, 7.6, 10.0, 15.0, 20.2, and 25.0 °C. LC50 at 96 h ranged from 0.7754 mg/l. at 6.5 °C to 0.0423 mg/l. H_2S at 25.0 °C (Table II). Fish used for tests at 6.5 °C were taken in January when lake water was 4 °C. Other tests were made on fish caught when lake temperature approximated test temperatures.

Six acute tests were done on wild stock and four on Duluth stock juveniles to compare relative tolerance of the two groups and to permit comparison of acute response and chronic safe levels (Table II). The mean 96-h LC50 of six tests with wild fish at 19.9–20.0 °C was 0.0554 mg/l. H_2S. Variation between tests was small and did not exceed 0.008 mg/l. Four tests run with Duluth stock at 19.8–22.0 °C were somewhat less than half as tolerant to H_2S as the wild stock at 96 h (Table II). The mean 96-h LC50 was 0.0243 mg/l. and the mean LTC in 8–10 days was 0.0180 mg/l. H_2S. Variation in LC50's between tests did not exceed 0.009 mg/l. at 96 h and in LTC's did not exceed 0.004 mg/l.

Four tests were conducted at 24 °C to determine whether fish reared in the wild under more rigorous conditions of competition and predation were more resistant to H_2S than fish reared in the laboratory. Eggs were collected in the field and reared to juvenile size in the laboratory. Two tests were conducted on these fish and at the same time two tests were run on fish naturally reared in the pond from the same stock and generation. No difference was found in the 96-h LC50 or LTC in 7–9 days.

Survival in Long-Term Exposure to Subacute Levels of H_2S. Chronic tests 1 and 2, each with two replications (series *a* and *b*), were started with wild stock juveniles (Table III). Test 1 ran for 191 days and test 2 for 345 days. After 51 days in both series of test 1, survival declined in the control and all test concentrations of H_2S. At 51 days survival in 0.0140 mg/l. H_2S in series *a* was 61% with 100% in the control. At 191 days the respective survivals were 6% and 65%. In series *b* survival through 51 days was essentially the same as the control in all H_2S treatments except 0.0121 mg/l., where it was substantially lower. Excessive loss in controls made comparisons doubtful for the remainder of the test.

Chronic test 2, series *a*, had reduced survival at 0.0293 mg/l. H_2S by the 37th day and thereafter, but at lower concentrations survival was similar to or better than the controls. In series *b*, survival in concentration of 0.0115 mg/l. H_2S was slightly lower than the control.

Chronic test 3 with three replications was started with Duluth stock sac fry and ran for 297 days (Table IV). In the three replications, survival was similar to that in the controls except at 0.0094 and 0.0101 mg/l. H_2S where survival was reduced to 60% and 40%, respectively, by the end of the test. Mortality of eggs and fry held in series *d* of test 3 for 80 days was not consistently different from controls in any H_2S concentration up to 0.0062 mg/l. H_2S.

Chronic test 4 was started with juveniles derived from spawnings from chronic test 3 and held for 80 days (series *d*) in concentrations up to 0.0062 mg/l. H_2S. At 0.0120 mg/l. in series *a*, survival was 71% of control after 196 days when this concentration was terminated; in series *b*, 76% of control at 0.0081 mg/l. after 274 days; and in series *c*, 52% of control at 0.0111 mg/l. after 274 days (Table IV). Maximum mortality at the highest levels was reached in 56 to 140 days and did not increase thereafter. Survival of eggs and fry generated in test 4 (series *d*) was 64% of controls after 80 days in 0.0076 mg/l. H_2S.

A chronic test was conducted with three concentrations of H_2S and one control with 4–19 juvenile fish per tank for 112 days to determine the effect of fish numbers on survival and growth. The number of fish in the tanks did not affect either factor.

Growth in Low Levels of H_2S. Growth of wild stock juvenile fathead minnows in various concentrations of H_2S was observed in chronic tests 1 and 2. After 107 days in chronic 1, series *a*, growth was adversely affected at 0.0140

Table II. Acute Toxicity of H_2S to Fathead Minnows[a]

Stage	No. of tests	Length, mm	Temperature, °C	Number of fish/chamber	LC50, mg/l.[b]		
					24 h	96 h	LTC(days)[c]
Egg	6	. . .	23.8–24.2	20–50	. . .	0.0536	0.0258 (5–8)[d]
Fry	3	5.6–5.9	24.0	20	0.0208	0.0107	0.0093 (6)
Wild juv.	1	47	6.5	40	. . .	0.7754	. . .
	1	50	7.6	40	1.0597	0.7761	. . .
	1	30	10.0	40	. . .	0.2040	. . .
	1	34	15.0	40	. . .	0.0798	. . .
	1	28.5	20.2	40	. . .	0.0477	. . .
	1	28.0	25.0	40	. . .	0.0423	. . .
Wild juv.	6	34.0–38.3	19.0–20.0	7–10	. . .	0.0554	. . .
Duluth juv.	4	32–39	19.8–22.0	11–18	. . .	0.0243	0.0180 (8–10)

[a] pH of all tests 7.9. [b] Where the LC50 is for more than one test the value given is the mean. [c] LTC value determined when no organisms died for 24 h. [d] Value for total incubation period.

Table III. Test Conditions, Survival (Percentage), and Growth (G) of Wild Stock Fathead Minnows with Long-Term Exposure to H_2S

Test and effect	Exposure, days	Temperature, °C	O_2, mg/l.	pH	H_2S concentration, mg/l. (SD in parentheses)				
1a		19.9–20.1	6.6	7.9	Control	0.0029	0.0106	0.0140	0.0190
					...	(0.0015)	(0.0057)	(0.0069)	(0.0082)
Survival	51				100	84	75	61	0
	191				65	76	68	6	0
Growth	107				2.23	1.99	2.24	1.87	...
Ib		19.8–20.1	6.6	7.9	Control	0.0023	0.0072	0.0091	0.0121
					...	(0.0015)	(0.0042)	(0.0044)	(0.0050)
Survival	51				100	90	100	96	59
	191				34	42	69	73	24
Growth	107				1.94	1.83	1.87	1.94	1.79
2a		21.2	7.5–8.3	7.7–7.8	Control	0.0007	0.0036	0.0101	0.0293
					...	(0.0009)	(0.0018)	(0.0040)	(0.0115)
Survival	37				80	100	100	89	20
	345				60	90	90	67	10
Growth	121				2.11	1.74	2.21	2.24	1.39
2b		21.2–21.3	7.6–8.1	7.7–7.8	Control	0.0006	0.0015	0.0033	0.0115
					...	(0.0006)	(0.0012)	(0.0018)	(0.0050)
Survival	37				67	89	89	80	60
	345				56	89	67	70	50
Growth	121				1.77	2.48	2.63	2.26	1.82

Table IV. Test Conditions, Survival (Percentage), Growth (G), and Fecundity[a] of Duluth Stock Fathead Minnows with Long-Term Exposure to H_2S

Test and effect	Exposure[b], days	Temperature, °C	O_2, mg/l.	pH	H_2S concentration, mg/l. (SD in parentheses)				
3a		23.0	6.4–7.1	7.7–7.8	Control	0.0006	0.0018	0.0049	0.0094
					...	(0.0004)	(0.0006)	(0.0012)	(0.0028)
Survival	297				100	90	100	90	60
Growth	112				1.34	1.24	1.09	1.28	0.98
Fecundity	297				1296	660	426	1512	1346
3b		22.5–22.7	7.0–7.4	7.8	Control	0.0006	0.0016	0.0039	
					...	(0.0004)	(0.0006)	(0.0015)	
Survival	297				90	80	80	100	
Growth	112				1.11	1.13	1.23	1.21	
Fecundity	297				1701	2614	806	1804	
3c		22.9–23.1	6.5–7.0	7.7	Control	0.0007	0.0018	0.0049	0.0101
					...	(0.0004)	(0.0006)	(0.0016)	(0.0030)
Survival	297				100	100	100	90	40
Growth	112				1.27	0.98	0.91	1.07	1.23
Fecundity	297				475	844	180	530	399
3d[c]		22.2–22.4	6.9–7.0	7.8–7.9	Control	0.0006	0.0011	0.0039	0.0062
					...	(0.0003)	(0.0005)	(0.0017)	(0.0017)
Survival	80				55	62	56	61	78
4a		24.0–24.2	6.1–6.8	7.7	Control	0.0012	0.0021	0.0053	0.0120
					...	(0.0008)	(0.0011)	(0.0024)	(0.0052)
Survival	274				100	100	100	100	0
Growth	56				1.19	1.16	1.23	1.05	0.65
Fecundity	274				452	906	445	334	...
4b		23.6–23.7	6.5–6.8	7.7	Control	0.0009	0.0018	0.0048	0.0081
					...	(0.0008)	(0.0008)	(0.0024)	(0.0038)
Survival	274				100	90	90	80	76
Growth	56				1.38	1.35	1.27	1.10	0.96
Fecundity	274				717	201	120	696	94
4c		24.0–24.3	6.2–6.8	7.7	Control	0.0010	0.0021	0.0066	0.0111
					...	(0.0008)	(0.0008)	(0.0042)	(0.0045)
Survival	274				90	90	80	0[d]	52
Growth	56				1.18	0.98	1.17	1.08	0.88
Fecundity	274				1461	1655	574	...	1258
4d		24.2–24.9	6.9–7.4	7.8	Control	0.0011	0.0014	0.0027	0.0076
					...	(0.0006)	(0.0008)	(0.0015)	(0.0035)
Survival	80				100	79	100	85	64

[a] Expressed as mean number of eggs spawned per female during the entire reproductive period. [b] Exposure times for test 4 do not include the 80 days of treatment in test 3*d*. [c] Started with eggs from test 3. [d] Mortality caused by low O_2.

Table V. Mean No-Effect Concentrations of H_2S (Mg/L.) for Survival, Growth, and Fecundity of Wild and Duluth Stocks of Fathead Minnows with Application Factors in Parentheses

Stock	96-h LC50	Effect criteria		
		Survival	Growth	Fecundity
Wild	0.0554	0.0083	0.0103	. . .
(Tests 1 & 2)		(.150)	(.186)	. . .
Duluth	0.0243	0.0036	0.0042	0.0059
(Tests 3 & 4)		(.148)	(.173)	(.243)

mg/l.; in series *b*, at 0.0121 mg/l. H_2S (Table III). In series *a* of chronic 2 fish grew approximately 33% less at 0.0293 mg/l. than in the control in 121 days but no reduction occurred at 0.0101 mg/l. In series *b* of chronic 2, percentage increment was not appreciably different from the control at 0.0115 mg/l. H_2S, and at lower levels growth was greater than in the control. Growth was inhibited at 0.0094 mg/l. H_2S in series *a* of chronic 3 (Table IV). In series *b* and *c*, concentrations of 0.0101 mg/l. and lower were equal to or lower than controls. Reduced growth occurred in test 4 at 0.0053 mg/l. H_2S in series *a*, 0.0048 mg/l. in series *b*, and 0.0066 mg/l. in series *c*.

Reproductive Success in Long-Term Exposure. Spawning success in chronic tests started with Duluth sac fry did not change consistently with H_2S concentrations as measured by the number of eggs deposited per female or total number of spawnings. For the entire reproductive period the total number of eggs per female varied from 180 to 2614 in 4 to 33 spawnings in different H_2S treatments. Mean number of spawnings per female varied from 1.25–13.50. Total eggs spawned per tank fell off at 0.0101 mg/l. H_2S in series *c* because there was mortality during the progress of the experiment. Some treatments had larger numbers of eggs per female than the controls. In the second cycle (chronic test 4), the number of eggs laid per female was smaller in most cases than in the first cycle but there was no consistent relationship between number of eggs spawned and H_2S concentration. During test 3 there was a delay of about 20 days in the start of spawning for all treatments as compared with the controls. For test 4 there was a delay of about 40 days for the highest H_2S levels but the other treatments were equal to the controls.

Days to Hatch in Various Treatments. Some eggs deposited in the three series (*a*, *b*, *c*) of chronic tests 3 and 4 were hatched in the same H_2S concentrations where they were deposited and some were removed from treatments and hatched in control water. Percentage survival of eggs to hatch in control and H_2S treatments varied from 44–92% in chronic tests 3 and 4. Eggs laid and hatched in the same H_2S concentration did not survive at different rates in different treatments or when hatched in control water during chronic test 3. In chronic test 4, eggs laid in H_2S and incubated in control water in most cases had lower survival than those laid and incubated in the same H_2S treatment. Survival rate was not directly related to H_2S concentration during incubation.

The length of fry at hatch did not vary significantly with H_2S concentration during incubation in either chronic test 3 or 4.

Discussion

Acute toxicity of H_2S to juvenile fish was greatly changed by temperature. Between 6.5 and 25 °C a 20-fold difference in sensitivity was noted. Eggs were twice as resistant as juveniles to H_2S. Juveniles were twice as resistant as 5–6 mm fry.

To determine no-effect concentrations of H_2S and application factors for use with acute test results, data from various tests were combined. Application factors were calculated to determine a multiplier which could be applied to acute tests to predict no-effect levels. Since acute reaction of different stocks may vary, the factor will remove the necessity for chronic tests on each stock.

A mean was calculated from the highest concentrations in each series of chronic tests 1 and 2 which had survival and growth equal to or greater than the controls in the respective tests (Table V). The no-effect levels were 0.0083 and 0.0103 mg/l. H_2S for survival and growth. Means for survival, growth, and fecundity were similarly calculated for tests 3 and 4. The no-effect concentrations were 0.0036, 0.0042, and 0.0059 mg/l. H_2S, respectively, for survival, growth, and fecundity. Although there was a marked difference in the sensitivity of wild and cultured stock, the application factors based on chronic and 96-h tests at the same temperatures were very similar for each criterion of effect.

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Improving Mass Transfer Characteristics of Limestone Slurries by Use of Magnesium Sulfate

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■ Poor mass transfer coefficients for limestone scrubbing slurries limit the effectiveness of spray-type scrubbers in removing SO_2 from power plant stack gases. Large resistances in the liquid phase, due to the need for limestone or calcium sulfite to dissolve during the absorption process, are the cause of this inefficiency. Experimental work is presented to show that these resistances can be largely eliminated by addition of magnesium sulfate to the slurry, enabling an efficiency to be achieved that approaches that of strong sodium carbonate solution. A detailed description of the chemical processes involved is given, accompanied by experimental data showing the effect of sulfate addition on the dissolved scrubbing capacity of the slurries. The magnesium sulfite ion pair, $MgSO_3^0$ is shown to be responsible for the increased scrubbing efficiency. As a bonus, it was found that slurries containing magnesium sulfate could be treated with air to convert sulfite sludge into filterable gypsum.

The ideal contactor for scrubbing SO_2 with a slurry is a curtain of spray that creates droplets that provide the surface area needed for effective absorption, then coalesce, and drain off to be replaced by new droplets. Spray towers and venturi scrubbers are well-known examples of this type of scrubber. Reactions in the liquid droplet must be very fast, however, because its lifetime is short. When a limestone slurry is used to absorb SO_2, the limestone must dissolve and the absorbent molecules or ions must diffuse to the surface of the droplet in order to keep the mass transfer going; if these reactions are slow, the efficiency of the contactor is much less than with a more rapid-acting absorbent.

Attempts to use limestone slurries in venturi scrubbers to remove SO_2 from stack gases have been very disappointing. Work reported by Gleason and McKenna (*1*) and Murthy and Harris (*2*) indicates SO_2 removal efficiencies of less than 30%. More recently, calibrations performed at the EPA-sponsored Shawnee pilot plant showed 45% SO_2 removal with limestone while strong sodium carbonate solutions gave 92% removal at the same conditions (*3*). Kerr (*4*) has correlated results from many such studies and attributed the poor performance of limestone slurries to large mass transfer resistances both in the liquid film and in solids dissolution.

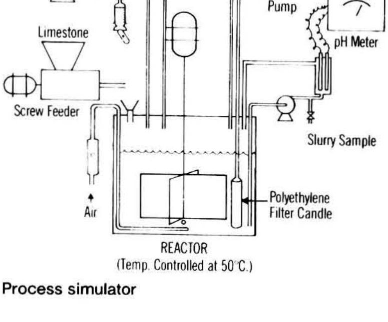

Figure 1. Process simulator

Results such as these have led to the use of contacting devices with complex internals, like marbles and plastic balls, to provide enough liquid surface area and residence time in the contacting zone. These devices, however, are prone to breakage and scaling. A more direct approach would be to improve the mass transfer characteristics of the limestone slurry so that venturi and spray scrubbers could be used. Simply, this means elimination of the need for solids dissolution in the contacting zone and increasing the concentration of absorbent species in the liquid phase so that rates of diffusion to the liquid film are increased. This has been done in the present work by maintaining a high concentration of sodium, ammonium, or (preferably) magnesium sulfate in the scrubbing liquid.

Experimental

Materials. In the bench-scale work a dolomitic limestone from Limecrest, N.J., which contained 83% $CaCO_3$ and 8.5% $MgCO_3$, was used. Stone from the same source was used in the batch-type venturi tests and in continuous pilot plant run H-1542-1B. A calcitic, New Mexico limestone supplied by the Gallup Sand & Gravel Co., which contained 81.0% $CaCO_3$ and 1.5% $MgCO_3$, was used for continuous pilot plant runs H-1541-1D and H-1541-3E.

Magnesium sulfate was Dow Chemical Co.'s USP "Epsom Salts" ($MgSO_4 \cdot 7H_2O$). The sodium sulfate and ammonium sulfate were both technical-grade anhydrous salts. Sulfurous acid was reagent grade 6% SO_2 solution.

Sulfur dioxide, nitrogen, and carbon dioxide were purified gases from The Matheson Co. The sulfur dioxide content of blends and calibration gases was determined by titration with sodium hydroxide after absorption in hydrogen peroxide.

Apparatus. Potentiometric titration of the clear liquid separated from simulated or actual limestone scrubbing slurries was performed with a Radiometer "Titrograph" recorder-programmer combined with a Model 26 pH meter, Model 11 Titrator, and Model SBR syringe buret. Solutions were protected from air oxidation by sweeping the titration vessel with nitrogen.

Packed-tower scrubbing of SO_2 with the clear liquid from simulated slurries was accomplished with a 2-in. diameter Pyrex column, packed to a height of 3 ft with ¼-in. Berl saddles. Temperature was controlled by 50 °C by steam addition to inlet gas blend. Analysis of the sulfur dioxide in outlet gas was made with a Du Pont Model 400 Photometric Analyzer.

Process simulation was accomplished with the apparatus shown in Figure 1. An electrically wound stainless steel vessel of about 5-l. capacity was equipped with an eight-blade agitator operated at 120 rpm and fed with limestone, sulfurous acid, and recycled filtrate. Automatic feed controls were sequenced by a cam timer. Provision was made to sparge air through the vessel when desired. Both clear liquid and slurry samples could be taken at any time with the net "make" of slurry being withdrawn manually from a valve in the slurry-pumping system at 1-h intervals. A continuous record of the slurry pH was obtained.

Venturi and venturi-spray scrubbers are shown in Figures 2 and 3. These units operated with a recirculating gas flow of 1000 scf/min, with the SO_2 absorbed being made up from weighed cylinders. The venturi pilot plant (Figure 2) was used in batch-type tests where a charge of limestone was utilized until depleted. The venturi-spray unit used continuous limestone feed.

Results and Discussion

Some boundary conditions are helpful in understanding the concept of a "dissolved scrubbing capacity" in the slurry. A typical liquid-to-gas ratio (L/G) of 65 gal/1000 scf brings 246 l. of liquid into contact with 1190 g-mol of flue gas. When the flue gas contains 3000 ppm SO_2, there are 3.57 g-mol of SO_2 to transfer or 0.0145 mol/l. If the dissolved scrubbing capacity of the slurry does not exceed this concentration by a comfortable margin, the liquid will be seriously depleted, and solids must dissolve and react with the SO_2 to keep the transfer going.

In Figure 4, potentiometric titrations of clear liquids separated from two simulated slurries are compared. The two samples were identically obtained except that one of the slurries contains magnesium sulfate at a formal concentration of 0.85 M. Obviously, a soluble base is titrated by the acid in the solution containing magnesium sulfate and, inasmuch as SO_2 will also react with this base, the titration represents the dissolved scrubbing capacity (DSC) of the slurry. The DSC is 0.035 N in the magnesium sulfate solution, but only 0.002 in the unpromoted slurry. Sodium and ammonium sulfate also produced enhanced DSC in the slurry.

Carrying substantial dissolved scrubbing capacity in the liquid phase of a slurry entering a scrubbing unit minimizes the change in pH between inlet and outlet. Figure 5 shows this effect demonstrated in the scrubbing simulator, where the sulfurous acid injected is equivalent to 800 ppm sulfur dioxide in a flue gas scrubbed at an L/G of 50 gal/1000 scf.

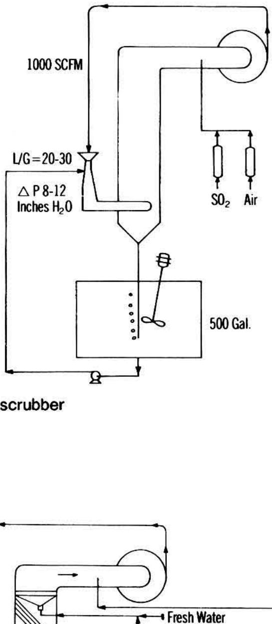

Figure 2. Venturi scrubber

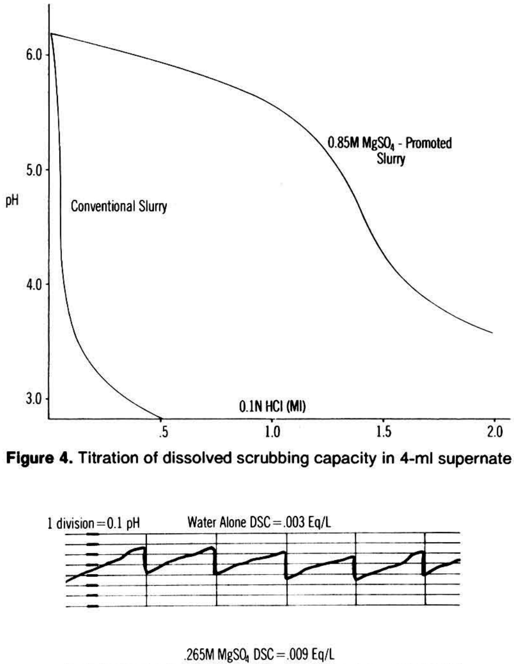

Figure 4. Titration of dissolved scrubbing capacity in 4-ml supernate

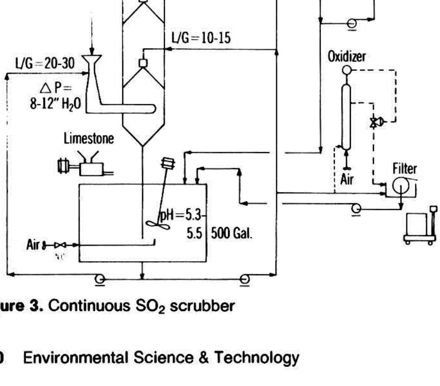

Figure 3. Continuous SO_2 scrubber

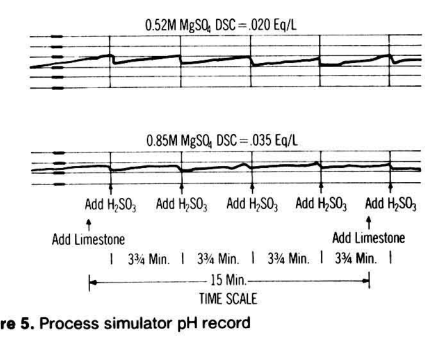

Figure 5. Process simulator pH record

When a packed tower is used, it is literally possible to titrate the SO_2 in flue gas with the dissolved scrubbing capacity of sulfate-promoted limestone scrubbing slurries. Table I gives the results of an experiment where the minimum liquid-to-gas ratio (L/G) was sought with supernatent liquid from three such slurries. It is seen that magnesium sulfate produced the highest DSC and remained an effective scrubbing agent at L/G's as low as 7.6 gal/1000 scf.

Table I. SO_2 Scrubbing with Slurry Supernate

Solution	L/G, gal/ mscf	Feed DSC[a] g-eq/l.	Stoich. factor[b]	SO_2 in, ppm	SO_2 out, ppm	% removal
3.1 mol $(NH_4)_2SO_4$	15.6	0.038	2.03	1044	0	100
	12.1	0.038	1.58	1044	0	100
	9.2	0.038	1.20	1044	0	100
1.2 mol Na_2SO_4	17.5	0.030	1.43	1300	0	100
	10.1	0.030	0.84	1300	480	63
	11.8	0.030	0.97	1300	120	91
0.93 mol $MgSO_4$	13.8	0.061	2.26	1300	0	100
	7.6	0.061	1.24	1300	0	100

[a] Dissolved scrubbing capacity. [b] Ratio of total equivalents of DSC in liquid to total moles of SO_2 in gas.

The basic species that make up the dissolved scrubbing capacity are ions and neutral molecules that differ in identity depending upon whether magnesium sulfate, sodium sulfate, or ammonium sulfate is used as a promoting agent. With sodium sulfate, the sulfite and bicarbonate ions derived from reaction of bisulfite ion with calcium carbonate predominate. With ammonium sulfate, free ammonia is also present, while with magnesium sulfate, the principal component of the DSC is believed to be the neutral ion pair, $MgSO_3{}^0$, based on the following observations.

1. Initial realization of the importance of ion pairing in magnesium sulfate solutions followed a series of experiments, where it was found that the solubility of magnesium sulfite increased from 0.09 M in water to 0.18 M in saturated magnesium sulfate solution. Without soluble complex formation, the magnesium sulfite solubility would be expected to decrease by at least an order of magnitude on addition of the common ion, magnesium.

2. The equilibrium constant for the $MgSO_3{}^0$ ion pair developed by Radian (5) indicates that the $MgSO_3{}^0$ concentration is 20 time greater than the $SO_3{}^{2-}$ concentration in strong magnesium sulfate solutions.

3. Comparison of potentiometric titration curves obtained with supernates from magnesium sulfate-promoted limestone scrubbing slurries with those from known solutions of magnesium sulfite and magnesium sulfate shows that the basic species being titrated behave identically.

4. Further confirmation was obtained by iodometric titration of the supernates, which shows that the total sulfite content ($MgSO_3{}^0$, $SO_3{}^{2-}$, and $HSO_3{}^-$) increases in a parallel fashion to the increase in dissolved scrubbing capacity obtained by adding magnesium sulfate.

The reaction sequence in an SO_2 scrubbing application using magnesium sulfate-promoted limestone starts with the ion pair, $MgSO_3{}^0$. Sulfur dioxide and water form H_2SO_3 that reacts with the $MgSO_3{}^0$ by

$$H_2SO_3 + MgSO_3{}^0 \rightarrow Mg^{2+} + 2HSO_3{}^- \tag{1}$$

When $CaCO_3$ is present, the $MgSO_3{}^0$ is regenerated by

$$Mg^{2+} + 2HSO_3{}^- + CaCO_3 \rightarrow MgSO_3{}^0 + Ca^{2+} + SO_3{}^{2-} + CO_2 + H_2O \tag{2}$$

Generally a holding tank is used in the scrubbing circuit which provides time for the regeneration reaction to take place.

The major precipitation reaction in most scrubbing applications is

$$Ca^{2+} + SO_3{}^{2-} + \tfrac{1}{2}H_2O \rightarrow CaSO_3\tfrac{1}{2}H_2O(S) \tag{3}$$

Some oxidation of sulfite to sulfate takes place in the scrubber due to the oxygen in the flue gas. This sulfate is precipitated as $CaSO_4{\cdot}2H_2O$.

$$SO_3{}^{2-} + \tfrac{1}{2}O_2 \rightarrow SO_4{}^{2-} \tag{4}$$

$$Ca^{2+} + SO_4{}^{2-} + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O \tag{5}$$

In some cases, when the rate of precipitation of $CaSO_3\frac{1}{2}H_2O$ is fast and oxidation is minimal, all of the sulfate may coprecipitate with the sulfite as the hemihydrate (6).

$$Ca^{2+} + SO_4{}^{2-} + \tfrac{1}{2}H_2O \xrightarrow{CaSO_3\frac{1}{2}H_2O} CaSO_4 \cdot \tfrac{1}{2}H_2O \tag{5a}$$

When this happens, the liquid is unsaturated with respect to $CaSO_4{\cdot}2H_2O$.

At steady state in a scrubbing process, the rates of precipitation of $CaSO_3\frac{1}{2}H_2O$ and $CaSO_4{\cdot}2H_2O$ are proportional to the relative supersaturation. The activity product for Ca^{2+} and $SO_3{}^{2-}$ is given by

$$(Ca^{2+})(SO_3{}^{2-}) = K_{sp}(CaSO_3\tfrac{1}{2}H_2O) \times r_{CaSO_3} \tag{6}$$

Where r_{CaSO_3} is the relative supersaturation. Similarly, for Ca^{2+} and $SO_4{}^{2-}$,

$$(Ca^{2+})(SO_4{}^{2-}) = K_{sp}(CaSO_4{\cdot}2H_2O) \times r_{CaSO_4} \tag{7}$$

Eliminating the calcium ion activity between Equations 6 and 7 gives the formulation:

$$\frac{(SO_3{}^{2-})}{(SO_4{}^{2-})\cdot} = \frac{r_{CaSO_3}}{r_{CaSO_4}} \times \frac{K_{sp}(CaSO_3{\cdot}\frac{1}{2}H_2O)}{K_{sp}(CaSO_4{\cdot}2H_2O)} \tag{8}$$

If activity coefficients for the $SO_3{}^{2-}$ and $SO_4{}^{2-}$ ions are combined with the ratio of solubility product constants to give a single practical constant, Equation 8 becomes

$$\frac{[SO_3{}^{2-}]}{[SO_4{}^{2-}]} = \frac{r_{CaSO_3}}{r_{CaSO_4}} \times k_1' \tag{9}$$

which tells us that increasing sulfate ion concentration gives an increase in sulfite concentration, yielding more DSC, provided the relative supersaturations of $CaSO_3$ and $CaSO_4$ remain the same.

In magnesium sulfate solutions most of the ions are tied up as ion pairs but an analogous equation is obtained.

$$\frac{[MgSO_3{}^0]}{[MgSO_4{}^0]} = \frac{r_{CaSO_3}}{r_{CaSO_4}} \times k_2' \tag{10}$$

The constant, k_2', can be considered the practical equilibrium constant for the reaction

$$MgSO_4{}^0 + CaSO_3\tfrac{1}{2}H_2O + \tfrac{3}{2}H_2O = MgSO_3{}^0 + CaSO_4{\cdot}2H_2O \tag{11}$$

The function of the magnesium sulfate in the liquid is to set the position of the equilibrium such that an appreciable concentration of the ion pair, $MgSO_3{}^0$, is achieved in a slurry under steady state conditions.

Demonstration

Although it had been predicted from fundamental considerations that the increased dissolved scrubbing capacity resulting from magnesium sulfate in the scrubbing liquor would turn an apparently poor liquid–gas contactor into a good one, it remained to be demonstrated by experiment. Figure 6 shows comparative results with a venturi scrubber using strong sodium carbonate solution, unpromoted limestone slurry, and magnesium-sulfate promoted limestone slurry. From these data, it was calculated that the overall mass transfer coeffi-

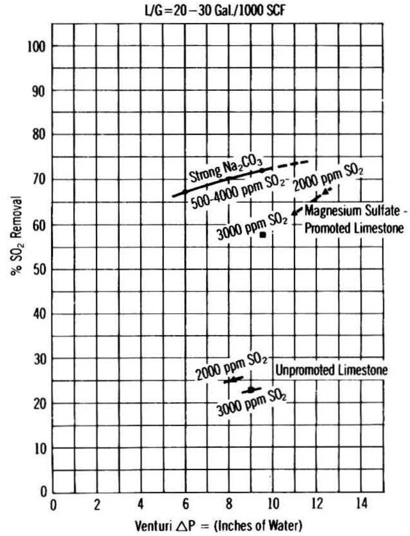

Figure 6. Venturi scrubbing of SO_2

cient with magnesium sulfate present was 3.3 times greater than in its absence.

Table II gives the conditions and results of runs made in the venturi-spray pilot plant at three different SO_2 levels. $MgSO_4$ was added to attain the required level. To approximate a power plant situation, $MgCl_2$ was added to simulate the effect of chlorine in the coal. In all cases, the minimum L/G, which would give specification SO_2 removal, was used. These results demonstrate that very high removals can be obtained easily with spray-type contactors over a wide range of SO_2 concentration.

One further benefit from the use of magnesium sulfate is the ability to oxidize the typical sulfite sludge produced in lime and limestone scrubbing to a stable gypsum product which has more favorable disposal properties. This is possible because the dissolved $MgSO_3^0$ is more readily oxidized than insoluble $CaSO_3½H_2O$. The equilibrium shown in Equation 11 provides the mechanism whereby solid $CaSO_3½H_2O$ is attacked by $MgSO_4^0$ during oxidation process to resupply $MgSO_3^0$ consumed by oxidation. The $MgSO_4^0$ is regenerated by the oxidation.

In the pilot plant a pressurized, air-sparged tower was used as an oxidizer. Experiments covered a range of air superficial velocity up to 0.4 fps, air pressure to 40 psig and slurry residence time of 0.5–2 h. Oxygen mass transfer rates approximated those expected for ionic sulfite solutions, with several of the runs producing complete conversion of the calcium sulfite in the slurry.

Conclusions

If a substantial concentration of magnesium sulfate is maintained in the liquid phase of a lime or limestone slurry used in absorbing SO_2, a scrubbing capability is developed by the liquid itself. Without such dissolved scrubbing capacity, calcium-based solids must dissolve in the gas–liquid contacting zone to neutralize the SO_2.

Eliminating the slow step of solids dissolution speeds the overall mass transfer process so that less slurry surface need be exposed or generated in the scrubbing zone and less liquid residence time is needed to obtain satisfactory SO_2 removal. The rapid increases in supersaturation with respect to calcium sulfite and calcium sulfate that occur when calcium solids are dissolved in the scrubber are avoided, alleviating problems associated with scale formation.

The action of the magnesium sulfate is to promote a high concentration of the ion pair, $MgSO_3^0$, in the slurry. This fact can be used to provide a route whereby calcium sulfite can be economically oxidized to gypsum through intermediate conversion to soluble $MgSO_3^0$.

Table II. Venturi-Spray Scrubber Results

Run number:	**H1541-1D**	**H1541-3E**	**H1542-1B**
Limestone:	**Calcitic (N.M.)**	**Calcitic (N.M.)**	**Dolomitic (N.J.)**
Gas rate, scfm	900	960	950
Liquid rate, gpm			
Venturi	20	20	30
Sprays—each nozzle	10	10	15
Inlet gas composition (dry)			
SO_2, ppm	970	1550	3110
O_2, %	5	6	3
CO_2, %	15	15	16
N_2	Bal.	Bal.	Bal.
Inlet slurry composition			
Total solids %, w/w	10	10	10
$MgSO_4$, mol/l.	0.40	0.49	1.03
$MgCl_2$, mol/l.	0.18	0.09	—
DSC, eq/l.	0.021	0.024	0.10
pH	5.4–5.5	5.4–5.5	5.3–5.4
SO_2 removal, %	92.7	93.4	90.2
Calcite utilization, %	81	72	71

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Photochemical Aerosol Formation

SO_2, 1-Heptene, and No_x in Ambient Air

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■ Aerosol formation was studied in a 96-m^3 Teflon bag containing unfiltered ambient air to which small amounts of SO_2, 1-heptene, and NO_x had been added. The contents were irradiated by sunlight. Gas phase concentrations were monitored continuously and a rate law was determined for the reaction of 1-heptene. By simultaneous measurements of the conversion of SO_2 and the formation of particulate sulfur, a sulfur balance was carried out on the system. The distribution of sulfur with respect to particle size, as well as total aerosol sulfur and carbon, was measured as a function of time during the experiments. The rates of formation of condensable species of both sulfur and carbon are consistent with a reaction between SO_2 and a reactive intermediate of the O_3–1-heptene reaction. The distribution of sulfur with respect to particle size shows a bimodal distribution about 0.2 μm.

The presence of SO_2 in photochemically reacting mixtures of NO_x and hydrocarbons has a marked effect on the nature of the aerosol which forms in such systems. The early literature on this subject is reviewed by Leighton (*1*). The SO_2 itself participates in the chemical reactions and its reaction products appear in the aerosol phase.

Smog chamber studies of irradiated mixtures of hydrocarbons, NO_x, and SO_2 (*2–10*) are useful in the study of such systems. Although SO_2 oxidation rates can be calculated from chamber data, previous investigators have not reported mass balances for sulfur. It is important to obtain a sulfur mass balance because oxidation rates determined from gas phase concentrations may include losses to the walls as well as to chemical reaction. Only Wilson et al. (*11*) conducted studies with natural sunlight or in the presence of ambient particulate matter. Such factors may be important because indoor lamps with intensity and/or spectrum differences from natural sunlight may promote one particular reaction mechanism over another. The presence of particulate matter allows heterogeneous processes (including condensation) to proceed at rates similar to those in the real atmosphere.

Of the aerosol parameters, only condensation nuclei and light scattering were measured in previous smog chamber studies with hydrocarbons, NO_x, and SO_2. No measurement of the distribution of sulfur compounds with respect to particle size has been made. Measurements have been reported of the total size distribution, as a function of time, in experiments with SO_2, propylene, and O_3 (*12*).

Photochemical reactions in polluted atmospheres have been reviewed by Altshuller and Bufalini (*13, 14*). Urone and Schroeder (*15*), Bufalini (*16*), and Calvert (*17*) have written reviews specifically on sulfur reactions in polluted atmospheres. There are diverse views regarding the relative importance of various SO_2 oxidation paths. The relatively slow rates of photooxidation of SO_2 in air exposed to light, and the catalytic influence of some solids and moisture on the rate of SO_2 oxidation indicate that heterogeneous oxidation paths are sometimes of controlling importance. In a photochemical atmosphere such as Los Angeles, the presence of many gas phase oxidants contribute to high SO_2 oxidation rates. Calvert (*17*) has reviewed the possible homogeneous SO_2 oxidation paths.

Pathways of possible importance in a photochemical atmosphere include:

1. Metal aided catalysis of SO_2 oxidation in liquid droplets.
2. Catalysis of SO_2 oxidation on the surface of soot particles (*18*).
3. Homogeneous gas phase oxidation of SO_2 by OH (*19*).
4. Homogeneous gas phase oxidation of SO_2 by an intermediate of the O_3, olefin reaction (*12, 20*).
5. Homogeneous gas phase oxidation of SO_2 by other reactive intermediates (such as HO_2, RO_2, and RO).

Computer simulations of the 1-butene–NO_x–SO_2 system indicate that items 3 and 4 play a dominant role in the oxidation of SO_2 in a system without particles (*21*).

Our experiments were designed to study the formation of sulfur-containing aerosols under conditions simulating the photochemical smog system. Small quantities of an olefin, NO, NO_2, and SO_2 were added to ambient air contained in a large bag, and irradiated by sunlight. The concentrations of the gas phase reactants were measured continuously, as well as certain physical properties of the aerosol. The sulfur distribution with respect to particle size was measured at five successive times during each experiment, and a mass balance was carried out on the sulfur.

Experimental System

The experiments were conducted on the roof of the Keck Laboratories at Caltech in a Teflon bag (average initial volume 96 m^3). The roof is 52 ft above the street level. To make the bag, FEP Teflon film sheets (10 panels, each 54 in. × 28 ft × 0.002 in.) were heat sealed together and the seams reinforced with mylar tape. Teflon was used because of its transparency to solar radiation (transmittance of greater than 75% of the ultraviolet, 92% of the visible, and 94% of the infrared) and its chemically inert nature (*22*). The bag has the shape of a pillow sealed at both ends. It was filled with ambient Pasadena air through a hole in the end of the bag using an 11-in. diameter attic fan. The hole was then sealed with a Plexiglas clamp, and gases under study were added through a Teflon port at ground level on one side of the bag. The contents of the bag were sampled continuously through a second port. Teflon and previously deposited particulate matter were the only materials that contacted the air inside the bag. Ropes across a wooden frame (held 2 ft off the ground by cinder blocks) supported the bag (Figure 1). Air circulating under the bag kept the maximum temperature attained inside the bag below 42 °C. The bag was held in place by a fishing net. Wind action on the bag and the temperature gradient within the bag kept the contents mixed during an experiment.

Chemicals were injected into the bag through the injector port with an auxiliary pump adding additional air to speed mixing. Using this auxiliary pump, complete mixing

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[1] Present address, Chevron Research Co., Richmond, Calif. 94802.

of added pollutants was obtained in approximately 5 min. Air for measurements was withdrawn continuously through a Teflon sampling tube that reached 4 ft into the middle of the reaction vessel. A 20-ft section of flexible black Teflon tubing (1 in. i.d.) carried the air to a glass manifold from which each instrument could sample for analysis. The measured response time of this sampling system was 20 s.

Continuous measurements were made of the following parameters, recorded with a digital printer: ozone, sulfur dioxide, condensation nuclei, b_{scat}, temperature, dew point, and broad-band solar radiation. Total hydrocarbons, methane, and carbon monoxide were also measured once every 5 min through an extra Teflon sampling tube at the end of the bag. Particles larger than 0.30 μm in diameter were measured as a function of time with an optical particle counter. However, the particle number distribution data obtained was not sufficient to calculate particle growth laws in the manner of Heisler (*23*), because most of the growth occurred below 0.3 μm. A description of the instruments and their characteristics is provided in Table I. Calibration of the gas phase instruments was performed before each series of experiments. A chemiluminescent NO_x monitor (Bendix Corp., Model 5513802 with a gold catalyst) also was used in the experiments, but both the NO and NO_x modes of the instrument showed interferences from other substances (*24*). Thus no values are reported for NO_x concentrations.

The chemiluminescent O_3 monitor (REM, Inc.) was calibrated using the California Air Resources Board recommended procedure. However, in light of recent findings (*25*), O_3 concentrations were corrected to an absolute value by cross-calibration with a Dasibi UV photometer (Model 1003-AH) which had been calibrated against the secondary O_3 standard of reference (*25*).

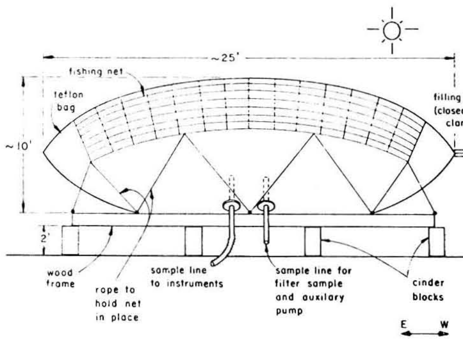

Figure 1. Diagram of the Teflon bag and supporting apparatus

The concentration of 1-heptene was determined using the total hydrocarbon mode of the gas chromatograph. The flame ionization detector does not respond to the oxygenated products expected with reactions of an olefin in photochemical smog (*26*). Therefore, all changes in total hydrocarbon response were assumed to be 1-heptene concentration changes. This assumption is validated by agreement of the measured O_3–1-heptene rate constant with the literature.

Aerosol samples were taken at the injection port using both a 47-mm in-line filter holder and a cascade impactor. The vaporization technique described by Roberts and Friedlander (*27*), was used to measure the concentration of sulfur in the aerosol. The term "aerosol sulfur" is used to denote the sulfur species concentration measured by this technique (any sulfur compound which evaporates or decomposes below 1200 °C). A Dohrman model DC-50 Total Carbon Analyzer was used to measure the aerosol carbon collected on glass fiber filters by a technique described by Grosjean (*28*). The term "aerosol carbon" is used to denote the concentration of carbon containing species in the aerosol (expressed as carbon), not the concentration of elemental carbon in the aerosol.

The procedure for a typical experiment was as follows: The bag was filled and emptied at least three times to remove residuals from the last experiment, filled about three-fourths full (all with the fan), and the end filling-hole was sealed off. The auxiliary pump was then used to fill the bag completely and mix the injected pollutant gases. NO was added first, in at least the concentration necessary to eliminate any ambient O_3 present; thus, any reactions of SO_2 or hydrocarbon with O_3 were prevented at the high concentrations present before complete mixing. NO_2 and SO_2 were added next and allowed to become mixed completely (about 5 min) before the hydrocarbon was added. After complete mixing of the hydrocarbon, the auxiliary pump was shut off and the aerosol sampling train was attached to that Teflon port. Monitoring of the progress of the bag run was continued until the bag volume had been reduced to about one-tenth of the initial volume. A drastic decrease in particle number caused by wall losses was evident when the volume was less than about 5 m^3.

Summary of Experiments

Experiments were carried out in the Teflon bag with sulfur dioxide, nitric oxide, nitrogen dioxide, and 1-heptene. A summary of four of the experiments, showing initial condi-

Table I. Instruments Used to Determine Concentrations in Teflon Bag Experiments

Measured parameter	Measurement principle (calibration method)	Instrument make and model
b_{scat}	Extinction coefficient due to light scattering (Freon)	Meteorology Research Inc., Model 1550. Integrating Nephelometer[a]
Condensation nuclei	Expansion cloud chamber-light scattering	Environment One Corp. Model Rich 100
Particles $\geq$ .3 μm	Optical light scattering (polystyrene latex spheres)	Modified Climet Instruments. Model CI-207. Particle Analyzer
O_3	Chemiluminescence reaction with ethylene (neutrally buffered potassium iodide solution, later corrected to UV photometry standard)	REM, Inc. Model 612 Atmospheric Ozone Monitor
Total hydrocarbons, methane, CO	Gas chromatography - flame ionization detector (certified gases)	Beckman Instruments. Model 6800. Air Quality Chromatograph[b]
SO_2	Flame photometry (SO_2 permeation tube)	Meloy Labs. Model SA-120. Sulfur Gas Analyzer
Temperature	Thermocouple	YSI Tele-Thermometer Model 43-TC
Dew point	Thermoelectric sensor	EG&G. Model 880-CI Dew Point Hygrometer[b]
Solar radiation	Broad band pryoheliometer	Epply. Pryoheliometer, No. 2977

[a] Loan, courtesy of Meteorology Research, Inc. [b] Loan, courtesy of the California Air Resources Board.

Table II. Summary of Teflon Bag Experimental Conditions

Run no.	Hydrocarbon	$[HC]_0$, ppm	$[NO]_0$, ppm	$[NO_2]_0$, ppm	$[SO_2]_0$, ppb	Δb_{scat}, 10^{-4} m^{-1}	k^a, %hr^{-1}	$[O_3]_{max}$, pphm	%RH	T, °C
C.04	1-Heptene	0.89	0.20	0.20	0.	2.4	0	53	45	31
C.95	1-Heptene	1.85	0.19	0.10	39.	9.5	25–82	41	16	35
C.96	1-Heptene	1.66	0.10	0.10	80.	14.5	21–99	33	14	38
C.97	1-Heptene	1.47	0.20	0.11	86.	14.0	27–72	26	16	36

[a] Pseudo-first-order rate constant for SO_2 loss: $d[SO_2]/dt, = -k[SO_2]$.

tions and the resulting maximum O_3 concentration, change in b_{scat}, and range of the rate of SO_2 loss, is given in Table II. Experiments were also run with cyclohexene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, and 1,7-octadiene as the hydrocarbon. A few experiments were run with the addition of SO_2 alone to ambient air. 1-Heptene was studied most extensively because it represents the middle range olefins present in the atmosphere. It forms organic aerosol and promotes formation of aerosol sulfur, and decays at a rate that allows study over a period of 2–3 h. The olefin–1-heptene has been found in gasoline, diluted auto exhaust, and in the ambient atmosphere.

While the 1-heptene concentrations used in these experiments were much higher than those measured in the atmosphere, they were of the order of the total atmospheric hydrocarbon concentrations. The concentrations of O_3, NO, NO_2, and SO_2 are comparable to ambient levels in Los Angeles. The 15–30% relative humidity values are typical of afternoon photochemical smog in Los Angeles. Total filter samples for aerosol chemical analysis and impactor samples were taken at 15–20-min intervals. A complete listing of the data is given by Roberts (*29*).

Estimates of the bag volume were made using the injected volume and the measured initial concentration of either SO_2 or 1-heptene. For the 13 experiments shown in Table II, the average initial volume using the initial SO_2 concentration was 96 ± 18 m^3. The spread in the measurement resulted because the bag was not filled to the same volume each time. The initial volume for each experiment (calculated using the initial SO_2 concentration) is used to calculate the initial concentrations of NO and NO_2.

The measurements of gas and aerosol sulfur during runs C.95 through C.97 were used to calculate sulfur recovery. Table III shows that the overall sulfur recovery (the sum of SO_2 and aerosol sulfur) was between 98 and 100% for the three experiments. Each is the average of five or six total filter samples and the corresponding gas phase SO_2 concentrations. The initial value is the SO_2 concentration just after the auxiliary filling pump has been turned off. Comparison of the measured particulate sulfur with the calculated particulate sulfur concentration using the initial SO_2 concentration and the decaying SO_2 concentration values shows excellent agreement (*27*).

Experiments with 1-Heptene

The starting conditions and other pertinent information for the 1-heptene experiments are given in Table II. The variations of concentration with time of SO_2, 1-heptene, O_3, b_{scat}, and CNC (condensation nuclei count) are given in Figure 2 for experiment C.95. The times of injection of the NO, NO_2, SO_2, and 1-heptene are noted.

A general discussion of the features of the 1-heptene experiments follows with C.95 as an example. Results for the other experiments were qualitatively similar. The initial decay in SO_2 concentration, before the 1-heptene was added, was the result of dilution from the auxiliary filling pump. The SO_2 decay was slight until the O_3 concentration became larger than 5 pphm, at which point there was a sharp downward trend in the SO_2 concentration. This characteristic was present in each of the experiments with SO_2 and is indicative of the involvement of the photochemistry in the oxidation of SO_2. The variation of the condensation nuclei concentration in experiment C.95 was especially interesting. There were three regimes of behavior of the total particle concentration: first, the large increase in the nuclei concentration just after the introduction of SO_2; second, another large increase in nuclei after the introduction of the 1-heptene; and third, the sharp drop in nuclei concentration accompanying the increase in SO_2 oxidation rate (and the increase of the O_3 concentration above 5 pphm). All three regimes were not found in all of the experiments because in some cases the 1-heptene was introduced shortly after the SO_2. However, all experiments show the sharp drop in the nuclei concentration at that same point. In fact, this was also the time that the 1-heptene began to be lost at a large rate from the gas phase, presumably by reaction with O_3. An increase in b_{scat} (decrease in visibility) usually began about 20 min after the O_3 concentration had gone above 5 pphm.

Thus, two major regimes were observed in these experiments: first, the concentrations of SO_2, O_3, 1-heptene, and b_{scat} are constant as the NO is converted to NO_2; and second, O_3 induces decay of both SO_2 and 1-heptene, and sub-

Table III. Overall Sulfur Recovery for Three Experiments with 1-Heptene

Run designation	$[SO_2]_0$		$[S_T]$, μg SO_2/m^3	Av % recovery
	Ppb	$\mu g/m^3$		
C.95	35.0	92.8	91.2 ± 6.6	98.4
C.96	79.5	210.7	211.3 ± 7.4	100.3
C.97	85.5	226.6	226.8 ± 13.3	100.1

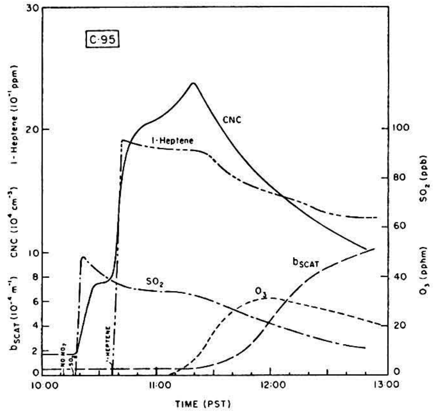

Figure 2. Concentration and light-scattering profiles for experiment C.95

Average of 16% RH and 35 °C

sequent aerosol formation. During the first regime, new particles are being formed at a high rate from both SO_2 and 1-heptene; however, a sharp drop in new particle formation is observed during the second photochemical regime. The large decrease in new particle formation occurs just as the oxidation rates of both SO_2 and 1-heptene sharply increased. This observation indicates that a more condensable species is being formed during the second regime or that new surface is then providing a sink for the condensable species so that new particle formation is suppressed.

Experiment C.04 showed that there was some aerosol formation in the 1-heptene system without SO_2, although the increase in b_{scat} occurs later than in the system with SO_2 (and after the O_3 concentration has reached its maximum).

Another feature of these experiments was the near-first-order decay of the SO_2 concentration during the photochemical regime. This is illustrated for experiment C.95 in Figure 3 where the log of the SO_2 concentration is plotted against time. The linear portion, indicating a first-order decay in SO_2 concentration, extends for about an hour during the experiment. Similar results were found in the other runs with this system.

Experiments also were carried out with NO, NO_2, SO_2, and the following hydrocarbons: cyclohexene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, and 1,7-octadiene. Three experiments were run with only SO_2 added to ambient air. In the experiments with cyclohexene and 1,7-octadiene, organic aerosol formation dominated aerosol sulfur formation. There was no measurable change in the SO_2 concentration when little O_3 (less than 5 pphm) was produced in the experiment with 2-methyl-2-butene. Experiments with SO_2 alone in ambient air showed comparably slow oxidation of SO_2 (less than 11% hr^{-1}).

Kinetics of Aerosol Formation

Recent studies have indicated that oxidation of SO_2 by some reactive intermediate of the O_3-olefin reaction can lead to the formation of aerosol sulfur (*8, 12, 20*). Other investigators have proposed the hydroxyl radical (*19*) or the hydroperoxyl radical (*30*) as a major contributor to the oxidation of SO_2 in the atmosphere. The photooxidation of SO_2 is probably not an important mechanism in the presence of the above photochemical agents, based on recently measured values of the quantum yield (*31, 32*).

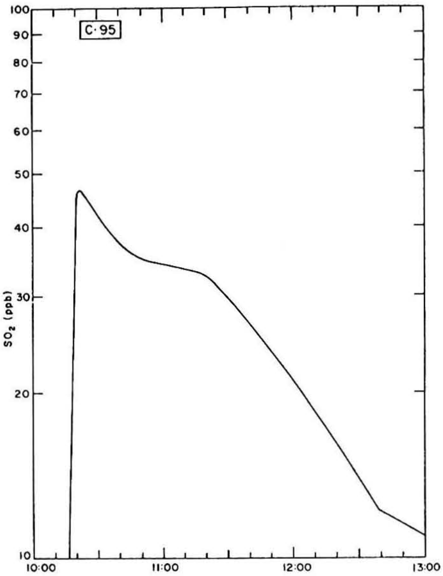

Figure 3. Concentration profile for experiment C.95 showing the near-first-order decay of SO_2

Our results could be explained by applying a general reaction scheme proposed by Grosjean (*33*) to the ozone–SO_2–1-heptene system. This reaction scheme involves the formation of a reactive intermediate (I) from the ozone attack on 1-heptene (Hp). The intermediate forms products, some of which are condensable, either by unimolecular (i) or bimolecular (j) pathways:

$$O_3 + \mathrm{Hp} \xrightarrow{k} \mathrm{I} \qquad \text{slow, the rate-determining step}$$

$$\mathrm{I} \xrightarrow{k_{1i}} \mathrm{P}_{1ik} \quad i = 1, N$$

$$\mathrm{I} + SO_2 \xrightarrow{k_{21}} \mathrm{P}_{21} + SO_3$$

$$\mathrm{I} + \mathrm{R}_j \xrightarrow{k_{2j}} \mathrm{P}_{2jk} \quad j = 2, M$$

This allows for N different unimolecular decompositions of I, and M different bimolecular reactions of I with species R_j. Each reaction can form a number of products, denoted by P_{1ik} and P_{2jk}. If I reaches a steady-state concentration,

$$[\mathrm{I}]_{ss} = \frac{k[O_3][\mathrm{Hp}]}{\sum_i k_{1i} + k_{21}[SO_2] + \sum_j k_{2j}[\mathrm{R}_j]} \tag{1}$$

The rate of formation of product P_{21} can thus be written at steady state as

$$\frac{d[\mathrm{P}_{21}]}{dt} = k_{21}\,[\mathrm{I}]_{ss}[SO_2] \tag{2}$$

$$= \frac{kk_{21}[O_3][\mathrm{Hp}][SO_2]}{\sum_i k_{1i} + k_{21}[SO_2] + \sum_j k_{2j}[\mathrm{R}_j]}$$

Integration from time 0 to time T, assuming $[P_{21}] = 0$ at time 0 results in:

$$[\mathrm{P}_{21}]_T = kk_{21} \int_0^T \frac{[O_3][\mathrm{Hp}][SO_2]}{\sum_i k_{1i} + k_{21}[SO_2] + \sum_j k_{2j}[\mathrm{R}_j]}\,dt \tag{3}$$

Letting α_{21} be the fraction of P_{21} which condenses, the aerosol carbon concentration is given by:

$$[\mathrm{AC}_{21}] = \alpha_{21}[\mathrm{P}_{21}] \tag{4}$$

If other P_{nik}'s form aerosol, there are similar expressions. Thus, for the total aerosol carbon (TAC) at time T:

$$[\mathrm{TAC}]_T = \sum_{i,k}[\mathrm{AC}_{1ik}] + \sum_{j,k}[\mathrm{AC}_{2jk}] \tag{5}$$

$$= k \int_0^T \frac{\left\{\sum_i \alpha_{1i}k_{1i} + \alpha_{21}k_{21}[SO_2] + \sum_j \alpha_{2j}k_{2j}[\mathrm{R}_j]\right\}[O_3]}{\sum_i k_{1i} + k_{21}[SO_2] + \sum_j k_{2j}[\mathrm{R}_j]}$$

For the heptene system, we also make the following simplifications:

(1) There is little aerosol carbon formed in the 1-heptene–NO_x system without SO_2, compared to the system with SO_2. The results of run C.04 described earlier as well as the work of Stevenson et al. (*34*), Wilson et al. (*7*), and

O'Brien et al. (*35*) show that this is a good assumption at the concentration levels used in this study. Thus,

$$\sum_i \alpha_{1i}k_{1i} + \sum_j \alpha_{2j}k_{2j}[R_j] \ll \alpha_{21}k_{21}[SO_2]$$

(2) Little of the reactive intermediate, I, reacts with SO_2. Cox and Penkett (*20*) have shown that there was no measurable difference in the variation with time of the O_3 and olefin concentrations, with and without SO_2. Thus,

$$k_{21}[SO_2] \ll \sum_i k_{1i} + \sum_j k_{2j}[R_j]$$

(3) The R_j are present in sufficient concentration such that their concentration is not depleted by reaction with I: $[R_j] \sim$ constant with time ($R_j = O_2$ is an example)

We are then left with the following expression for the aerosol carbon concentration at a given time T:

$$[TAC]_T = \frac{kk_{21}}{\sum_i k_{1i} + \sum_j k_{2j}[R_j]} \int_0^T \alpha_{21}[O_3][Hp][SO_2]dt \qquad (6)$$

Thus, the aerosol carbon should be a linear function of the integral of the product of the ozone, 1-heptene, and sulfur dioxide concentrations. This also assumes that α_{21} is not a function of time.

The same type of analysis can be performed to determine the aerosol sulfur concentration at time T. A steady state concentration for I implies that:

$$\frac{d[SO_3]}{dt} = k_{21}[I]_{ss}[SO_2] \qquad (7)$$

Making the same assumptions concerning the reactions of the intermediate (Equations 1–3), integration from time 0 (no SO_3) to time T results in an expression for the concentration of aerosol sulfur:

$$[AS]_T = \frac{kk_{21}}{\sum_i k_{1i} + \sum_j k_{2j}[R_j]} \int_0^T \alpha_{SO_3}[O_3][Hp][SO_2]dt \qquad (8)$$

where α_{SO_3} represents the fraction of SO_3 formed, which results in aerosol sulfur. Therefore, both the aerosol carbon and the aerosol sulfur should be linear functions of the integral of the product of the ozone, 1-heptene, and SO_2 concentrations.

The gas phase and aerosol phase measurements for experiments C.04, C.95, C.96, and C.97 were analyzed within the framework of the aerosol formation kinetic scheme. Integrated forms (Equation 3) were used instead of differential forms (Equation 2) because of the continuous data for the gas phase species. The data points shown in the figures are computed for the midpoint of the aerosol samples taken during the experiments. Integrations were done with a planimeter.

The 1-heptene depletion rate can be used to determine the apparent O_3–1-heptene rate constant, assuming that 1-heptene only reacts with O_3:

$$\frac{d[Hp]}{dt} = -k[O_3][Hp] \qquad (9)$$

Integration from time 0 to time T results in:

$$[Hp]_0 - [Hp]_T = k\int_0^T [O_3][Hp]dt \qquad (10)$$

Figure 4 shows that the change in the 1-heptene concentration is a linear function of the integral of the product of the O_3 and 1-heptene concentrations after a short induction period. A least-squares fit to the linear section of the data yields an average O_3–1-heptene rate constant for these four experiments of 13.5×10^{-3} ppm^{-1} min^{-1}. This agrees well with the value of Cadle and Schadt (*36*), 12×10^{-3} ppm^{-1} min^{-1}, measured in a contaminant-free system. Although no other measurements have been made of the O_3–1-heptene rate constant, the Cadle and Schadt (*36*) value for the O_3–1-hexene rate constant (15×10^{-3} ppm^{-1} min^{-1}) agrees well with the value recently determined by Japar et al. (*37*) of 16.1×10^{-3} ppm^{-1} min^{-1}.

The aerosol carbon and sulfur measurements can be used to test the aerosol kinetic scheme using Equations 6 and 8. Figure 5 shows the aerosol carbon concentration, as a function of the integrated product of the O_3–1-heptene and SO_2 concentrations, for experiments C.95, C.96, and C.97. The linearity of the relationship over most of the range indicates that, in the 1-heptene–NO–NO_2–SO_2 system, the formation of aerosol carbon is consistent with the reaction of SO_2 with a reactive intermediate of the O_3–1-heptene reaction. The upward bend of the aerosol carbon concentration near the end of experiments C.96 and C.97 indicates that an aerosol carbon formation pathway different from the one postulated in the above assumptions is becoming significant.

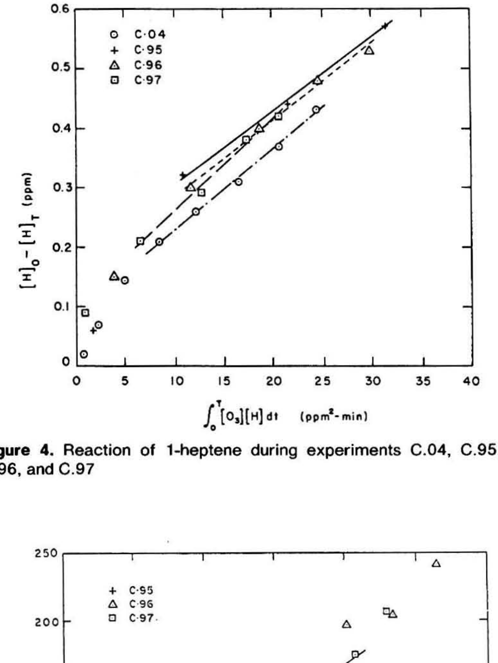

Figure 4. Reaction of 1-heptene during experiments C.04, C.95, C.96, and C.97

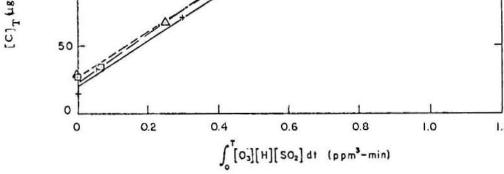

Figure 5. Formation of aerosol carbon during experiments C.95, C.96, and C.97

Based on the form of Equation 8, a plot of aerosol sulfur is shown in Figure 6. There was less than 2 $\mu g/m^3$ of aerosol sulfur (as SO_4^{2-}) in the first sample of each experiment. The fast rise in the aerosol sulfur concentration at the beginning of each experiment results from an SO_2 oxidation mechanism other than the O_3–olefin reactive intermediate. However, after this short induction period, there is a linear dependence of the aerosol sulfur concentration on the integral of the product of the O_3–1-heptene and SO_2 concentrations. The linear dependence is consistent with the assumptions made concerning aerosol sulfur formation.

Equations 2 and 9 suggest that for a particular experiment, the aerosol carbon and 1-heptene concentrations would be related:

$$[TAC]_T - [TAC]_0 = \alpha\{[Hp]_0 - [Hp]_T\} \qquad (11)$$

Figure 7 shows the formation of the aerosol carbon as a function of the 1-heptene reacted. Each experiment shows approximate linearity. The quantity, α, is the fraction of reacted 1-heptene that results in aerosol carbon. For the three runs this fraction ranged from 5–14%. Because most of the aerosol carbon is formed in a reaction with SO_2, α depends on the SO_2 concentration.

The olefin may reaction with species other than O_3, such as O atoms, or OH and HO_2 radicals. SO_2 may also react with these species instead of with the intermediate of the O_3–olefin reaction. The rise in both aerosol sulfur and carbon observed initially (Figures 5 and 6), which is not explained by our kinetic scheme, may result from such reactions.

Distribution of Sulfur with Respect to Particle Size

The distribution of sulfur with respect to particle diameter was measured as a function of time during the 1-heptene experiments using a low-pressure, single-(round)-jet, multistage cascade impactor (*29*). Design and calibration of a low-pressure impactor has been reported in the literature (*38–42*). However, no investigator has reported mass or chemical size distribution data using such a device.

The low-pressure impactor consisted of 4 stages and a restricing orifice (operated at choke flow) upstream of the first stage (orifice diameter of 0.008 in.). The theoretically predicted size ranges (50% cutoff sizes) for the after filter and four stages were as follows: less than 0.09 μm, 0.09–0.20 μm, 0.20–0.37 μm, 0.37–0.86 μm, and greater than 0.86 μm in diameter. The impactor was calibrated with polystyrene latex spheres of diameter 0.088–0.716 μm by counting the collected spheres with an electron microscope. The experimental efficiency curves for the 2d and 3d stages show good agreement with the theoretically predicted 50% cutoff values. Buchholz (*41*) found that bounce-off and wall losses were of little importance for submicron particles in a low-pressure impactor.

The sulfur size distribution function (logarithmic coordinate for d_p) can be determined from impactor data by assuming that there is a particle diameter below which the mass of sulfur can be neglected. The value of 0.02 μm was used for this purpose in constructing the bar graph distributions.

To obtain a continuous aerosol sulfur distribution function with respect to particle diameter, a cumulative distribution plot was prepared and then differentiated. The resulting continuous sulfur distribution functions are undoubtedly inaccurate because of the differentiation process; however, by redesign of the low-pressure impactor, it should be possible to obtain more accurate continuous distribution functions.

The data for run C.95 are shown in Figure 8 both as bar graphs and continuous distribution functions. Similar re-

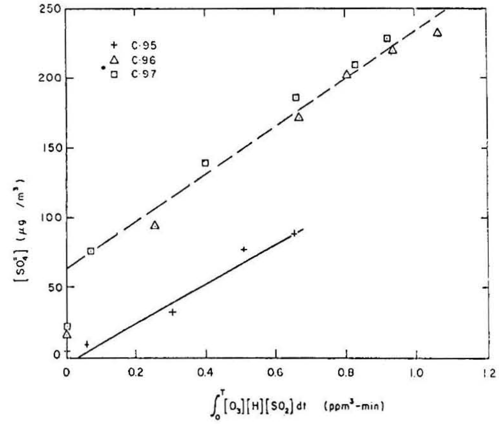

Figure 6. Formation of aerosol sulfur during experiments C.95, C.96, and C.97

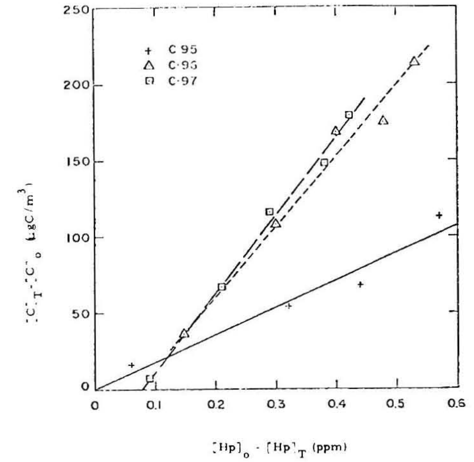

Figure 7. Formation of aerosol carbon as function of reacted 1-heptene during experiments C.95, C.96, and C.97

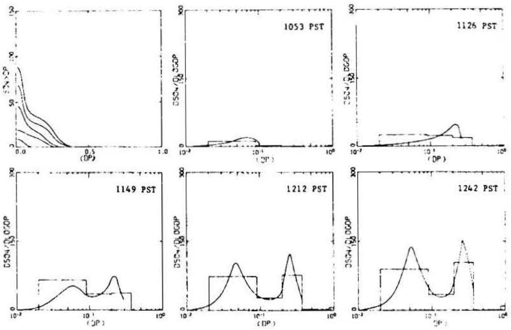

Figure 8. Sulfur size distribution as function of particle size during experiments C.95

Area under the curve represents the total mass of sulfur (reported as sulfate) over any size range

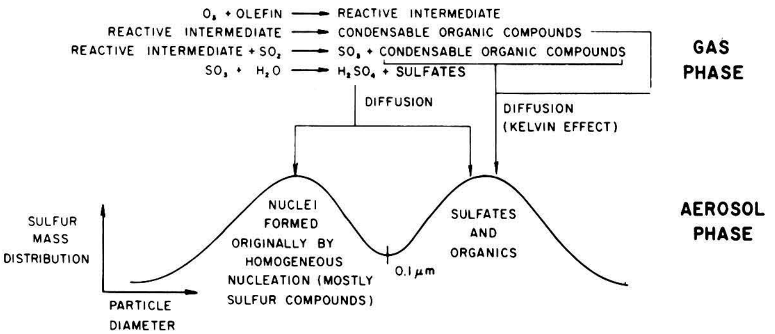

Figure 9. Schematic diagram of gas-to-particle conversion in the SO_2, olefin, NO_x system. Only limited portions of the proposed scheme have been experimentally verified and the diagram should be regarded as tentative

sults were found in runs C.96 and C.97. The first sample contained a small amount of particulate sulfur (all below 0.2 μm). Then a bimodal distribution developed (one mode below 0.1 μm, the other between 0.2 and 0.4 μm) and the two modes grew to larger sizes by continued conversion from the gas phase. Runs C.96 and C.97 resulted in the growth of sulfur to larger particle sizes than in C.95.

In the previous section, the formation of most of the aerosol carbon and aerosol sulfur was explained by the reaction of SO_2 with a reactive with aerosol carbon (compare Equations 6 and 8). It was found that the aerosol sulfur in the size range above 0.2 μm was a linear function of the total aerosol carbon. In fact, the ratio of the upper mode (>0.2 μm) to total aerosol sulfur is 0.33 ± 0.07 throughout the three 1-heptene–SO_2 experiments. Thus, one-third of the converted SO_2 appears in particles larger than 0.2 μm, and two-thirds in particles smaller than 0.2 μm.

In experiments with cyclohexene, cyclopentene, and 1,7-octadiene, Heisler (*23*) found that the average critical size for aerosol carbon is in particles greater than about 0.2 μm, thus coinciding with the upper mode in the sulfur size distribution. The upper mode is probably produced by growth of sulfur containing species along with the organic species, while the lower mode results from the growth of sulfur species upon the particles formed in the initial nucleation period of the experiment. A schematic diagram of the aerosol formation process is shown in Figure 9.

Summary

Aerosol formation studies were carried out in a large Teflon bag irradiated with natural sunlight. Sulfur dioxide, nitrogen oxides, and various olefins were added to unfiltered ambient air and allowed to react for up to 3 h. The concentrations used were typical of average Los Angeles conditions, with the exception of the olefins. Olefin concentrations were about 100 times higher than individual ambient concentrations, although only two to five times higher than total olefin ambient concentrations. Sulfur mass balances during the experiments were excellent; measured gas and aerosol sulfur concentrations accounted for all of the initial SO_2 present.

The rate of formation of aerosol containing carbon and sulfur is consistent with a reaction between SO_2 and a reactive intermediate of the O_3–1-heptene reaction. A sharp increase in the SO_2 oxidation rate occurred when the O_3 concentrations exceeded 0.05 ppm, and a kinetic scheme is proposed for aerosol formation. The distribution of sulfur with respect to particle size changed with time, eventually becoming bimodal about 0.2 μm. The concentration of aerosol sulfur in the upper mode was closely related to the total aerosol carbon, and probably resulted from the deposition of sulfur containing compounds on the organic fraction of the aerosol in the size range above 0.2 μm. Thus it is likely that the nature of the aerosol initially present in such systems will have a significant effect on the distribution of sulfur with respect to particle size.

Large numbers of new particles were generated during the early stages of the experiments, but no new particles were generated after the O_3 concentration exceeded about 0.05 ppm. Different mechanisms probably control SO_2 oxidation for O_3 concentrations above and below 0.05 ppm.

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Fate of Crude Oil Spilled on Seawater Contained in Outdoor Tanks

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Before the possible short- and long-term environmental effects of marine oil pollution can be adequately evaluated and predicted, detailed information on the fate of spilled oil is required. The fate of spilled oil is very complex. Once spread on the sea surface, oil is immediately and simultaneously affected by a wide variety of processes that include evaporation, accommodation into underlying water, biological decomposition, and chemical degradation.

Within the past few years, considerable scientific attention has been devoted to the fate of oil added to seawater. Experiments have been conducted both in the laboratory (*1–9*) and in the field with intentional oil spills (*1, 10–12*) and seeps (*13*). Despite the marked variability of analytical and experimental procedures used in these investigations, several general conclusions emerge: 1. Evaporation of volatile hydrocarbons is rapid and probably accounts for the greatest loss. 2. Ecologically significant quantities of oil can penetrate into the water column in three principal forms: particulate, solubilized (colloidal), and truly soluble. 3. The most abundant hydrocarbons accommodated in seawater appear to be the medium molecular weight aromatics (two- and three-ring compounds). 4. The relative importance of the numerous weathering processes is influenced greatly by the composition of spilled oil and environmental factors such as turbulence and temperature.

Our interest in the fate of oil spills has centered on the possible levels and forms of oil pollution that can be expected to occur in seawater and possibly affect marine organisms. Our initial work (*4*) involved laboratory experiments conducted in separatory funnels. These experiments provided information on the concentrations of particulate and subparticulate oil that can be accommodated in seawater under different experiment conditions. Realizing the limitations of laboratory experiments of this type, we continued our work by studying

■ The fate of crude oil spilled on seawater was studied in outdoor tanks. Concentrations of oil in the surface film, water column, and sediment were monitored for as long as three months by fluorescence spectroscopy. About half of the spilled oil formed tar balls or was stranded on the walls of the tank. It is estimated that less than 5% of the oil entered the water column and sediments. The concentration of oil in the water column was as high as 2–3 mg/l. during the first few days. Oil could still be detected in the seawater (about 30 μg/l.) and sediment (about 10 μg/g wet sediment) after three months. The concentrations observed were in the same range as reported in polluted environments and are potentially deleterious to some marine organisms.

the fate of small oil spills in large outdoor tanks containing sediment. Although not an exact replication, the conditions of these experiments approach those usually encountered in coastal environments where stranded oil is present. More realistic conditions can only be obtained by studying actual spills which poses considerable logistic problems.

Methods

Experiments were conducted in two circular tanks (1 m deep and 4 m in diameter) placed just outside our laboratory on the shore of Bedford Basin (Figure 1). The bottom of each tank was covered with about 5 cm of sand obtained from a local building supply dealer. Tanks were filled with surface water (upper 1 m) from Bedford Basin, delivered by pump, to within 10 cm of the top (about 8000 l./tank). Several days were allowed for suspended matter to settle before experiments were begun.

Six experiments were run (Table I). In the first four, oil was added to one tank while the second served as a control. Since concentrations in the control tank were relatively low and remained constant during these experiments, no control was used in Experiments 5 and 6.

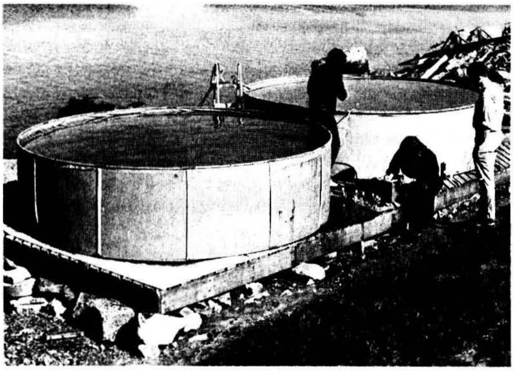

Figure 1. Photograph of tanks in which fate of crude oil spills was investigated. Tanks are located on the shore of Bedford Basin, just outside the laboratory

Surface film samples were collected by immersing a glass test tube to a depth of 5.5 cm and slowly withdrawing it. The surface of the test tube was washed twice with 5 ml of hexane and the rinse collected in a glass bottle. This sampling technique is essentially identical to the glass plate technique of Harvey and Burzell (*14*) reported to be efficient for sampling microlayers less than 100 μ thick (*15*). The tube collected the surface film from an area approximately 33 cm^2. Three such samples were collected from each tank every sampling date.

Water samples were collected by quickly immersing a 1-l. glass bottle attached to a metal rod to a depth of 0.5 m and allowing it to fill. This device was lowered and retrieved through that part of the surface that had the least amount of visible oil (concentrations in water samples collected with a siphon placed in the tank before oil was added were similar, indicating that contamination by entrainment of surface film was minimal). Water was transferred to glass separatory funnels and extracted twice with 40 ml of methylene chloride. Bottles were rinsed with methylene chloride to recover adsorbed material, and the rinse was added to samples. Methylene chloride was removed in a rotary evaporator at 30 °C and the residue taken up in 10 ml of hexane. Two water samples were collected from each tank on every sampling date.

Sediment was collected with a siphon that, to avoid contamination from the surface film, was placed in the tank before oil was added and was never removed. About 300 g of sediment were removed from an area approximately 100 cm^2 on each sampling date. Two grams were extracted with 1 ml of distilled water and 10 ml of hexane using the procedure of Hargrave and Phillips (*16*).

The hexane extracts were analyzed by fluorescence spectroscopy using the techniques described by Gordon and Keizer (*17*). Two types of information were obtained: estimated total oil concentrations and synchronous excitation of emission spectra (SEES).

Fluorescence spectroscopy is not a perfect method for

Table I. Details of Six Experiments Conducted to Study Fate of Crude Oil Spilled on Seawater

		Water temp., °C			
Experiment	Dates	Start	End	Amount and type oil added	Notes
1	5–21 June 1973	14	19	100 ml Tia Juana crude	One tank oiled, other control
2	3–12 July 1973	21	25	100 ml Tia Juana crude	One tank oiled, other control
3	13 Aug.–30 Nov. 1973	24	5	700 ml Tia Juana crude	One tank oiled, other control
4[a]	27 Dec. 1973–Jan. 1974	2	−1.5	700 ml Guanipa crude	One tank oiled, other control
5	17 June–25 Sept. 1974	19	16	1000 ml Guanipa crude	Both tanks oiled, no control
6	1 Oct.–1 Nov. 1974	12	3	1000 ml Guanipa crude	Single tank

[a] Ended prematurely when water froze and tank ruptured.

measuring petroleum hydrocarbon concentrations (*18*). Concentrations obtained with this technique are only estimates. However, fluorescence spectroscopy is most accurate when used in experiments such as those discussed in this paper when (1) the concentrations being measured are high, (2) the origin of the hydrocarbons being detected is known and a sample is available for calibration purposes, and (3) concentrations can be corrected for naturally occurring fluorescence observed in controls. The only serious error in the concentrations determined might result from changes in the fluorescence characteristics of the oil during weathering (evaporation, photooxidation, bacterial oxidation, and so forth). Therefore the accuracy of concentrations probably decreased to an unknown degree during the course of each experiment.

All solvents were redistilled in glass and all materials were thoroughly rinsed with solvent before use. Visual observations were recorded and photographs taken during all experiments. The pH was determined in Experiment 1, and oxygen was measured in Experiments 1–3 with a Radiometer blood-gas analyzer.

Results

Generally speaking the six experiments produced similar results. The differences observed were due mainly to the quantity of oil added and the duration of the experiment. Most of the quantitative data presented originated from Experiment 5 which was the most complete.

Surface Film. Within minutes after being poured on the water surface in the center of the tank, the oil spread unevenly over the entire surface. Some areas had a thick layer of oil while others had only a thin irridescent film. By the end of the first day (6–8 h after addition), the wind had driven most of the oil to the leeward edge of the tank where some adhered to the tank wall. After several days, the entire inner circumference of the tank was coated with oil at and just above the water surface. On approximately the third day, the oil slick started to break up and form discrete streaks and blobs which in time developed into tar balls, often around a nucleus such as a wood chip or feather. By the tenth day, there were no visible slicks or films. Except for tar balls, the water surface was clear. By the end of the longer experiments (Nos. 3 and 5), the oil coating the tank wall had become crusty on the surface. This oil was scraped from the walls at the termination of Experiments No. 3 and 6, combined with the tar balls, and weighed. In Experiment 3, 269 g or 38% that had been added was recovered in this form, while in Experiment 6, 640 g or 76% was recovered (more than half was in the form of tar balls).

Oil behaved much differently in the surface film during Experiment 4. Oil was added when the air temperature was −1 °C and the water temperature was 2 °C. Instead of spreading rapidly as it did in the other experiments started at higher temperatures, the oil spread very slowly and tended to form large blobs. There was much less tendency to form irridescent films.

The visual observations were closely paralleled by the concentrations of oil detected in the surface film (Table II). The highest concentrations occurred the first day, some exceeding 10 mg oil/cm^2 (corresponding to a film thickness of about 0.12 mm). Slightly lower concentrations persisted until Day 9. As noted visually, the distribution of oil on the surface was very patchy; consequently concentrations at any time during this period were quite variable as shown by the excessive standard deviations in Table II. After Day 9, when an oil film was no longer visible, concentrations dropped sharply and by Day 24 and thereafter they approached original background levels.

The disappearance of oil from the surface film is also demonstrated by the SEES (Figure 2). Guanipa crude dissolved in hexane yielded two well-defined peaks: one at approximately 320 nm which is produced by two-ring aromatic compounds (naphthalenes and perhaps oxygenated derivatives) and another at about 350 nm which is produced by three- and four-ring aromatics (and as anthracene, phenanthrene, chrysene, and perhaps oxygenated derivatives). The peak at 280–290 nm is produced mainly by benzenes in the redistilled hexane, though some could have come from the oil. These two peaks were detectable in the surface film for at least 17 days. From Day 24 onward, spectra were similar to the preoil spectrum.

Water Column. Concentrations reached several hundred µg/l. within 30 min (Table II). The highest concentrations, 2–3

Table II. Average Oil Concentrations, Estimated by Fluorescence Spectroscopy, Observed in Surface Film, Water Column and Sediment During Experiment 5

Standard deviations are given in parentheses

	Surface film[a]		Water column		Sediment	
Day	n	µg/cm^2	n	µg/l.	n	µg/g wet sediment
1 (before Oil[b]	5	0.1 (0.05)	2	15 (4)	—	—
1 (30 min)	5	5659 (8500)	4	231 (203)	—	—
1 (5 h)	6	5900 (7270)	2	2575 (3270)	2	13 (14)
2	4	800 (1340)	4	78 (11)	2	4 (3)
3	6	1390 (2180)	4	164 (60)	2	22 (4)
4	6	2780 (4110)	4	67 (5)	2	32 (6)
5	6	1760 (2000)	4	59 (5)	2	16 (3)
9	6	2870 (4860)	4	89 (25)	2	54 (55)
17	6	164 (327)	4	80 (6)	2	31 (9)
24	6	0.2 (0.04)	4	66 (6)	2	74 (67)
31	6	1.4 (1.5)	4	60 (7)	2	33 (14)
45	6	0.4 (0.06)	4	41 (3)	2	7 (6)
59	6	0.2 (0.07)	4	25 (2)	2	8 (5)
73	6	0.2 (0.07)	4	26 (7)	2	12 (6)
79	6	0.2 (0.05)	4	21 (3)	2	6 (1)
101	3	0.1 (0.05)	2	34 (1)	1	13

[a] Including occasional tar ball. [b] i.e., control.

mg/l., occurred during the first few days. For the next 30 days, average concentrations stayed in the range of about 60–160 μg/l. From Day 31 onward, the concentrations gradually dropped and approximated 30 μg/l. at the termination of the experiment (Day 101). Most of the variation in replicates can be explained by the nonhomogeneous distribution of oil in seawater (*18, 19*).

The data from the other experiments (Table I) demonstrated the same relative changes with time, but the concentrations observed were directly related to the amount of oil initially added. The initial and control concentrations in all experiments averaged 3 and 6 μg/l.

The two characteristic SEES peaks of Guanipa crude are also observed in the water column (Figure 3). After 5 days, the 350 nm peak (three- and four-ringed aromatics) began to drop relative to the 320 nm peak (two-ringed aromatics) and at the end of the experiment it was no longer visible. Therefore, during the course of the experiment the proportion of two-ring aromatics in the water column increased relative to the higher molecular weight aromatics. Such an enrichment was not observed in the surface film.

There was no detectable difference in dissolved oxygen in Experiments 1–3 between control and oiled tanks; oxygen concentrations in seawater remaining near saturation. In Experiment 1, there was no observed difference in pH (8.2–8.3).

Sediments. Oil appeared in the sediment within 5 h and concentrations tended to increase steadily during the first week (Table II). The highest concentrations occurred between Days 4 and 31, thereafter they dropped. Much of the variation between concentrations can be attributed to a nonhomogeneous distribution of oil on the sediment. Maximum concentrations were on the order of 100 μg/g of sediment, while initial and control tank concentrations were generally less than 1 μg/g of sediment. A detectable amount of oil remained in the sediment at the end of the experiment. The characteristic peaks of Guanipa crude were present in the SEES obtained at the end of the experiment (Figure 4), and, as observed in the water column, there appeared to be an enrichment of the naphthalenes.

Oil Budget. From the concentrations listed in Table II and knowing the dimensions of the tank, it is possible to calculate the approximate amount of oil contained in the surface film, water column, and sediment on each sampling date during Experiment 5 (Table III). It should be noted that the oil stranded on the tank wall and incorporated into tarballs is not included in these figures. The relative amounts of these two forms increased during experiments.

Initially, all the oil was contained in the surface film, but the amount began to drop immediately with the onset of weathering. It is interesting to note, however, that it was not until after Day 17 that the water and sediment contained more oil than the surface film. The greatest amount of oil in the water column occurred at 5 h. From Day 4 onward, the total amount of oil in the sediment exceeded that in the water. At the termination of the experiment, most of the oil remaining in the tank (except that stranded on walls or incorporated into tar balls) was incorporated in the sediment. On Day 17 less than 1% of the oil added could be found in the surface film, water column, and sediment; from Day 59 onward, less than 0.1%. If we judge from the results of Experiments 3 and 6, probably about half the added oil was stranded on tank walls or formed tarballs during this experiment. The remaining oil (about 50%) was presumably lost by evaporation or degraded by biological and chemical processes.

Discussion

The environmental conditions of these tank experiments are not an exact replication of conditions to which oil would be exposed after a spill on natural waters. Water turbulence, oil slick spreading, and dilution of those oil components accommodated into water were reduced considerably. Due to the presence of the tank wall, the conditions of these experiments are more similar to those encountered in coastal environments, where oil can be stranded along the shoreline, than in open water away from land. Despite their recognized limitations, experiments such as these can provide valuable in-

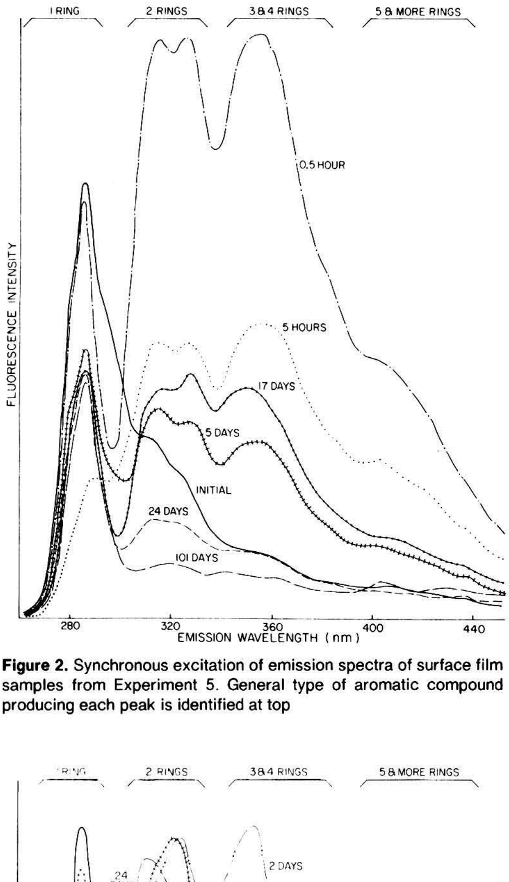

Figure 2. Synchronous excitation of emission spectra of surface film samples from Experiment 5. General type of aromatic compound producing each peak is identified at top

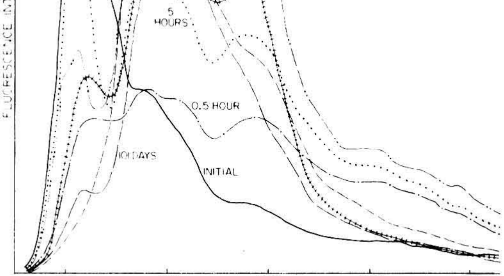

Figure 3. Synchronous excitation of emission spectra of water samples (0.5 m) from Experiment 5. General type of aromatic compound producing each peak is identified at top

formation on the possible behavior and fate of oil spills, especially in coastal areas.

It is clear that spilled crude oil can penetrate into the water column within minutes and that the highest concentrations in the water will probably occur during the first few days. Oil will take longer to reach the sediment, and the highest concentrations will probably not be attained until about the second or third week after the spill (the exact time is undoubtedly dependent on such variables as water depth, currents, and tides). After about three weeks, most of the oil remaining at the water surface will have been incorporated into tarballs or stranded on shore lines; no appreciable surface film will be present. However, despite the absence of a surface film of oil, appreciable quantities of oil will persist in the water and sediment for at least three months. The behavior of other oils in similar experiments and the behavior of the same crude oil at different levels of turbulence and temperature can be predicted reasonably well (*1–4*).

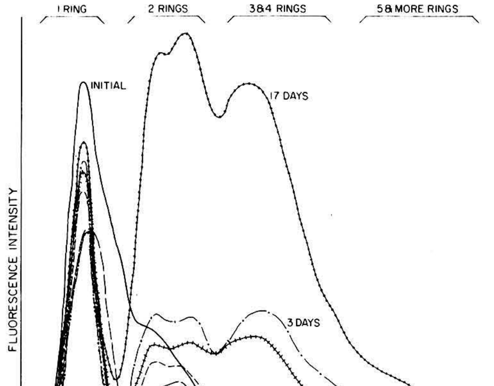

Figure 4. Synchronous excitation of emission spectra of sediment in Experiment 5. General type of aromatic compound producing each peak is identified at top

Table III. Estimated Amounts of Oil Contained in Surface Film, Water Column, and Sediment of Experiment 5 on Each Sampling Date

Oil contained in tarballs and coated on walls of tank is not included. Judging from the results of Experiments 3 and 6, approximately half of the oil was in these forms at the end of this experiment. Total amount of oil initially added was 843 g

	G/tank				
Day	Surface film	Water	Sediment	Total	% added
1 (30 min)	706	1.8	—	708	84
1 (5 h)	738	20.5	0.5	759	90
2	100	0.5	0.1	101	12
3	174	1.2	0.8	176	21
4	348	0.4	1.2	350	42
5	220	0.4	0.6	221	26
9	359	0.6	2.0	362	43
17	21	0.5	1.1	2	0.2
24	0.01	0.4	2.7	3	0.4
31	0.2	0.4	1.2	2	0.2
45	0.04	0.2	0.3	1	0.1
59	0.01	0.1	0.3	0.4	0.05
73	0.01	0.1	0.4	0.5	0.06
79	0.01	0.1	0.2	0.3	0.04
101	0.0	0.2	0.5	0.7	0.08

It is impossible to calculate the exact amount of spilled oil that entered the water column and sediment. The data listed in Table III represent only the amounts present in the surface film, water column, and sediment at sampling times and reflect the balance between the processes of supply and removal of oil at that time. They provide little information about the dynamics of weathering. The data in Table III, however, suggest that most oil entering the water column did so during the first few days: After only 5 h, at least 20.5 g had been accommodated. Most likely, oil was continually introduced into the water column during the rest of the first week, albeit at a lesser rate, while the surface film persisted. The total amount of oil entering the water column was probably less than 50 g or no more than about 5% of the oil spilled. Due to weathering in the water column (both physical/chemical and biological), the amount of spilled oil reaching the sediment must have been considerably less. In actual spills, the percentage of oil entering the water column and sediments will vary according to oil type and environmental conditions (*1–4*).

The ecological impact of an oil spill depends not on the total amount of spilled oil that enters the water column and sediment but on the concentration and persistence of toxic components (low- and medium-weight aromatic compounds) that can cause acute or sublethal effects. The oil concentrations observed in these experiments are similar to concentrations observed in the vicinity of oil spills and in chronically polluted harbors. For example, the concentrations of hydrocarbons in polluted seawater generally range between 1 and 800 μg/l. (Table IV). With regard to sediments, Hargrave and Phillips (*16*) report average concentrations in polluted sediment from a Bermuda beach and Chedabucto Bay, N.S., of 329 and 143 μg oil/g wet sediment, respectively. It is difficult to evaluate much of the oil toxicity literature because insufficient attention was given to determine the actual oil concentrations at which biological effects were observed. It does appear, however, that the oil concentrations observed in our tank experiments (Table II) and in polluted environments (Table IV) are high enough to cause sublethal effects in phytoplankton, lobster larvae, and snails (Table V).

Our experiments provide further evidence that the medium molecular weight aromatic compounds in oil can readily enter the water column and sediments and persist for relatively long periods of time. The SEES (Figures 2–4) suggest that in our experiments two-ring aromatic compounds persisted at least 17 days in the surface film and three months in the water column and sediments at concentrations not exceeding those of estimated total oil (Table II). This observation is somewhat contrary to the inference made by Harrison et al. (*11*) that naphthalene should disappear in 3–8 h, depending upon wind conditions. The difference could be caused by either the presence of stranded oil in our tank experiments (which also occurs naturally in coastal areas) or the relative insensitivity (∼1 mg/l.) of the analytical techniques used by Harrison et al. (*11*).

Our earlier experiments (*4*) indicated that 87–98% of the oil accommodated in seawater after seven days was in a particulate form greater than 1 μm in diameter. A slightly lower percentage, approximately 75%, was reported by Boehm and Quinn (*5*) in similar experiments with a No. 2 fuel oil. Water samples from the tank experiments were not filtered, except

Table IV. Oil Concentrations Reported in Surface Seawater from Areas Subjected to Different Degrees of Oil Pollution

All concentrations represent estimates obtained using fluorescence spectroscopy except those of Ahmed et al. (*19*) determined by ir

Area	Range of concentrations, $\mu g/l$	Reference
Boston Harbor	816–114	(*19*)
Halifax Harbor	72–2	(*20*)
Bedford Basin	60–0.5	(*21*)
Chedabucto Bay[a]	41–16	(*22*)
Halifax-Bermuda Section	<1	(*18*)

[a] Three months after Arrow disaster.

Table V. Approximate Oil Concentrations at Which Sublethal Effects Begin to Appear in Different Organisms

In all cases, oil concentrations in experiment containers were estimated by fluorescence spectroscopy

Organism	Sublethal effect	Oil concn, $\mu g/l$.	Reference
Marine phytoplankton	Change in photosynthetic rate	50	(*23*)
Lobster larvae	Rate of development	200	(*24*)
Intertidal snails	Crawling rate	800	(*25*)

on Day 79 of Experiment 5. At that time, only 10% of the total oil accommodated in seawater was retained on a 1.2-μm Millipore filter. It thus appears that the ratio of particulate to subparticulate oil changes during weathering, leading to a predominance of truly dissolved compounds. This is presumably due in part to the removal of particulate oil from the water by various mechanisms (adsorption to settling particulate matter naturally present in the water column, ingestion by filter feeding organisms, such as copepods [demonstrated by Conover (*26*)] which were present in the tank, and so forth).

We have no data on the behavior of the aliphatic hydrocarbons during these experiments. They no doubt were accommodated into seawater, most likely in a particulate form or solubilized by the dissolved organic matter (*27*). Their half-life in the water column must be less than that of aromatic hydrocarbons because of their greater susceptibility to biological decomposition (*28*) and their tendency to associate with particulate matter which settles.

Between 40 and 80% of the spilled oil was "stranded" (i.e., tarballs and coated on the tank wall), while probably less than 5% entered the water column and sediments. The stranded oil was not isolated from the water column, contact being maintained through wave action and a fluctuating water level caused by evaporation and precipitation. The conditions of these experiments could be very similar to conditions encountered by oil spilled in coastal environments where a large portion can be stranded along the coastline. In the natural environment, stranded oil is not isolated from the marine environment. It can weather slowly and be reintroduced into the inter- and subtidal environments by way of the sediments (*29*).

Tank experiments such as these can provide useful information on the behavior and fate of oil spills. Caution however must be used in extrapolating results to the natural environment. The technique is particularly useful for comparing the behavior of different oils or the effects of different environmental parameters or treatments (temperature, suspended matter load, presence of organisms, etc.). It has already been used to study the effectiveness and toxicity of an oil dispersant (*30*).

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Sources of Polonium-210 in Atmosphere

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■ Mean tropospheric aerosol residence times determined from cosmic ray-produced isotope activity ratios, fallout, and $^{210}Po/^{210}Pb$ ratios are concluded to be in error. Thus, complementary sources of ^{210}Po in the atmosphere must exist. Results presented substantiate dust storms, coal-burning power plants, forest fires, and plant exudates as sources of atmospheric ^{210}Po. Preliminary estimates of the magnitude of these and other possible complementary sources of atmospheric ^{210}Po are made. The most important sources appear to be soil particles and plant exudates, both of which are natural sources. The largest anthropogenic source is associated with phosphate fertilizer production. Together, the complementary sources account for most of the ^{210}Po in the troposphere. Thus, a shorter residence time of 4–6 days appears reasonable.

^{222}Rn and its radioactive daughters are used as indicators of residence times of tropospheric aerosols. The decay scheme for ^{222}Rn is shown in Figure 1. Atmospheric residence times for aerosols can be calculated from the relationship:

$$dN_B/dt = N_A\lambda_A - N_B(\lambda_B + \lambda_R) = 0 \qquad (1)$$

where A and B represent the parent and daughter isotopes. The mean aerosol residence time, τ_R, is the reciprocal of the removal rate, λ_R, by all processes such as washout, rainout, and dry deposition. Theoretically, the activity ratio, $N_B\lambda_B/N_A\lambda_A$, for any isotopes in the series with somewhat differing radioactive decay rates, λ, can be used to determine aerosol residence times. In practice, $^{222}Rn/^{210}Pb$ and $^{210}Bi/^{210}Pb$ activity ratios generally yield residence times of a few days (*1–3*), whereas $^{210}Po/^{210}Pb$ ratios yield apparent residence times of a month or more (*4–6*). This discrepancy has led to contradictory conclusions regarding the occurrence of ^{210}Po in the troposphere and varying aerosol residence times.

If it is assumed that all of the ^{210}Po originates from the decay of ^{222}Rn in the atmosphere (*7*), then the divergent residence times, calculated from the various activity ratios, must represent mixing of air masses with different aerosol residence times (*6, 8*). Junge (*9*) ascribed a residence time of a few days to surface air and one month to the troposphere as a whole. Cosmic ray measurements (*10, 11*) and fallout data (*12*) were interpreted in a manner which appeared to support this concept, and an increased residence time with altitude in the troposphere has been assumed to be the case by several authors.

Moore et al. (*13*) have shown that $^{222}Rn/^{210}Pb$, $^{210}Bi/^{210}Pb$, and $^{210}Po/^{210}Pb$ activity ratios, when considered separately, each yield the same apparent residence time for all altitudes within the troposphere. However, some divergence of residence times still exists between the various ratios. Also, a recent review by Martell and Moore (*14*) demonstrates that the earlier fallout and cosmic ray data yielded questionable estimates of aerosol residence times and are subject to reinterpretation, whereas more recent data are compatible with a tropospheric residence time of only a few days.

Although the intermixing of tropospheric air masses of differing aerosol ages cannot be disproved by analysis of ^{222}Rn daughters in single air masses, a large air mass existing as an identifiable entity for longer than a few days must spend some time over an ocean. Equation 1 assumes a constant vertical flux of ^{222}Rn, and since the oceanic flux is negligible compared to the continental flux, this assumption is not fulfilled. Thus, all residence times calculated from activity ratios of ^{222}Rn and its daughters are, at best, only approximate. Those calculated from $^{210}Po/^{210}Pb$ ratios appear to be the least reliable (see below).

The above considerations lead us to conclude that tropospheric aerosol residence times are approximately 4–6 days, and there is mounting evidence that a large portion of tropospheric ^{210}Po originates from complementary sources other than tropospheric ^{222}Rn decay. The $^{210}Po/^{210}Pb$ activity ratio for a one-month residence time is 0.105; for a 5-day residence time it is 0.010. If the shorter residence time is correct, the amount of ^{210}Po grown from ^{210}Pb in the atmosphere is approximately 10% of the total tropospheric ^{210}Po, and a large majority of the tropospheric ^{210}Po must be due to complementary sources. The existence of such sources has been discussed by Martell and Poet (*15*), Martell (*16*), Vilenskiy (*17*), Mattsson (*18*), and Moore et al. (*19*).

More direct evidence of complementary sources of atmospheric ^{210}Po appeared desirable. Therefore, we have made a number of measurements of ^{226}Ra, ^{210}Po, and ^{210}Pb in the atmosphere and in surface soils (*20*) and have estimated that approximately 60% of the ^{210}Po in clear air over the continental United States is derived from the entrainment of soil dust. Results presented in this paper show that dust storms, coal-burning power plants, forest fires, and plant exudates are also complementary sources of ^{210}Po. Some preliminary estimates of the magnitude of these and other possible complementary sources of atmospheric ^{210}Po are attempted below.

Experimental Methods and Results

Data presented in Table I consist of ^{210}Pb and ^{210}Po concentrations of pine needles and grass collected near the NCAR laboratory in August 1970. Samples representative of differing exposures and times of growth were collected. The grass was cut approximately 5 cm above ground level and included a variety of wild grasses common to this mesa area. All samples were dried at 80 °C overnight. Carriers were added, and the

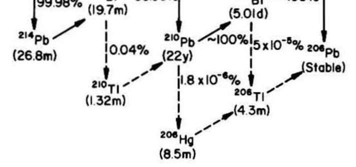

Figure 1. ^{222}Rn decay scheme

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Table I. ^{210}Pb and ^{210}Po Deposited on Pine Needles and Grass

		Concn, pCi/g		Activity Ratio
	Growth period[a]	^{210}Pb	^{210}Po	$^{210}Po/^{210}Pb$
A.	3 mo	0.31	0.138	0.45
	3 mo	0.70	0.336	0.48
	4–6 yr	1.77	1.30	0.73
	Dead, under tree	3.10	2.46	0.79
B.	3 mo, west side	0.35	0.093	0.27
	3 mo, east side	0.45	0.224	0.50
C.	3 mo	0.42	0.177	0.42
	3 mo, dead	0.69	0.663	0.96
D.	3 mo	0.67	0.276	0.41
	2 yr, dead	0.76	0.437	0.58
E.	2 yr	0.22	. . .	. . .
	3 yr	0.20	. . .	. . .
	4–5 yr	0.28	. . .	. . .
	Grass, 3 mo	0.91	0.234	0.26

[a] Letters designate different trees from the same area.

samples were then wet ashed with fuming HNO_3 and H_2O_2. To determine the enrichment factor for these isotopes deposited on the surface of the pine needles, the waxy coating was removed from the needles by shaking them in a separatory funnel with three aliquots of ethyl acetate and determining the specific activity of ^{210}Pb on the combined ethyl acetate extracts.

Data presented in Table II show ^{210}Pb, ^{210}Bi, and ^{210}Po concentrations of aerosols collected in areas of slash burning in Oregon and near the Four Corners, N.M., power plant. Procedures for the collection of aerosol samples by aircraft have been described elsewhere (*13*). The slash-burning samples were collected using Delbag 99/98 filters, and the power plant samples were collected using IPC 1478 filters. In both cases, samples were collected upwind of the plume and then in the plume by flying through the plume in a figure eight pattern. Since it is somewhat difficult to determine the exact boundaries of the plume, the samples do contain clear air aerosols collected outside the plume as well as aerosols collected in the plume itself. In the case of the power plant, the upwind sample may be somewhat contaminated with plume material since the plume was shifting with time.

Isotopic measurements were also made for a series of samples collected during a well-developed dust storm near Big Springs, Tex., in April 1973. Results are shown in Table III. The samples were collected using Delbag 99/98 polystyrene microfiber filters.

Procedures for the chemical analysis and radioactive assay of the various isotopes are described elsewhere (*3*). One sigma counting errors for all the data presented are less than 10% of the values listed.

Discussion

Complementary sources of long-lived ^{222}Rn daughters in the atmosphere can seriously influence their concentration and limit their usefulness in estimating aerosol residence times, if sampling is done in the vicinity of such sources. Aerosols from these sources are spread many kilometers downwind from the source and hence may become mixed with other pollutant sources to yield a diffuse background of pollutant ^{222}Rn daughters. The isotope most drastically affected in concentration is ^{210}Po due to its low natural atmospheric concentration and its high enrichment relative to ^{210}Pb and ^{210}Bi in pollutant sources.

Table II. Isotopic Composition of Plume Samples

Location[a] km	Concn, pCi/100 m^3			Activity ratios	
	^{210}Pb	^{210}Bi	^{210}Po	$^{210}Bi/^{210}Pb$	$^{210}Po/^{210}Pb$
	Slash-burning plumes				
9.3u	0.93	0.61	0.036	0.66	0.04
7.4d	1.36	1.04	0.254	0.76	0.19
1.4d	1.09	1.00	0.423	0.92	0.39
11.1u	1.95	1.13	0.107	0.58	0.06
11.1d	1.46	0.84	0.135	0.58	0.09
1.4d	1.49	1.18	0.277	0.79	0.19
8.8u	0.47	0.15	0.045	0.32	0.10
7.2d	0.58	0.18	0.099	0.31	0.17
1.6d	0.56	0.51	0.179	0.91	0.32
9.6u	0.84	0.27	0.050	0.32	0.06
6.4d	1.02	0.77	0.135	0.75	0.13
0.8d	0.92	0.60	0.131	0.65	0.14
	Power plant plume				
9.3u	1.38	0.61	0.088	0.44	0.06
18.5d	1.98	0.67	0.367	0.34	0.19
5.6d	1.39	0.63	0.154	0.45	0.11

[a] Distance: u, upwind; d, downwind in the plume.

Production figures needed to make estimates of the magnitude of such complementary sources are most often expressed on an annual basis for the United States as a whole. For this reason we have expressed the pollutant flux of ^{210}Po in a similar manner.

Total ^{210}Po Flux

The concentrations of ^{222}Rn and its long-lived daughters vs. altitude over the United States are reported by Moore et al. (*13*). The ^{222}Rn profiles correspond to a turbulent diffusion coefficient, D, of $\sim$650 m^2 min^{-1}. This value is in general agreement with other published estimates for vertical mixing in the troposphere above 1 km (*21*).

Surface air concentrations, C_o, of ^{210}Po (*3, 13*) are approximately 9×10^{-4} pCi m^{-3}. The ^{210}Po flux, F, is given by

$$F = C_o(D\lambda_R)^{1/2} \quad (2)$$

where λ_R is the tropospheric aerosol removal rate. For λ_R = 0.2 days^{-1}, the calculated flux is 2.7×10^{-4} pCi m^{-2} min^{-1}, or for the continental United States (area, 7.7×10^{12} m^2), 1100 Ci/yr. This value includes the ^{210}Po due to all sources. That

Table III. Isotopic Composition of Texas Dust Storm Samples[a]

Altitude, km	Concn, pCi/100 m^3 STP			Activity ratios[b]	
	^{210}Pb	^{210}Bi	^{210}Po	$^{210}Bi/^{210}Pb$	$^{210}Po/^{210}Pb$
0	2.90	3.03	0.900	1.04	0.31
3.4	0.83	0.54	0.129	0.65	0.35
4.0	0.46	0.34	0.078	0.40	0.17
3.0	0.61	0.43	0.197	0.71	0.32
4.6	0.47	0.32	0.105	0.68	0.22
9.4	0.33	0.24	0.037	0.73	0.11

[a] Level indicated as 0-km altitude was 3 m above ground level. The 9.4-km level was taken in transit from Boulder to Texas and upon return. The other samples were taken on two sequential days. [b] Apparent residence times indicated by $^{210}Po/^{210}Pb$ ratios are: 0.1, 30 days; 0.2, 60 days; 0.3, 95 days; 0.4, 145 days.

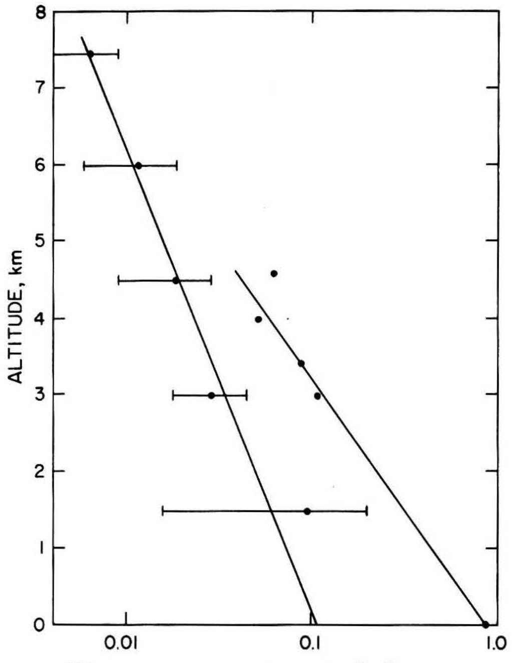

Figure 2. ^{210}Po concentration vs. altitude for clear air (|–●–|) and fully developed dust storm (●) samples. Error bars represent one standard deviation from the mean and include data from 13 profiles. Dust storm data are for individual samples

this average ^{210}Po flux may be quite variable with time and location is evident from the actual data below.

Soil Flux

The vertical profile of ^{210}Po concentration vs. altitude for the dust storm samples is compared to that for clear air in Figure 2. The data for clear air include 13 profiles taken over Utah, Nebraska, Colorado, and Kansas. The error bars represent one standard deviation from the mean value. An estimate of the ^{210}Po due to stratospheric influx made by Moore et al. (*13*) indicates this component to be less than 10% of the total ^{210}Po in clear air below about 8 km. The dust storm concentrations (values without error bars) are much higher than those for clear air samples. The distribution of ^{210}Po with altitude and ^{90}Sr concentrations and ^{90}Sr/^{210}Pb ratios determined for these samples indicate a surface source and not a stratospheric source for this material. The ^{210}Bi concentrations included in Tables II and III allow comparison of ^{210}Bi/^{210}Pb ratios to ^{210}Po/^{210}Pb ratios. The ^{210}Bi/^{210}Pb ratios are greater near the source of material; however, this ratio appears to be less affected by pollutant sources except when very close to the source. Thus, the ^{210}Bi/^{210}Pb ratio is a better indicator of tropospheric aerosol residence times than the ^{210}Po/^{210}Pb ratio.

Because the storm developed rapidly and lasted only a few days and also because the mean airborne particle size is larger than that during less turbulent atmospheric conditions, most of the dust storm particles should have residence times less than a few days.

The concentration, C, of ^{210}Po at an altitude H above ground level is related to the concentration, C_o, at ground level by

Table IV. Approximate ^{210}Po Fluxes from Various Sources for Continental United States

Source	Flux, Ci/yr
Natural sources	
Soil particles	660
Plant exudates	460
Stratospheric	40
Forest fires	10
Anthropogenic sources	
Phosphate fertilizer dispersion	50
By-product gypsum	5
Lead production	6
Cement and other metal production	1
Fossil fuel burning	10
Total flux calculated from clear air profiles	1100

$$\frac{C}{C_o} \cdot \frac{\rho}{\rho_o} = \exp\left[-H(\lambda_R/D)^{1/2}\right] \qquad (3)$$

where ρ is the density of the atmosphere. When a value of D = 650 m^2 min^{-1} is used in the above equation, the resulting aerosol residence time is 2.4 days. The ^{210}Po flux given by Equation 2 is then 4×10^{-3} pCi m^{-2} min^{-1} or about 15 times that for clear air. That the ^{210}Po concentrations determined on sequential days are similar suggests that the steady-state conditions assumed in Equations 2 and 3 are maintained. F is directly proportional to D, and since D is probably underestimated for such turbulent conditions, the calculated ^{210}Po flux is a minimum value.

Although the above data provide evidence that dust storms are sources of ^{210}Po in the atmosphere, estimation of the annual flux for the United States is not possible because the frequency and magnitude of such dust storms are not known. Based on ^{226}Ra concentrations in atmospheric samples, we have estimated that approximately 60% of the ^{210}Po is due to entrainment of soil particles (*20*). A value of 660 Ci yr^{-1} is therefore included in Table IV.

Plant Exudates

The retention of radioactive aerosols by vegetation has been discussed by Chamberlain (*22*) and by Chadwick and Chamberlain (*23*). For rapidly growing plants the aerosols appear to have a residence time on the plant of 20–50 days. The residence time increases for slower growing plants of different varieties or when growing conditions become less favorable, such as late in the growing season or in winter when the plants are dormant. Chamberlain indicates that ^{210}Pb is more strongly retained by foliage than most other elements.

The evidence for the removal from plant surfaces of radionuclides in company with submicron organic plant exudates is indirect but impressive. Went et al. (*24*) have shown a correlation between airborne submicron particles and density of vegetation. They have suggested (*25*) that these particles result from condensation of volatile organic material released from the plant surfaces. There is also evidence (*26*) that wax particles can be lost from the surface of many plants. These small particles of epicuticular wax presummably can be removed by stress conditions such as leaf expansion during active growth or by normal weathering due to wind action and abrasion. Martin and Juniper (*26*) suggested that half of the waxy material on leaves may be lost in this manner. Moorby and Squires (*27*) were able to demonstrate the transfer of ^{89}Sr from labeled plants to uncontaminated plants and to air filters. They suggested that the radioactivity was lost from the leaf surface in association with small wax particles, but could not provide conclusive evidence for this mechanism. Chadwick and Chamberlain (*23*) assumed the same mechanism for loss of radionuclides from plant surfaces.

In somewhat similar experiments, Beauford et al. (*28*) were able to show that ^{65}Zn was translocated through plants from the roots and released to the atmosphere. They collected particles with an impactor and found the ^{65}Zn to be associated with submicron particles. Also, they found by electron microscopy needle-like particles up to 2000 Å long and 300 Å wide which had been given off by the plants. These particles appeared similar to particles found on leaf surfaces. Whether the radioactivity is associated with these particles is still not certain. Beauford et al. (*28*) also considered that the ^{65}Zn might be contained in water given off by the plant, but could find no correlation between the amounts of water and ^{65}Zn collected. Thus, the release of organic matter and radionuclides from plants surfaces does occur. It appears that they are released together, but more conclusive evidence would be beneficial.

The data in Table I, although quite variable, support the trends suggested above. Based on the ^{210}Po/^{210}Pb ratio for the older needles, the apparent residence time of these isotopes on pine needles is about 2 years. The ^{210}Po/^{210}Pb ratio for more recent growth is lower, indicating the equilibrium between deposition and removal has not yet been established. Also, the deposition appears to vary quite widely depending on exposure conditions. Trees A–D were located on an exposed mountain ridge, whereas tree E stood within a clump of other trees in a protected area. The grass sample has a much higher ^{210}Pb content in spite of its short growth period. This is attributed to the higher concentration of radon, and its short-lived daughters within the grass stand in close proximity to soil, the source of emanating radon.

The experiments in which the specific activity of the waxy material was determined indicated that approximately half of the ^{210}Pb is in the waxy outer coating which is only 1% of the total pine needle weight. This is probably a minimum percentage of ^{210}Pb because some of the aerosol material may have been redeposited on the stripped pine needles rather than follow the organic phase during its removal. Similar enrichments were found by Martell (*29*) for material removed from tobacco plants by brushing the leaves and by sonic cleaning. The specific activity of the total needles was 0.50 ± 0.03 pCi/g, whereas the specific activity of the waxy material averaged 22.1 ± 0.1 pCi/g for two samples. Thus, airborne ^{222}Rn daughters are deposited on vegetation surfaces, and the ^{210}Po slowly grows in toward equilibrium with ^{210}Pb. These isotopes may then become airborne associated with particles in the aerosol size range, either by exudation from surfaces or as the result of forest fires.

A crude estimate of the flux of ^{210}Po into the atmosphere from plant exudates and decomposed vegetation can be obtained with the data of Went (*25*) who estimated that terpene-like hydrocarbons and others released to the atmosphere by plants amount to roughly 17 million tons/yr for the whole earth. If we omit the amount estimated for steppes, the fractional amount estimated for the continental United States is 8 million tons/yr. The data above indicate a specific activity of approximately 22 pCi/g on pine needle surfaces. If this represents exuded material, the flux of ^{210}Po to the atmosphere from this source is ~176 Ci/yr. More recently, Rasmussen and Went (*30*) have estimated the global production of organic aerosols to be 43.8 million tons/yr or 2.6 times the above value. The ^{210}Po flux calculated for the continental United States is 460 Ci/yr based on the above data.

Forest Fires

The samples reported in Table II are from controlled slash burning. This type of fire was selected rather than uncontrolled forest fires for sampling, because they could be predicted in advance and aircraft sampling would not interfere with fire control operations. The material burned represents leaves, branches, underbrush, and forest litter which remain after logging operations. The activity ratios in the upwind samples are typical for clear air. In the smoke plume, the ratios are elevated, the ^{210}Po/^{210}Pb ratios being most affected due to the low initial ^{210}Po concentration in the atmosphere, the greater ^{210}Po/^{210}Pb ratio in the source material, and the volatility of Po.

Statistics on forest fires given by the U.S. Department of Agriculture (*31*) show that 1.43 × 10^6 ha burned in 1971 and 0.92 × 10^6 ha in 1972. Thus, about 1.2 × 10^6 ha are burned annually. Estimates of material burned range from 2 to 4 tons/ha for grassland and 100 to 160 tons/ha for timber. Most of the radon daughters are deposited on the leaves and needles of trees and on grass close to the ground. This material then contributes to the soil mat and forest litter, which account for a large portion of the material burned in a forest fire. Assuming combustion of about 11 tons/ha with a specific activity of 0.9 pCi ^{210}Po/g and assuming that 100% of this ^{210}Po reaches the atmosphere, the ^{210}Po flux from forest fires is 10 Ci/yr.

Stratospheric Source

Radioactive aerosols in the lower stratosphere have residence times which increase with altitude apparently between about two months and two years (*14*). For these residence times, the ^{210}Po will more nearly approach secular equilibrium with ^{210}Pb. The stratosphere can therefore act as a source of tropospheric ^{210}Po with a contribution to the ^{210}Po in the troposphere which varies quite widely. Lambert and Nezami (*32*) assume that the fraction of tropospheric ^{210}Po which mixes down from the stratosphere is 5–50%. Our own estimates range from 1.5 (*3*) to 7% (*19*).

Both Marenco and Fontan (*7*) and Nevissi et al. (*6*) have found high ^{210}Po/^{210}Pb ratios in rain samples which they interpret as indicative of longer tropospheric aerosol residence times. However, it seems more reasonable to attribute such increased ratios to stratospheric air intrusions into the troposphere during the passage of frontal systems. In fact, Marenco and Fontan (*7*) show that higher ^{210}Po/^{210}Pb ratios and ^{210}Po concentrations are associated with "storm" conditions as opposed to "rain" and "no rain" conditions. Recently, Gavini et al. (*8*) have presented evidence indicating the intrusion of stratospheric air into the troposphere and subsequent scavenging of the intrusion during thunderstorms. Thus, it would appear that the stratosphere may account for a large fraction of the ^{210}Po in the troposphere under certain conditions, but that much of this excess ^{210}Po will be quickly removed. Only a small percentage of tropospheric ^{210}Po originates in the stratosphere on the average. In terms of flux, 4% of the total tropospheric ^{210}Po would involve an effective downward flux of 40 Ci/yr over the continental United States.

Fossil Fuel Burning

Data in Table II confirm that coal-burning power plants are sources of ^{210}Pb and its daughters. In such effluents the ^{210}Po/^{210}Pb ratio is much higher than in clear air samples. ^{226}Ra concentrations were also determined for these samples and show an increase similar to that observed for ^{210}Po (*20*). Although samples of the aerosol at the stack were not available from the Four Corners plant, samples were analyzed from the precipitator outlet of the Valmont coal-burning power plant in Boulder, Colo. This involved material that normally escapes the precipitator and is released to the atmosphere. The ^{210}Po/^{210}Pb ratio in this material was 1.1, much higher than normally found in atmospheric aerosol particles. This measurement is based on collections in a region of relatively high temperature, and it is possible that a large portion of the ^{210}Po passed through the collector as volatile and gaseous compounds. This result therefore substantiates the enrichment of volatile ^{210}Po over ^{210}Pb in effluents from coal-burning plants mentioned by Martell (*16*) and Peirson et al. (*5*).

The total amount of coal consumed in the U.S. in 1972 was 3.8×10^8 tons (*33*). Jaworowski et al. (*34*) indicated about 0.1 pCi ^{210}Po/g of coal, and Mattsson (*18*) reported about 10 times higher values. Our own analyses indicate approximately 0.3 pCi ^{210}Po/g coal. This value gives rise to a total ^{210}Po flux of 10 Ci/yr, assuming 10% of the ^{210}Po in coal is emitted.

Potash Fertilizer Production

During 1972 approximately 38.5 million tons of phosphate rock were mined in the United States (*33*). Phosphate rock contains approximately 40 pCi ^{226}Ra/g rock, and about 60% of this activity is found in the by-product gypsum (*35*). The remaining ^{226}Ra activity in phosphate fertilizer is dispersed over croplands and lawns. Based on the above figures, the amount of ^{226}Ra dispersed would be 616 Ci/yr in the U.S. This figure is a maximum, however, as not all phosphate rock is converted to fertilizer. About half of the phosphate rock mined is used to produce other commodities such as phosphoric acid (*33*). Thus, a reasonable figure for the U.S. is 308 Ci/yr. The U.S. produces approximately 45% of the world supply of phosphate fertilizer. Therefore, the total dispersed worldwide is 680 Ci/yr. Jaworowski (*36*) estimated the worldwide amount to be 400 Ci/yr. Because the mining of phosphate rock has nearly doubled in the U.S. alone since the early 1960's, these estimates agree reasonably well.

If ^{226}Ra from fertilizer were evenly dispersed over the U.S., the amount would be approximately 40 pCi/m^2. The resuspension factor, K, is defined as follows (*37*):

$$K = \frac{(\text{pCi/m}^3)\ \text{air}}{(\text{pCi/m}^2)\ \text{soil}} \tag{4}$$

Resuspension factors for newly deposited material on cultivated fields are in the range of 10^{-6}. This yields 4×10^{-5} pCi/m^3 air near the surface or 50 Ci/yr for a flux into the atmosphere over the United States (Equation 2).

Although it is not known how the ^{210}Pb is distributed between the phosphate fertilizer and the by-product gypsum, if a ^{210}Pb/^{226}Ra activity ratio of unity is assumed, the ^{210}Po would soon be in equilibrium with the ^{210}Pb, and the flux calculated for ^{226}Ra would apply to ^{210}Po.

For unfertilized, undisturbed soil sites, natural radionuclides such as ^{226}Ra have smaller resuspension factors ($\sim 10^{-9}$), and the natural ^{210}Pb/^{226}Ra ratio near the soil surface is greater than unity (*20*). Since the above soil flux value and atmospheric ^{226}Ra concentrations applicable to natural, undisturbed areas were used to calculate the ^{210}Po flux due to soils (*20*), the flux calculated for dispersed fertilizers is in addition to the natural soil flux.

The calculation of the ^{210}Po flux due to fertilizers does not include the activity which remains with the gypsum, nor does it account for fertilization over many years; thus, the figure must be a conservative estimate. The contribution due to airborne ^{210}Po from the by-product gypsum is arbitrarily taken to be 10% of the corresponding ^{210}Po flux due to phosphate fertilizer. Although the gypsum fraction has a higher ^{226}Ra activity than the fertilizer, it is assumed to contribute less to the atmospheric ^{210}Po flux because it is left in large, unconsolidated piles or dumped into swamps, ditches, or bodies of water, rather than widely distributed over croplands.

Other sources of ^{210}Po include the manufacture of phosphorus, animal feed supplements, and some phosphate fertilizer production. In these processes the phosphate rock is heated to a very high temperature, and ^{210}Po is vaporized and released. The Atomic Energy Commission (*38*) has made a preliminary study of releases involved in such processes, and the Environmental Protection Agency is continuing such studies (*39*). No reliable estimates of the magnitude of these sources can be made at present.

Lead Production

Marenco and Fontan (*7*) report a value of approximately 100 pCi ^{210}Po/g lead for tetraethyl lead in gasoline. Our own value is 8 pCi ^{210}Pb/g lead. Although gasoline combustion can result in significant local lead pollution, it does not make a significant contribution to ^{210}Po in the atmosphere. However, the overall lead production in the U.S. is many times that used in gasoline additives. Lead undergoes a high-temperature smelting process and thus may release ^{210}Po. The production of new lead in the U.S. in 1972 was 1.41 million tons. If we assume 8 pCi ^{210}Po/g lead and a total release of ^{210}Po to the atmosphere, the ^{210}Po flux from this source is 11 Ci/yr. Although it is likely that the fraction released is somewhat less than 100%, this does not include releases from old lead that is repurified. Thus, assuming about 50% of the ^{210}Po is released, the ^{210}Po flux is 6 Ci/yr.

Cement Manufacture

Jaworowski (*36*) estimated that the global flux of ^{226}Ra into the atmosphere from cement production was 0.8 Ci/yr for 1965. Since this process involves a high-temperature roasting step, the amount of ^{210}Po released is probably much higher than the amount of ^{226}Ra released. In addition, the production of cement has undoubtedly increased since 1965. Therefore, the value of 1 Ci/yr may be taken as a conservative estimate of the U.S. ^{210}Po flux.

Other Possible Sources

Estimates have been made above for ^{210}Po fluxes from three commercial manufacturing sources. These represent only a few of the sources which involve high-temperature processing of materials containing ^{226}Ra and ^{210}Pb. Other sources of ^{210}Po may be iron, aluminum, and copper production. Unfortunately, data are not available to make estimates of ^{210}Po releases from these sources.

One important source which has been purposely omitted is uranium ore mining and milling. Although this is a large potential source, the amounts of ^{210}Po released to the atmosphere from these operations appear to be rather small. This may be due to the fact that the mill tailings from uranium production are rather well consolidated and hence are not subject to appreciable wind erosion. We base this supposition upon the fact that our own sampling for ^{226}Ra (*20*) is remotely downwind of such operations in Colorado, and we find that the ^{226}Ra specific activity of airborne dust in both air and rain samples resembles that of local soils and never exhibits the much higher values to be expected for uranium mine tailings.

Concluding Remarks

The above approximate estimates of the magnitude of complementary sources of airborne ^{210}Po are admittedly highly uncertain. Even so, it may be concluded that the combined magnitude of these sources is so large that the major portion of the ^{210}Po in the troposphere obviously does not arise from the decay of atmospheric ^{222}Rn. Thus, the use of ^{210}Po/^{210}Pb ratios to determine tropospheric aerosol residence times is not justified. The magnitude of these complementary ^{210}Po sources depend on geographical proximity to the source and on meterological conditions. Taken together, these numerous complementary sources are widely dispersed and thus add generally to the ^{210}Po in the atmosphere. Further studies of these pollutant sources and their possible biological effects should be made.

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Oxidation of Contaminative Methane Traces with Radio-Frequency Discharge

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■ An 11.8-mHz glow discharge was used to oxidize trace levels of methane in oxygen. The concentration of methane can be reduced by three orders of magnitude. The effects of power (0–400 W), flow rate (10–10^3 cc-STP/min) and concentration (70–8000 ppm) were investigated at pressures ranging from 50 torr to almost 1 atm. No organic reaction products were detected in the treated gas stream. The process may prove useful for the removal of atmospheric trace contaminants at ambient pressure.

The removal of trace contaminants from the atmosphere is an important environmental problem. In buildings, harmful or toxic gases can accumulate and cause discomfort or create a health problem. The life support systems of spacecraft and submarines must maintain the concentrations of certain trace contaminants well below hazardous levels. Then too, trace contaminants ideally should be present in only truly negligible quantities in the zero air used for standardization of air monitoring equipment.

We report here our initial study in which a radio-frequency discharge was used to reduce the concentration of a trace organic contaminant, methane, by three orders of magnitude and up to pressures near atmospheric. Methane was chosen for these experiments because it is relatively unreactive; thus the oxidation of methane would indicate the possibility of removing other, more reactive materials. At the same time methane is easy to work with since it is neither toxic nor corrosive. This report is limited to oxygen, which has been used in space cabin atmospheres.

Recently, Bailin et al. (*1*) described the use of a microwave discharge for the partial removal of toxic vapor simulants. The cold plasma used in their experiments operated only at pressures less than 100 torr; apparently this would make the process unattractive for many practical applications.

Apparatus

The flow apparatus is shown in Figure 1. A mixture of dry oxygen and methane is formed in a dynamic dilution system. The bulk of this mixture is vented and a small side stream is

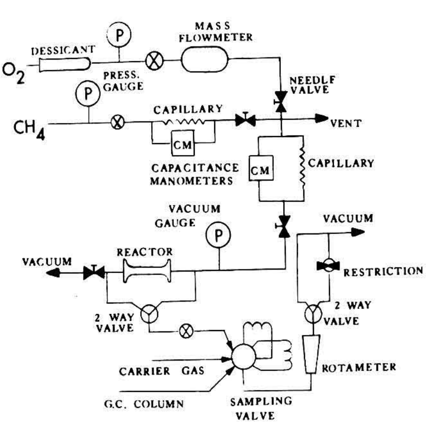

Figure 1. Flow system

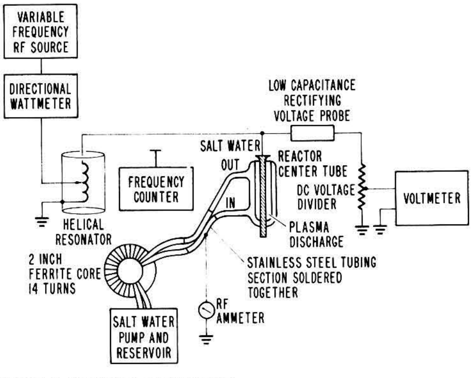

Figure 2. Electrical arrangement

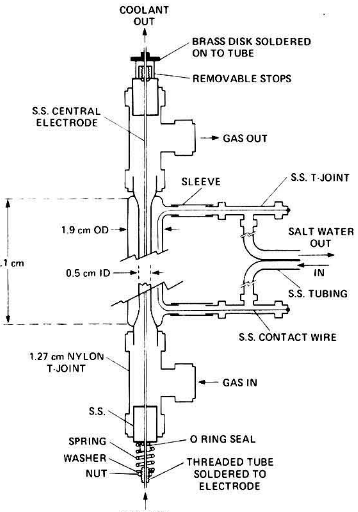

Figure 3. Processing reactor. Central electrodes of 0.079, 0.159 and 0.318 cm O.D. were used

metered into the discharge reactor. Products are analyzed using a gas chromatograph with a dual thermal conductivity/flame ionization detector. A 0.159-cm i.d., 3.18-m stainless steel Poropak Q column was used in the Perkin-Elmer Model 900 chromatograph at 38 °C. Input to the column was controlled by a Carle microvolume valve using two sampling loops. At any time one loop was switched into the gas chromatograph while the second could be simultaneously evacuated and filled with a fresh sample.

Figure 2 shows the electrical arrangement. Power from a conventional radio frequency transmitter at 11.8 mHz is supplied to a helical resonator to generate sufficient voltage for high-pressure operation. The theory and operation of this system have been described elsewhere (2). A coaxial geometry is used for the processing reactor as shown in Figure 3. The hollow cylindrical central electrode was convectively cooled by a flow of compressed air or distilled water. Saturated salt water circulating through the outer jacket of the reactor acts as a combination electrode/coolant. Stainless steel contact wires help maintain resistance between the reactor jacket and stainless steel tubing section in the figure at 1 ohm or less.

The saltwater cooling line is connected through a ferrite/liquid choke as shown so that an RF ammeter can be connected between the discharge electrode and ground to measure the total current. The arrangement permits an accurate determination of the electrical plasma operating parameters (2).

Three different central electrode diameters, 0.079 cm, 0.159 cm, and 0.318 cm o.d. were used in these experiments. The inner quartz tube surrounding the central electrode was 0.5 cm i.d., and the length of the coaxial discharge zone between this tube and the electrode was 9.1 cm.

Experimental

The discharge was operated between 50 and 600 torr with the inner electrodes of different diameter. In initial experiments, the glass reactor was constructed from Pyrex instead of quartz as shown in Figure 3. Pyrex was less satisfactory because, at very high powers and pressures, a hot spot would occasionally develop on the inner wall of the glass tube containing the plasma. This was symptomatically evident as an orange incandescent point which, after a time, caused the reactor to rupture, apparently from thermal stress. This condition did not occur with the quartz reactors.

Distilled water was a better coolant than air for the inner electrode. When the inner electrode tube was cooled using air, uneven heating led to a slight buckling and the tube could not be held straight by the tension of the spring pulling it through the O-ring seal (Figure 3). Also, with air, several times a hot incandescent spot developed on the inner tube at high power and pressure. If the discharge was not shut off immediately when the spot appeared, the electrode tube would finally rupture and release compressed air into the reactor. This did not occur with water cooling.

The highest pressure used in these runs was limited to 600 torr so that there would be no discharge from the leads connecting the reactor to the RF source. The pressure of 600 torr was not an experimental limitation of the reactor and we consider that the pressure could be readily increased to atmospheric provided the electrical leads were suitably insulated.

Results

The discharge emitted a bluish to purplish glow under all of the conditions and under some circumstances a number of brighter wispy blue spots were visible at different points on the inner electrode. In general, the discharge did not completely fill the reaction region. For instance, with the 0.159-cm central electrode, the discharge extended axially only for about 5 cm during a run at 200 torr and 60 W. This region of active discharge lengthened axially with increasing power and decreasing pressure.

Figures 4 through 6 present typical methane removal data. Several features characterized all of the data: the fraction of contaminant removed increases with power (Figure 4); the fraction of contaminant removed increases noticeably with decreasing flow rate (Figure 5); the fraction of contaminant removed at a given power and flow rate is insensitive to concentration (Figure 6). At constant power and pressure, the physical and electrical characteristics of the discharge were insensitive to flow rate so that the axis of Figure 3 (flow rate) is inversely proportional to residence time. Under many conditions, a three-order-of-magnitude reduction in contaminant concentration was measured. At low methane concentrations, the analytical accuracy was limited by the precision and sensitivity of the chromatographic system; this accounts for some of the scatter in the data and for the uncertainty at the highest degrees of removal shown in Figure 5.

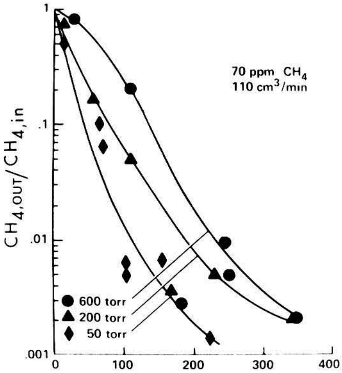

Figure 4. Methane removal vs. power with a 0.318-cm electrode. Oxygen flow rate was 110 cm^3-STP/min with 70 ppm methane

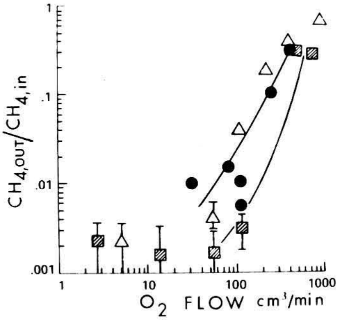

Figure 5. Effect of oxygen flow rate on methane oxidation at 50 torr ▨ 0.079 cm electrode, 110 W, 70 ppm CH_4; △ 0.159 cm electrode, 100 W, 120 ppm CH_4; ● 0.318 cm electrode, 105 W, 70 ppm CH_4

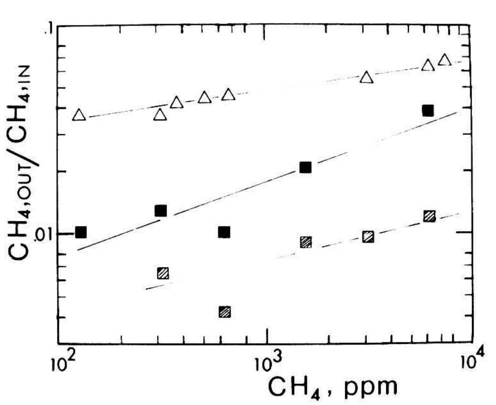

Figure 6. Effect of concentration on methane oxidation at 50 torr and 110 cm^3-STP/min oxygen
▨ 0.079 cm electrode, 108 W; ■ 0.079 cm electrode, 75 W; △ 0.159 cm electrode, 100 W

No organic compounds other than methane were observed in the chromatograms of gaseous reactants or products. However, the inner wall of the 0.5-cm i.d. quartz reactor tube (Figure 3) developed a faint, transparent brownish coating indicating the probable deposition of a thin polymeric film. This coating was confined to the plasma-containing zone of the tube and there was no evidence of discoloration or contamination elsewhere.

After a new reactor was inserted and a coating had formed, the visible tint did not perceptibly darken or otherwise change even after weeks of use. Apparently the film soon reaches a steady state thickness such that the rate of deposition is balanced by oxidation or other removal processes. Therefore we do not consider this film to be a product of the continuous reaction. Since no organic products have been observed in the gaseous effluent stream, it is believed that the final oxidation products were CO_2 and water in accordance with the following discussion.

The possible formation of carbon monoxide, formic acid, or formaldehyde cannot be ruled out from the chromatographic analyses since the TC and FID detectors were insensitive to these materials at the trace levels of this work; methanol would have been detected. However, a number of previous workers have reported that the primary reactions leading to destruction of methane by atomic oxygen or the hydroxyl radical

$$O + CH_4 = CH_3 + OH \tag{1}$$

$$OH + CH_4 = CH_3 + H_2O \tag{2}$$

have a rate constant which is 3 to 4 orders of magnitude smaller (at 300 K) than that for reactions between O or OH and CH_2O (*3*):

$$O + CH_2O = CHO + OH \tag{3}$$

$$OH + CH_2O = H_2O + CHO \tag{4}$$

The latter reactions also have a lower activation energy. Additional evidence for the absence of such compounds is presented below.

Discussion

There is evidence (*3–5*) that any CO formed would be rapidly oxidized to CO_2 via

$$CO + O + M = CO_2 + M \tag{5}$$

and

$$CO + OH = CO_2 + H \tag{6}$$

This is supported by the work of Buser and Sullivan (*6*) who found that the mass action product in their closed dc glow discharge system:

$$K_{\text{effective}} = \frac{[CO_2]}{[CO][O_2]^{1/2}} \tag{7}$$

reached a steady state value. Although this reaction quotient was less than thermodynamic equilibrium, it nevertheless obeyed Le Chatelier's law and was nearly constant above 0.5 torr. Furthermore, Reaction 5 as well as $K_{\text{effective}}$ and the true thermodynamic equilibrium constant for

$$CO + \frac{1}{2}O_2 = CO_2 \tag{8}$$

are favored by increasing total pressure.

Several kinetic studies also provide indirect evidence that CO_2 and water should be the principal products under the present conditions of higher pressure and extremely small $[CH_4]/[O_2]$. Avramenko et al. (*7*) reported that the major products formed from the low pressure (~1 torr) reaction between O atoms from a discharge in O_2 with CH_4 added downstream were formaldehyde and CO. Smaller amounts of H_2O_2 were also noted under some conditions.

However, Wong and Potter (*8, 9*) found no formaldehyde during their later studies of the same reaction at ~1 torr. On-line mass spectrometric analyses of the reactants (CH_4,O,O_2) and products revealed that with high O_2 concentrations ($[CH_4]/[O_2] < 20\%$), carbon dioxide and water were the major products while traces of CO and H_2 were observed. At low O_2 concentrations ($[CH_4]/[O_2] > 1$), CO and water were the major products and the trace components were CO_2, H_2, and H atoms.

Table I. Proposed Kinetics for Methane Oxidation

Reaction	References
$e + O_2 = O + O$	(*17, 18*)
$\left.\begin{matrix}O\\OH\end{matrix}\right\} + CH_4 = CH_3 + \left\{\begin{matrix}OH\\H_2O\end{matrix}\right.$	(*3*) (*3*)
$CH_3 + O_2 + M = CH_3O_2 + M$	(*3*)
$CH_3O_2 + CH_3O_2 = \left\{\begin{matrix}CH_3OH + CH_2O + O_2\\2CH_3O + O\\CH_3O_2CH_3 + O_2\end{matrix}\right.$	(*14*) (*14*) (*14*)
$CH_3O_2 + HO_2 = CH_3O_2H + O_2$	(*3*)
$\left.\begin{matrix}O\\OH\end{matrix}\right\} + CH_3OOCH_3 = CH_3O + CH_2O + \left\{\begin{matrix}OH\\H_2O\end{matrix}\right.$	— —
$\left.\begin{matrix}O\\OH\end{matrix}\right\} + CH_3OOH = CH_2O + \left\{\begin{matrix}2OH\\OH + H_2O\end{matrix}\right.$	— —
$2CH_3O = CH_3OH + CH_2O$	(*14, 16*)
$CH_3O + CH_3O_2 = CH_3O_2H + CH_2O$	(*14, 16*)
$CH_3O + O_2 = CH_2O + HO_2$	(*3*)
$\left.\begin{matrix}O\\OH\end{matrix}\right\} + CH_3OH = CH_2OH + \left\{\begin{matrix}OH\\H_2O\end{matrix}\right.$	(*15*) —
$O_2 + CH_2OH = CH_2O + HO_2$	(*13*)
$O + CHO = \left\{\begin{matrix}CO_2 + H\\CO + OH\end{matrix}\right.$	(*3*) (*3*)
$O_2 + CHO = HO_2 + CO$	(*3*)
$\left.\begin{matrix}O\\OH\\OH_2\end{matrix}\right\} + CH_2O = CHO + \left\{\begin{matrix}OH\\H_2O\\H_2O_2\end{matrix}\right.$	(*3*) (*3*) (*3*)
$OH + CO = CO_2 + H$	(*3*)
$O + CO + M = CO_2 + M$	(*3*)
$O + O + M = O_2 + M$	(*4, 5*)
$O + O_2 + M = O_3 + M$	(*3*)
$O + O_3 = 2O_2$	(*3*)
$O \xrightarrow{\text{surface}} O_2$	(*19*)
$O_3 \xrightarrow{\text{surface}} 2O_2$	(*12*)
$H + O_2 + M = HO_2 + M$	(*3*)
$O + OH = H + O_2$	(*3*)
$O + HO_2 = OH + O_2$	(*3*)
$O + H_2O_2 = \left\{\begin{matrix}HO_2 + OH\\H_2O + O_2\end{matrix}\right.$	(*3*)
$OH + H_2O_2 = HO_2 + H_2O$	(*3*)

Avramenko et al. (*7*) did not report the relative concentrations of their reactants. In view of Wong and Potter's analyses it seems possible that the different product distribution obtained by Avramenko could be due to a larger ratio of $[CH_4]/[O_2]$.

It should be noted that the limited production of undesirable products would not necessarily make the process unattractive for contaminant control. If the reaction products are themselves oxidized by the discharge at a high enough rate, their steady state concentration with recycle may be at an acceptable level.

Based on previously reported kinetics, we propose the reaction sequence in Table I to describe the CH_4 oxidation process in an RF discharge. Taken together, these reactions will result in the overall conversion of CH_4 into CO_2 and water, providing there is a sufficient excess of O atoms and O_2. Beginning with the initial reaction between O and CH_4, the criteria for including a reaction were that it result in the removal of a reactant or intermediate produced in other steps, and that it be more rapid than competing reactions that were not included or else be comparable in rate to competing reactions that were included. In selecting these governing reactions, we have taken $[O_2] \gg [O]$ and assumed $[O] > [OH]$ and OH_2. Additional heterogeneous reactions not shown in the table may be significant, but very little quantitative information on such reactions is available. The reaction of OH with CH_3OH has not been studied but should be faster than O + CH_3OH by anology to the corresponding reactions with dimethyl ether (*10*). The reactions of O and OH with methyl and dimethyl peroxide have not been reported but should be at least as fast as the methanol H-atom abstraction.

The initiation through step 1, an electron molecule reaction, is a characteristic feature of electrical discharge reactions. For the quantitative evaluation of the rate of this step and the overall rate of reaction, information on the spacial and energy distribution of electrons is needed (*11*). These kinetics will be dealt with in a subsequent paper.

Conclusions

Almost complete removal of a sample trace contaminant, methane, through the use of a radio frequency discharge has been demonstrated from 50 torr up to almost atmospheric pressure in an oxygen atmosphere. The initial results appear promising and further developments in reactor design, the use of air atmospheres, and determining the degree to which undesirable minor products can be produced may lead to the use of an RF discharge in several environmental applications.

Acknowledgment

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NOTES

Evaluation of Continuous Mercury Monitor on Combustion Sources

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■ A continuous mercury monitor was evaluated at two fossil fuel–fired boilers. Within the accuracies of the measurements, the continuous analyzer and either the wet chemical mercury sampling procedure or mercury material balance calculations were in agreement. The system can be operational in 5½ h from a cold start. The time includes installation (20 min), 4 h to preheat catalytic converter (combusts organics which might be present), and 1 h to calibrate the system. The system once operational requires minimum attention.

The measurement of toxic materials emitted from energy transformation processes is a necessary part of any environmental assessment of those processes. The emission rates of the trace constituents of coal and/or oil is dependent upon the source of the fuel and the degree of fuel preparation. Studies by the Illinois Geological Survey (*1*) have shown the variability of the mercury content within run-of-mine coal and the variability of the coal mercury content between different mines. Since the mercury emission rates vary as a function of the mercury content of the coal, the continuous or semicontinuous analysis of the toxic stream components is of great importance.

A study (*2*) has recently been made to evaluate various commercially available total mercury vapor monitors. The instruments in question were evaluated at a chlor-alkali plant, a zinc smelter, and a mercury processing plant. Since the results obtained were encouraging, a study was initiated to evaluate one of the mercury monitors on a coal-fired utility boiler and on an oil-fired experimental burner.

Experimental

The instrument selected for field evaluation was the Geomet Model 103 Mecury Monitor. The monitor is designed to measure elemental mercury in the vapor phase. A flow diagram of the monitoring system developed for use on the combustion sources is shown in Figure 1.

The Geomet Model 103 Mercury Monitor samples flue gas at a nominal rate of 4.8 l./min. The mercury vapor is collected by amalgamation on two silver grids. At the end of the preselected sampling period, these grids are sequentially heated to desorb the collected mercury. The vapor is then analyzed using the UV absorption line at 253.6 nm. The total sampling time can be varied from 0–30 min.

The first site at which the mercury monitor was evaluated was a coal-fired utility boiler which generates 138 MW of electric power. After calibration, using procedures recommended by the manufacturer, flue gas monitoring was initiated. The flue gas conditions are given in Table I.

Manual samples for mercury vapor were acquired simultaneously with the instrumental data using a technique developed earlier in our laboratory (*3*). The sampling period for the manual procedure was about 20 min. The Geomet was

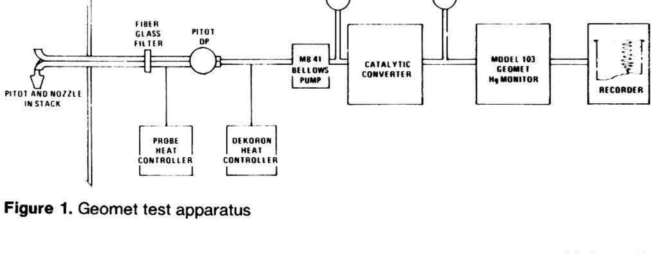

Figure 1. Geomet test apparatus

Table I. Flue Gas Conditions

Temperature, °C	162
Velocity, cm/s	3400
Composition	
CO_2, vol %	15.1
O_2, vol %	4.1
H_2O, vol %	6.0
SO_2, ppm	1200–1300

Table II. Comparison of Instrumental and Manual Mercury Vapor Sampling Techniques

Test	Manual procedure, $\mu g/m^3$	Geomet, $\mu g/m^{3a}$
1	8.6	4.0
2	5.3	6.0
3	6.2	7.2
Av	6.7 ± 1.7	5.7 ± 1.6

[a] The values are averages of at least three instrument readouts.

operated on a 5-min sampling period. A minimum of three instrument readings were obtained for each manual sample acquired. The results of both the manual and instrumental tests are given in Table II.

A second test was performed on an oil-fired experimental burner at the EPA's Industrial Environmental Research Laboratory at Research Triangle Park, N.C. The concentration of mercury vapor detected by the monitor was compared to the total level of mercury in the fuel as fired. The material balance calculations for mercury, based on detected mercury levels in the flue gas, indicated that 0.112 ppm (w/w) of mercury was present in the fuel oil. The analysis of the fuel oil using standard procedures indicated that the fuel oil contained less than 0.2 ppm of mercury.

To bring the sampling system and the analysis system online from a cold start requires about 5½ h. Twenty minutes are required to install the device, 4 h are required to preheat the catalytic converter, and 1 h is required to calibrate the system. (This is a three-point calibration curve.) The system is very stable and requires minimum attention when it is in continuous operation. (Recalibrate once a week with routine system monitoring twice a day.) During 80 h of operation on the two-fossil fuel combustion sources, no apparent problems with the sampling system or the instrument occurred.

Conclusion

The studies performed with the Geomet analyzer indicate that mercury concentration data can be obtained on a semicontinuous basis from utility boilers. The analyses can be performed without dilution of the flue gas and with minimal interference from other flue gas constitutents. A study (*4*) by TRW Systems Group has shown that 90+% of the mercury contained in fossil fuels is emitted as the elemental vapor upon combustion. Instruments such as the Geomet analyzer can be highly useful in the evaluation of mercury emissions from high-temperature energy transformation processes.

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Average Tropospheric Concentration of Carbon Tetrachloride Based on Industrial Production, Usage, and Emissions

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Carbon tetrachloride along with fluorocarbon-11 and fluorocarbon-12 has been identified as a long-lived chlorinated species capable of surviving reaction and removal processes. Carbon tetrachloride has a very long lifetime in the troposphere based on the only significant known reaction process—the extremely slow rate of reaction with OH radicals (*1*) permitting diffusion of this molecule well into the stratosphere. Possible losses into the oceans or by removal by precipitation processes are uncertain at present. Gas chromatographic measurements by Lovelock et al. (*2*) and Wilkness et al. (*3*) for 1971–72 averaged 73 ppt. However, carbon tetrachloride concentrations measured over the Atlantic in October 1973 averaged 138 ppt and concentrations of carbon tetrachloride measured near the U.K. in a flight on June 6, 1974, into the stratosphere ranged from about 120 ppt near the surface down to 95 to 100 ppt at the tropopause (*4*). Hanst and co-workers (*5*) using an infrared FTS technique have analyzed samples at East Coast U.S. sites in 1975 and obtained minimum carbon tetrachloride concentrations in the 70–80-ppt range as low as reported earlier by Lovelock (*2*) and Wilkness et al. (*3*). Grimsrud and Rasmussen (*6*) have reported carbon tetrachloride concentrations of 120 ± 15 ppt. It has not been clear from these results whether these concentrations of carbon tetrachloride could be accounted for by anthropogenic emissions or whether significant natural sources of carbon tetrachloride may exist.

An independent computation of average tropospheric concentration of carbon tetrachloride can be made assuming that anthropogenic sources of carbon tetrachloride are the sole source of tropospheric carbon tetrachloride. This computation requires a reasonably accurate estimate of

■ The anthropogenic contribution of carbon tetrachloride can be computed from U.S. and worldwide production and usage patterns since early in the present century. Based on the estimates and the range of uncertainties in losses, the current concentration levels of carbon tetrachloride in the troposphere would range from 60–80 ppt. The current emission losses for carbon tetrachloride would increase the tropospheric concentration by about 1 ppt per year. These estimates are compatible with many of the ambient air measurements reported. It is impossible to reconcile the variations with time of the tropospheric concentrations of carbon tetrachloride reported in some of the recent measurements with these anthropogenic losses.

historical production of carbon tetrachloride, usage patterns, and subsequent emissions to the atmosphere. The U.S. production of carbon tetrachloride from 1922 on has been provided by the U.S. Tariff Commision (*7*). An estimate for 1914 and 1919 were available from other sources (*8, 9*). Earlier and missing years of production were estimated by interpolation.

Usage of carbon tetrachloride in the U.S. into the 1930's involved the following application: dry cleaning and spotting, fire extinguishers, machinery cleaning, metal degreasing, agricultural fumigant, and other industrial uses (*8*). Almost all uses would have resulted in an almost immediate or delayed loss (fire extinguishers) to the atmosphere. Very few uses, such as some very limited production of chloroform from carbon tetrachloride, would have not involved a loss to the atmosphere. A 95% loss factor was selected as reasonable and possibly conservative. An additional loss approaching 100 million lb could have occurred if essentially all of the carbon tetrachloride produced during this period were lost to the atmosphere. The detailed usage pattern for carbon tetrachloride in the U.S. for 1940 through 1949 is available (*9*). The use of a 5% loss factor (carbon tetrachloride production, transfer losses along with small usages in fumigants, fire extinguishers, and pesticides spray) for 1965–74 is a compromise among various estimates of 2.4, 9, and 13% for losses associated with recent production (*10–12*). This range of estimates causes a range of uncertainty from −200 million lb to +900 million lb in Table I.

Before 1960 production of carbon tetrachloride outside of the U.S. was small (*8*). Annual production of carbon tetrachloride in France, Italy, and West Germany did not exceed 2 million lb in 1954 (*8*) although German production began about 1890. In the U.K. and Europe carbon tetrachloride was used primarily for fire extinguishers and as a spotting agent until fluorocarbon production became significant. If non-U.S. production and loss to the atmosphere was only 2 million lb a year over a 50-year period, an additional 100 million lb would have been emitted to the atmosphere. Since 1960, production of fluorocarbons outside the U.S. has amounted to about 6100 million lb (*10*). Carbon tetrachloride production and fluorocarbon production are proportioned between U.S. and worldwide amounts. That is, other countries have been producing about 55% of worldwide production of both carbon tetrachloride and fluorocarbons. Therefore, it appears reasonable that almost all of the carbon tetrachloride produced since 1960 abroad has been used as a starting material for fluorocarbons. Use of the production loss estimate of 2.4% leads to a lower limit of 140 million lb of carbon tetrachloride outside of the U.S. An overall minimal historical increment for non-U.S. tetrachloride losses would be about 240 million lb. When added to the total in Table I, the estimate of total worldwide emissions would be 3.9 million lb. The range of uncertainties is such that losses could range as high as 5.0 billion lb.

If a residence time of several hundred years for carbon tetrachloride is correct, this is essentially an infinite lifetime for purposes of estimating an average tropospheric loss. Most losses are immediate. Losses from fire extinguishers have a delay time, but this also is insignificant since this usage was more important in past decades. Because most of the losses occurred over a period 10 to 35 years in the past, northern and southern hemisphere concentration should be very nearly the same if anthropogenic losses dominate. The estimated average tropospheric concentration by 1975 would range from 65–88 ppt. This range overlaps the earlier estimates (*3, 4*) gas chromatographic and more recent infrared results (*5*) from analysis of tropospheric samples, but falls significantly below other more recent values (*4, 6*). It also ignores the correction for the amount of carbon tetrachloride in the stratosphere. The assumption of the same mixing volume for carbon tetrachloride in the stratosphere and troposphere would lead to almost 10% of the CCl_4 molecules or photolysis products being in the stratosphere which reduces the tropospheric concentration estimate to that amount—down to 60–80 ppt.

It should be noted that, based on even the upper estimate of total emissions (5 billion lb), half of the present integrated emissions had been lost to the atmosphere 20 years ago and one-quarter over 30 years ago. The losses per year have decreased because of the marked shift in usage patterns. The present loss rate would correspond to an increase of no more than 1 ppt per year in tropospheric carbon tetrachloride concentrations.

This anthropogenic contribution is consistent with the lower ambient air measurement results but does not ac-

Table I. U.S. Production and Atmospheric Emissions of Carbon Tetrachloride

(In millions of lb)

Year(s)	U.S. production	U.S. emissions by time period	U.S. cummulative emissions[a]
1907–13	20 est.	19[b]	19
1914–21	80 est.	72[b]	91
1922–30	180	171[b]	262
1931–39	530	450[c]	712
1940–49	1685	1100[d]	1812
1950–53	940	470[e]	2282
1954–62	2579	800[f]	3082
1962–64	1539	150[g]	3232
1965–74	8682	434[h]	3666

[a] Lower range of estimated losses (see text). [b] 95% of all production lost to atmosphere. [c] An average of 10% of production used as starting material for fluorocarbons; 95% of remaining production lost to atmosphere. [d] An average of 33% of production used as starting material for fluorocarbons; 95% of remaining production lost to atmosphere. [e] An average of 45% of production used as starting material for fluorocarbons; 95% of remaining production lost to atmosphere. [f] An average of 66% of production used as starting material for fluorocarbons; 95% of remaining production lost to atmosphere. [g] An average of 80% of production used as starting material for fluorocarbons; 95% of remaining production lost to atmosphere. [h] From 80–95% of production used as starting material for fluorocarbons, losses to atmosphere taken as 5% of production.

count for the higher tropospheric concentration values and the increases reported for carbon tetrachloride between 1971 and 1975 from Lovelock's results. Other hypothetical processes involving reactions of chlorin with organic materials in water also would be unlikely to cause such rapid increases. It also is difficult to conceive of a natural source which would not make a significant contribution in the early 1970's but would contribute significantly a few years later. It appears urgent to determine the accuracy of the available ambient air analytical results for carbon tetrachloride in the 100-ppt range so as to resolve whether or not natural sources of carbon tetrachloride are required to account for the global background of carbon tetrachloride.

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Coping with Spills of Silicone Fluids

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■ Laboratory simulations were made of roadway spills using polydimethylsiloxane fluids of 1- to 100 000-centistoke (cS) viscosity. Sliding friction of rubber on concrete and asphalt wet with fluid has been measured and used as a model of road traction. Various cleanup procedures have been evaluated; the effectiveness of each method was judged both visually and by the degree of recovery of dry traction. Water spills have been simulated in the laboratory, and cleanup procedures using oil containment and recovery devices are found to be applicable.

Because polydimethylsiloxane fluids are being shipped and used more and more widely, it seems inevitable that eventually some quantity will be spilled or accidentally imposed on roads or streams. In the event of a road spill, the first concern is whether the slipperiness of the spilled fluid presents a significant hazard. Another concern is how to clean up spills on roads or waterways. Still a third deals with the effect of the fluid on the environment. The object of this investigation was to develop ways of coping with massive spills of silicone fluids. In this report we focus primarily on the more widely used intermediate viscosity grades of fluid (50–10 000 cS) which to some extent resemble mineral oil in consistency and physical properties, and are more likely to present a cleanup problem than the extremely low- or high-viscosity polymers.

Toxicity of the fluid need not be of particular concern; the polydimethylsiloxanes are relatively inert chemically and among the least toxic materials as regards skin contact or ingestion (*1, 2*). Laboratory experiments with several environmental species have indicated a low degree of hazard for the species studied (*3*). It is, however, important not to confuse this class of siloxanes with organosilicon monomers that may have different toxicological properties and chemical reactivity. Only the lower viscosity grades (less than 5 cS) of the fluids are volatile enough to cause a potential flammability problem (Table I), although almost any silicone fluid will burn under proper circumstances. (CO_2 or foam extinguishers are recommended.)

Experimental

Spills were simulated in the laboratory to determine optimum cleanup procedures. For study of water spills, a shallow polyethylene basin (75 × 110 × 10 cm) was filled with tap water. A polydimethylsiloxane fluid (200 ml, to form a film ~0.2 mm thick) was then applied. The silicone, which has a density less than that of water, first spread rapidly in an extremely thin surface film until constrained by the basin. The

Table I. Typical Physical Properties of Polydimethylsiloxane Fluids (*4, 5*)

Viscosity at 25 °C cS	Flash point, open cup, °C	Specific gravity @ 25 °C	Boiling point, °C	Vapor pressure at 25 °C, mm Hg
1.0	37	0.818	150 @ 760	6
5.0	135	0.920	120 @ 0.5	$<10^{-3}$
10	165	0.940	>200 @ 0.5	—
50	280	0.960	>200 @ 0.5	—
100	300	0.968	—	—
350	>315	0.972	—	—
1 000	>315	0.972	—	—
10 000	>315	0.973	—	—

bulk of the fluid then spread slowly to cover the surface. Two drops of Shell Oil Herder (*6*) were applied at one end of the rectangular pool. (This chemical was chosen as being representative of proprietary oil containment materials; no endorsement or preference is implied. Before any such material is used in a spill situation, the manufacturer's literature should be consulted.) The time required for the polydimethylsiloxane fluid to contract a new equilibrium state (a thick circular film covering very little area) was measured. Then OilSnare (*7*), a collection of oleophilic hydrophobic plastic fibers designed for adsorbing oil from water while remaining afloat, was weighed, moved through the collected silicone fluid for 10 min, removed, and allowed to drain for 30 s. The snare was weighed again to determine the amount of silicone recovered. The liquid entrapped was typically 90% silicone fluid and 10% water.

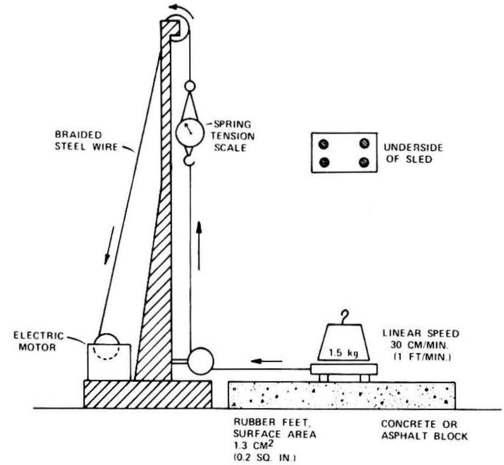

Figure 1. Keil tester adapted to measurement of sliding fraction

An apparatus was built to measure sliding friction to rubber on concrete and asphalt surfaces. A Keil tester, equipped with a 5.7-rpm electric motor and tension scale was equipped to pull a weighted sled horizontally (Figure 1). The feet of the sled were made from tire tread rubber and had a total contact area of 1.3 cm^2. The weight of the sled was 1.5 kg, giving a contact pressure of approximately 1.1 kg/cm^2, roughly the same as that of many highway vehicles.

Sliding friction of the sled was measured by pulling the sled with the tester at 1 ft/min and measuring its resistance with the spring scale. Scale readings varied by about ±5% as the sled traversed the surface of the pavement, and an average was estimated. Readings in the range of 1200 g were found for dry unworn concrete and 1300–1400 g for used asphalt paving. Fluid was then spilled on the surface and the friction again measured. After the surface was treated to clean up the spill, the sled feet were cleaned thoroughly with Chlorothene (1,1,1-trichloroethane) and friction was measured a third time. The effectiveness of cleanup was judged both visually and by the degree of recovery of the original friction reading. The set of initial scale readings (dry pavement) was used to calculate the statistical confidence limits shown in Table III.

Sand, sawdust, cement, and commercial oil absorbent [Zorb-All (*8*) was selected as typical of available materials] were evaluated for effectiveness in removing silicone fluids from concrete and asphalt. Each material was put down on the spill, allowed to stand for a measured period of time, and then swept off.

The soil spill was monitored by periodically removing a plug of soil to a depth of 70 cm, sectioning the plug into 2.5-cm sections, extracting the silicone fluid from the soil with a measured amount of methyl isobutyl ketone, and determining the concentration of silicone in the extract by atomic absorption spectrometry (*9*).

Results and Discussion

Spills on Water. Because polydimethylsiloxane fluids float on water, a spill can be contained by floating booms or dikes (*10*). Or, if containment equipment is unavailable or impractical, the silicone can be concentrated by applying a surface-active chemical designed for this purpose around the perimeter of the spill. Such materials have a high spreading pressure (42 dyn/cm), and force the silicone (spreading pressure $\sim$10 dyn/cm) (*11*) to contract into a small, low surface area pool. A monomolecular layer of polydimethylsiloxane fluid contracts to cover a surface area about 10^6 times less when thus treated. Very little surface-active material is required (8 l. per linear mile of oil slick or <0.1 ppm).

Once the silicone fluid has been concentrated, it can be removed from the water surface by systems such as are used for petroleum spills (*10*). These include pumps, skimmers, physical absorbents, and oleophilic hydrophobic fibers (*12*) that are fabricated into floating ropes.

These ropes are moved through the oil-laden water, to a machine with wringer rollers and a holding tank, and back into the water. This technique is effective for crude oil spills (*13*), and is equally useful for silicones (Table II).

Once collected, the fluid may be reclaimed or incinerated in a suitable burner. Silicone fluids are usually diluted to 10% or lower concentration with scrap solvent for incineration. However, control of the particulate SiO$_2$ formed by the combustion is necessary.

Table II. Evaluation of Containment and Recovery Procedures for Polydimethylsiloxane Fluids

Polydimethylsiloxane fluid viscosity, cS	Approximate spreading rate of monomolecular silicone film m/s	Application of Oil Herder, silicone contraction time, s	Application of OilSnare, g silicone removed per g of snare
5	>5	3	1.0
100	>2	6	2.6
1 000	~1	15	4.3
10 000	~0.3	35	8.3

Spills on Roadways. The chief concern in a roadway spill is the loss of tire traction caused by the lubricating action of the silicone fluid. As it turns out, silicone fluids have about the same degree of lubricity as motor oil as regards rubber on concrete or asphalt.

Several viscosities and types of fluids were tested on concrete and asphalt. Loss of traction (measured by the procedure described in the Experimental Section) varied with the viscosity of the fluid, as shown in Table III. These data also show that traction decreases with increasing viscosity, down to a minimum traction.

Procedures evaluated for removal of fluids from pavement include physical absorbents and high-pressure water flush. It is assumed in all cases that the flow of material is halted and any large amounts of spilled fluid have been collected and transferred to a suitable container. This discussion pertains to removal of the remaining film of fluid to restore normal traction to the pavement.

Although dry sawdust is fairly effective for absorbing fluids,

Table III. Spill Traction

		Smooth concrete		Worn asphalt paving	
Material	**Viscosity**	**Scale reading**	**Percent of dry traction**	**Scale reading**	**Percent of dry traction**
None (dry surface)	—	1200 ± 190[a]	100	1330 ± 250[b]	100
Polydimethyl-siloxane fluid	1 cS	1100 1200	100	1400 1500	100
	5 cS	1200 1200	100	1300 1400	90
	50 cS	950 1000	81	1200	86
	100 cS	700 800	73	1000	75
	350 cS	400	33	800 900	68
	1 000 cS	300	27	600	46
	5 300 cS	250 300	22	400	33
	10 000 cS	350	30	400	33
	100 000 cS	250	20	—	—
Water	1 cps	1100 1200	100	1400 1600	100
SAE 30 motor oil	210 cps	400 400	33	500	42

[a] Number of data points = 14; average = 1203; repeatability of single measurement = 186.8 (95% confidence limit); standard deviation = 86.5; relative standard deviation = 7.19. [b] Number of data points = 10; average = 1330; repeatability of single measurement = 256.8 (95% confidence limit); standard deviation = 113.5; RSD = 8.54.

sawdust is usually damp and therefore unsatisfactory because the adsorbed water inhibits absorption of silicone.

Sand was also found unsatisfactory, chiefly because it has little absorptive capacity.

Cement (mortar) powder worked very well at removing fluids from concrete and asphalt. If water is also present, however, the cement can harden and its removal becomes difficult.

A porous, baked diatomaceous earth designed especially for oil absorption is commercially available and proved to be convenient and safe. In a typical experiment, after a spill of 100 cS of polydimethylsiloxane fluid was made on a concrete surface, an index of 60 indicated significant loss of traction. The oil-absorbing powder and cement powder were used to treat different areas of the spill. After 1 h, the materials were swept off and traction indices of 85 and 90 were measured for the absorber and cement, respectively. An additional half hour of treatment with fresh material gave indices of 100 for both treated areas, indicating full recovery.

The time required to remove polydimethylsiloxane fluid from pavement with physical absorbents depends on the viscosity of the fluid and the amount of fluid present. Figure 2 demonstrates that fluids with viscosity of 100 cS or lower can be removed rapidly (1 or 2 h). Fluids of 100–500 cS can be removed effectively in 3–4 h, or in less time if fresh absorbent is periodically applied to the surface. Fluids of 500 cS and higher viscosity take longer for removal. Periodic replenishment with new absorbant hastens recovery. Absorbents were not very effective for the 100 000-cS fluid.

A polydimethylsiloxane fluid of any viscosity can be removed quickly by the application of a solvent followed immediately by a physical absorbent. The solvent used in experimental investigations was Chlorothene (1,1,1-trichloroethane). Any solvent that easily dissolves silicones would be effective; other factors which must be considered are flammability, toxicity, and effect on the environment. Solvents should not be used on asphalt surfaces, however, as they will dissolve the asphalt. It should be noted that most polydimethylsiloxane fluids will not soften asphalt; in fact, silicone fluids affect asphalt much less than motor oil.

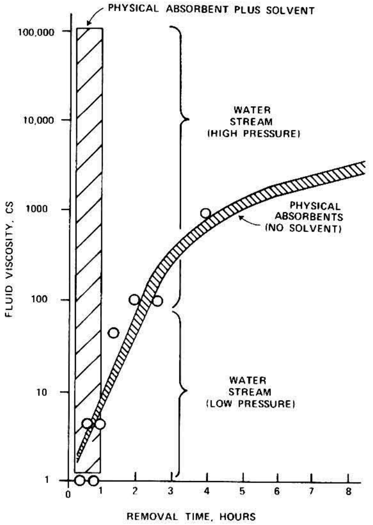

Figure 2. Removal time for polydimethylsiloxane fluids on pavement as a function of fluid viscosity, using different removal techniques

A high-pressure stream of water is effective in displacing fluids of all viscosity grades from concrete and asphalt. Streams at 1800 psi were forceful enough to remove 100 000 cS of polydimethylsiloxane fluid completely from concrete. Water streams of less force, such as those available from municipal fire-fighting equipment, are not so efficient but are useful in removing fluids of lower viscosity. Containment and disposal of the displaced fluid are problems that still remain, however, and unless these problems can be overcome, water flushing cannot be recommended.

Spills on Soil. A 5-gal spill of 100-cS polydimethylsiloxane fluid on 1 m^2 of sandy soil has been monitored for two years.

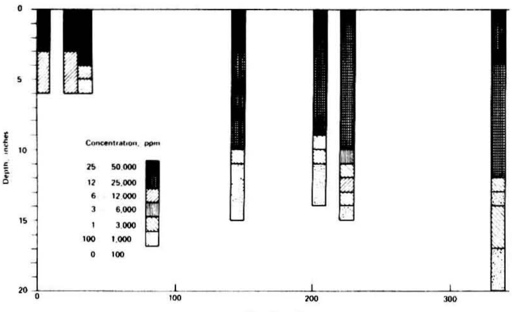

Figure 3. Depth profile of 100-cS polydimethylsiloxane on soil as a function of time after spill

Results show a gradual downward migration to a depth of 50 cm during this time period (Figure 3). No significant lateral movement of the fluid was found. Vegetation within the spill area is sparse.

Laboratory experiments with columns of soil showed that migration rates are dependent in a complex way on the kind of soil (sand, clay, or loam), its moisture content, and the amount of watering. In general, dry soils seem to have a greater absorptive capacity and hold silicone fluids more tenaciously than wet soils.

The soil thus appears to act as its own absorbent, and if the presence of fluid is objectionable, the soil can be removed to a landfill area and replaced with fresh soil.

A more complete report on studies of the movement and interaction of polydimethylsiloxane fluids with soils will be published elsewhere.

Conclusions

Polydimethylsiloxane fluids in spill situations behave much the same as motor or mineral oil of comparable viscosity. The same cleanup procedures are applicable.

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CORRESPONDENCE

SIR: Dr. Holland and I were much disappointed to see the publication of the article "Determination of Nitrate in Water Samples Using a Portable Polarographic Instrument", *Environmental Science and Technology,* **9**, 1075 (1975), without reference to our own earlier paper.

Since this paper was received November 6, 1974 and our paper, "Development of a Portable Polarograph for Determination of Aldehydes in Automotive Exhaust and Production Plant Samples", *ibid.*, **9**, 127 (1975), was received on April 18, 1974, and accepted on October 21, 1974, it is extremely difficult to understand why you did not call our paper to the attention of the authors of the nitrate paper.

By way of explanation, you should understand that the phrase "peak-seeking circuit" has different meanings in the respective papers. In our paper we are referring to the capture, during each scan, of the maximum current flow value as a potential. In contrast, Young et al. are smoothing out the output of the dropping mercury electrode.

Please note that our paper makes reference to our patent application. That application has since issued as U.S. Patent No. 3 922 205. Since the authors of the nitrate paper were not alerted by your office and no attempt made to cross reference our papers, we fear your readers have been misled into believing they are free to build and use a portable polarograph with our peak-seeking circuit. However, the commercial model is being supplied to the trade by a licensee of The Dow Chemical Co.

James D. McLean

Analytical Laboratories
574 Building
The Dow Chemical Co.
Midland, Mich. 48640

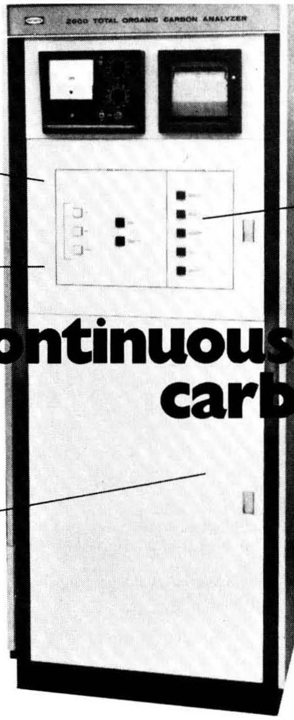
SIR: The paper "Development of a Portable Polarograph for Determination of Aldehydes in Automotive Exhaust and Production Plant Samples" appeared after our paper was submitted and while it was in review. Our failure to insert a reference to the above paper in our revision is an oversight for which we apologize.

The emphasis of our paper should not be taken as the instrument (which is pretty standard OA circuitry), but as the demonstration of the utility of the $ZrOCl_2$ catalytic method coupled with background compensation for the determination of nitrate in complex samples.

The clear message of both papers would seem to be that with the widespread availability of inexpensive, lightweight, and reliable circuits, the polarographic methods for a number of species of environmental interest should be re-examined.

Robert H. Philp, Jr

University of South Carolina
Columbia, S.C. 29208



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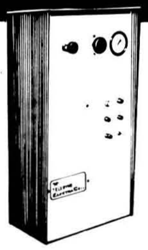

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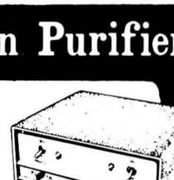

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INDUSTRY TRENDS

Camp Dresser & McKee Inc. has acquired Accu-Labs Research, Inc. (Wheat Ridge, Colo.). Accu-Labs provides fuels testing, radionuclide determination, and other laboratory services.

UOP Inc. (Northampton, England) will supply a 100 000-acfm multicyclone centrifugal collector to clean fumes from a large foundry in England's Midlands. It will remove ¾ ton/h of iron oxide dusts.

The **Pacific Environmental Laboratory**, a division of **Kennedy Engineers,** Inc., has begun operations at Tacoma, Wash., to perform water quality and wastewater analyses for service in the Pacific Northwest.

Environmental Data Corp. (Monrovia, Calif.) has received orders exceeding $430 000 for *in-situ* stack-gas monitoring instruments from utilities and smelters throughout the U.S.

John Deere (Moline, Ill.) has introduced the world's first fully automatic-drive crawlers. The bulldozer and loader are 110 hp; the operators need no longer worry about up- and down-shifting.

Monitor Labs, Inc. (San Diego, Calif.) has sold a large air monitoring system to HYDROMET, the Russian agency responsible for analysis and monitoring of air and water pollutants.

Andco Inc. and **The Carborundum Co.** have concluded a new licensing agreement that gives Andco rights to the Torrax Solid Waste Conversion System in the U.S., and other industrialized countries. A 200 tpd Andco-Torrax unit is nearing completion in Luxembourg.

Dames & Moore (Los Angeles, Calif.) is conducting oil shale development studies for the Rio Blanco Oil Shale Project and C-b Shale Oil Project at Piceance Creek Basin, Colo.

Exxon USA (New York, N.Y.) announced that it has reduced energy consumption at its U.S. refineries to 16% below what it was in 1972. This represents a saving of more than 6 million bbl/yr of oil.

Fluor Canada, Ltd. is engineering contractor for a $30 million project to increase ethane recovery at Dome Petroleum Limited's 1.5 billion standard ft^3/day turbo expander gas processing plant at Empress, Alta.

L. B. Foster Co. (Pittsburgh, Pa.) has acquired Hydro-Ash Inc., a designer of utility and industrial air pollution control systems, and builder of pneumatic ash handling and conveying systems at coal-burning plants.

Gustav Getter Associates (New Rochelle, N.Y.) has received a U.S. Navy award for design of a "Hush House" that houses jet aircraft during engine testing to quiet the roar to levels acceptable to the nearby community. The Hush House is at Miramar, Calif.

Mikropul Corp. (Summit, N.J.) has received a contract in excess of $6 million for a dry scrubbing system to control particulate and gaseous fluoride emissions from the primary aluminum reduction plant of Ormet Corp., at Hannibal, Ohio.

A.B. Curls & Associates Inc. (Lakeland, Fla.) was appointed Florida sales "rep" for Marconaflo Inc. Emphasis will be on "Dynajet" product and slurry systems for phosphate industry material reclamation and transfer.

Dravo Corp. announced that a 6-mgd wastewater treatment system it designed and built for Alton Box Board Co. (Jacksonville, Fla.) has gone on stream. Alton produces 750 tpd of kraft linerboard.

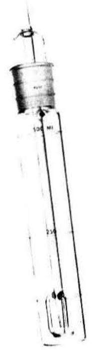
Sala Magnetics, Inc. (Cambridge, Mass.) has completed a 1-mgd magnetic filtration pilot plant that can remove fine, even weakly magnetic contaminants from industrial process and waste streams. The firm is a subsidiary of Sala International (Sweden).

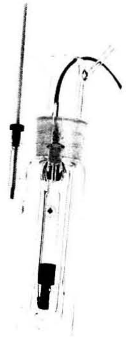
Dorr-Oliver Inc. has installed a fluid-bed system in a new pilot plant of Alumet Co. (Golden, Colo.) to make alumina from naturally occurring alunite ore, rather than bauxite. The process is based on technology licensed from the U.S.S.R.

The Dow Chemical Co. (Midland, Mich.) will market an advanced means of concentrating dissolved solids, developed by Asahi Chemical Industry Co., Ltd. (Tokyo, Japan).

AG Brown Boveri & Cie. (Baden, Switzerland) has acquired a majority holding in the Kent Group (England), which is active in instrumentation, control systems, and process automation.

Airco, Inc. (Montvale, N.J.) said that it expects to be in full compliance with present air and water pollution abatement regulations at all of its existing facilities by the end of 1977. The cost was $87 million for the last 8 yrs, and will be $7 million for the next 2 yrs.





Synergo Co. (Philadelphia, Pa.) is designing wastewater facility improvements for Pennwalt Corp. Chemicals Division to collect and cleanse storm water runoff and process wastewater before discharge into the Houston (Tex.) Ship Channel.

UOP Inc. will supply monolithic catalysts and converters to Dr. Ing. h.c.F. Porsche AG of Stuttgart, W. Ger. These exhaust pollution control units will be installed on Porsche 924 sports cars for sale in the U.S. this summer.

Sybron Corp. (Rochester, N.Y.) had sales of almost $558 million in 1975, a record. Of this total, $154.2 million was for process and water and wastewater treatment equipment.

Radian Corp. (Austin, Tex.) has received what it calls a "most important" contract from the U.S. ERDA to provide analytical chemical support for *in situ* coal gasification (without mining) experiments underway at Hanna, Wyo.

Stone & Webster Engineering Corp. (Boston, Mass.) was selected by ERDA to study tidal power technology worldwide, and ascertain whether research and development could improve its economical effectiveness. Passamaquoddy Bay, Me., and Cook's Inlet, Alaska, will be assessed.

Research-Cottrell, Inc. announced that its full-size electrostatic precipitator test facility, the nation's first, is "open for business" at R-C. It was built at a cost of more than $300 000.

Geraghty & Miller (Port Washington, N.Y.) will test disposal of treated municipal wastewater through a 6500-ft deep well located outside Orlando, Fla.

Combustion Equipment Associates, Inc. and **Occidental Petroleum Corp.** have made a joint venture, CEA/OXY Resource Recovery Associates, to design, construct, own, and operate solid waste recovery systems in the U.S. CEA/OXY will construct a $52 system at Bridgeport, Conn.

The Black Clawson Co. (New York, N.Y.) announced that work has begun on a $500 000 addition to its research and development facilities at Middletown, Ohio, aimed mainly at improving pulping and waste treatment. Expected completion is early next year.

Belco Air Pollution Control Corp. (Livingston, N.J.) has an $8.3 million contract to design, supply, and build an air pollution control system at Unit 1 at Nearman Creek for the Board of Public Utilities of Kansas City, Kan.

AB Svenska Flaktfabriken (Sweden) announced that its agreement with The Carborundum Co. to make and market electrostatic precipitators based on Flakt technology will be terminated as of this month. On-going projects, however, will be executed as planned.

Agar Instrumentation Inc. (Houston, Tex.) will provide 205 density meters to Consolidated Gas (Clarksburg, W. Va.) to help measure energy flow of gases for buying and selling purposes.

Cryogenic Technology, inc. (CTi, Waltham, Mass.) has a $2 million contract to construct two environmental protection systems for Taiwan Power Chinsan 1 and 2 nuclear power plants.

TRW Systems and Energy (Redondo Beach, Calif.) has been awarded a $215 190 contract to develop utilization plans for additions to the East Mesa, Calif. experimental geothermal test facility. ERDA made the award.

Hardee's Food Systems, Inc. (Rocky Mount, N.C.) announced successful design, installation, and operation of an air quality control system called the CONQUEROR, developed by Hardee's, a fast food restaurant chain, with the aid of Monsanto EnviroChem Systems, Inc.

NEW PRODUCTS

Process control systems
The computerized system for the pulp and paper industry offers savings in chemicals, energy and water and reduces corrosion and effluent discharge according to the manufacturer. Systematix Controls Inc. **128**

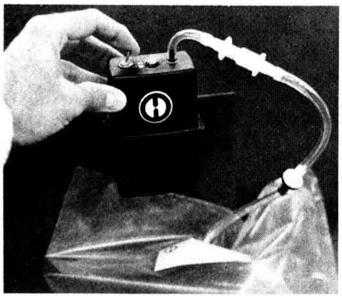
Water purifier
The mini unit, suitable for the home, boat or motor home, provides 30 gal/h of purified water. The purifier uses ozone as the purifying agent. Alron Industries, Inc. **129**

Precipitator
Units, installed on paint booth exhausts, meet air pollution regulations and recover valuable coloring agents without cross-contamination. Units feature dry collection and recovery systems. Beltran Associates, Inc. **130**

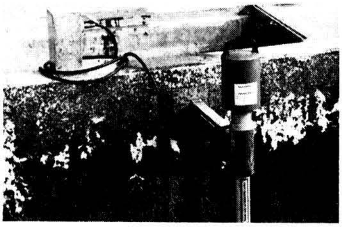
pH flow cell
The flow cell, especially designed to be used with the company's combination pH electrode, can be used at temperatures and pressures up to 65 °C and 100 psig, respectively. Sensorex **131**

Cyclone separators
The units act as pre-coolers and collect 17% of all particles 1 μ in size and up to 94.9% of all particles 22 μ or larger under specified conditions. Total efficiency is 55.4%. Fisher-Klosterman, Inc. **132**

Spray module cooling system
System consists of a series of self-contained floating units that spray and cool hot water in a flowing channel. The system is suited for closed-loop recirculating cooling systems. Ceramic Cooling Tower Co. **133**



Pulse pump
The pump with an air sample bag is designed for short-term field studies. Hourly average air samples, collected in the bag, may be analyzed later at a central laboratory. The pump's flow rate is 2–20 l/h. Environmental Measurements, Inc. **102**



Dissolved oxygen system
Consists of the Züellig dissolved oxygen probe, which requires no membranes or electrolytes, a solid-state analyzer equipped with analog output signals, relay contacts and a variety of displays. Great Lakes Instruments, Inc. **103**

Flowmeter
Designed for use in sanitary sewers, the unit may be used in pipes from 8–60 in. in diameter. It measures velocity by using the electromagnetic flow principle and depth with the use of a bubble sensor. Marsh-McBirney, Inc. **101**

Survey flowmeter system
The system is capable of providing measuring surveys in any type of flume or weir. The portable flowmeter may be used for open-channel monitoring because it does not require contact with the stream and is unaffected by floods, freezing rain, debris, or water quality. Stevens International, Inc. **104**

Activated carbon
The new active, highly adsorbent carbon is produced from high-sulfur petroleum coke. The surface area of this amorphous carbon is 2500 m^2/g. Samples are now being used in small-scale commercial demonstrations. Amoco Research Corp. **105**

Gas specific gravity transducer
The unit has an accuracy of 0.1%, will make continuous on-line measurements in hazardous locations, has a digital output signal, and will automatically compensate for gas compressibility. Solartron Electronic Group, Ltd. **106**

Mass spectrometer data system
The system offers an expanded software capability, a 19 000-spectra chemical library and a semiconductor memory minicomputer. Hewlett-Packard Co. **107**

Multiple-path flowmeter
The sonic flowmeter, suitable for most liquid applications, incorporates a digital processor that integrates velocities measured along four or more parallel paths to calculate volume flow. Accuracy is claimed to be better than 1%. Ocean Research Equipment, Inc. **108**

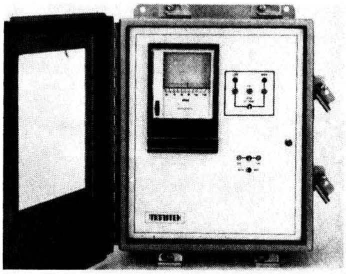
Water analyzers
Designed for continuous, unattended service, the units can monitor temperature, conductivity, pH, dissolved oxygen and other parameters. Any of up to nine sensors can be accommodated in any combination. Raytheon Co. **109**

Aerosol mass monitor
The portable unit measures respirable dust concentration; all particles less than 3.5 μ are weighed. Dust concentrations in mg/m^3 are displayed on a digital readout. Thermo-Systems Inc. **110**

Flowmeter
The instrument is designed for metering low flow rates—0.1–130 scf/h air, and 0.01–30 gph water. The flowmeter will accept any standard connector. Matheson Instruments **111**

Particulate monitor
Unit can selectively detect ash, smoke and dust particles. The principle of surface ionization is used to produce electrical pulses that correlate with particle size. Both count rate and total ion current are displayed. Extranuclear Laboratories, Inc. **134**

Tube fittings
Configurations include connectors, elbows, unions and union tees. Fittings are designed for tubing systems that handle corrosive media that are toxic and hazardous. Crawford Fitting Co. **136**



Monitor/controller
The instrument will work with pH, CRP, or pION probes or probe transmitters, and can be fitted in new and existing systems. Measured values are indicated directly on analog meter or strip chart recorders. Monitor Technology, Inc. **112**

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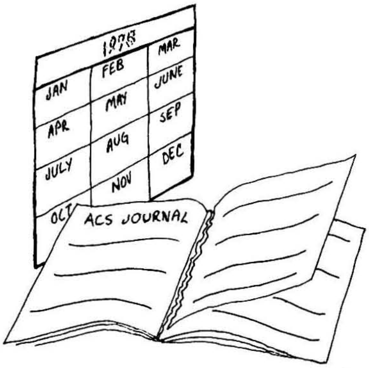
TIMELY TEARSHEETS



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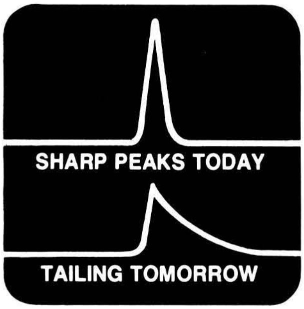

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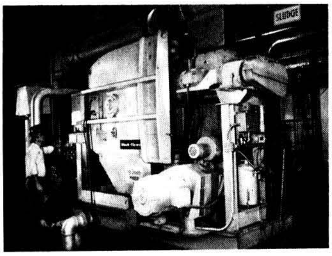
These polypropylene samplers are designed for trace metal samplings. One model with a removable bottom weight doubles as a collecting vessel with a 1200-ml capacity. Other models with fixed bottom weights have 1400-ml and 2000-ml capacities. All units can be used with or without a BOD bottle. Lab-Line Instruments, Inc. **113**

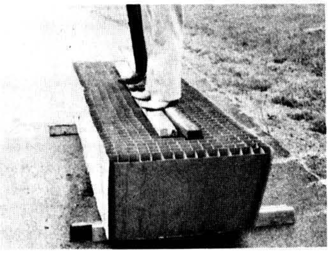
Water quality analyzer
Records data on temperature, conductivity, dissolved oxygen and pH in fresh or salt water. The instrument features digital readout, AC/DC operation and an internal recharging unit. Martek Instruments Inc. **114**

Continuous gas monitors
Monitors process streams, stack gas or ambient air. The photoionization detection principle allows the unit a measuring range of 0.1–1500 ppm. h·nu Systems, Inc. **115**



Dewatering press
The cone-type press was designed for use in pulp and paper; municipal solid waste, sewage and water treatment; and chemical process industry applications. The Black Clawson Co. **116**

Pyrometer
The bipolar digital unit measures several types of thermocouples in degrees C, F or Kelvin with an accuracy better than 0.3%. Other features are automatic zero and polarity. Newport Laboratories, Inc. **117**



Floc barrier
Constructed of corrosion resistant material, the barrier finds application in water treatment and chemical service facilities. The unit is purported to increase the capacity of existing clarifiers and reduce the size of new ones. Ecodyne Corp. **118**

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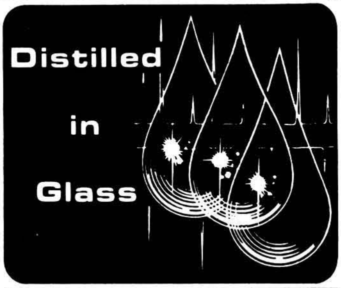

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CIRCLE 6 ON READER SERVICE CARD

NEW LITERATURE

Gas purification. Booklet, "Matheson Gases and Equipment for Analytical Instrumentation," covers a wide range of pure gases and gas mixtures, as well as flow control and purification equipment. Matheson **151**

Pipe flanges. Catalog lists an extensive line of pipe flanges that meet American Water Works Association (AWWA) and American National Standards Institute (ANSI) specifications. The Mundo Corp. **152**

Audiometric testing. Bulletin 5.0102.0 describes the company's new Model 401-A-SE "spaSAVER" audiometric testing room. Sound (free) field and hearing aid evaluations, air and bone conduction tests, and speech tests are possible. Less than 19 ft^2 of floor space. Industrial Acoustics Co., Inc. **153**

Water reclamation. Bulletin 5391 is a 1976 buyers guide to water treatment and waste reclamation equipment. Many products and processes are discussed. The Permutit Co., Inc. **154**

Electrostatic precipitators. Catalog lists precipitators with 99+% efficiencies, and operable at the above 850 °F. Collecting structures have no moving parts. Western Precipitation Division, Joy Manufacturing Co. **155**

Energy saving. Bulletin 755, "Energy Management", details and illustrates major approaches to saving fuel and reducing expenses, and tells how the company provides comprehensive service in these areas. Betz Environmental Engineers, Inc. **156**

Water systems products. Catalog lists waste treatment products, well points and screens, valves, pump and tank accessories, and other related products. Clayton Mark **157**

Particle classifiers. Electromagnetic sieve shaker/micromill combination can classify particles down to 5 microns and grind to below 2 microns. Usable as wet or dry sieve. Micro Materials Corp. **158**

Corrosive material pumps. Bulletins 355 and 321 list and describe pumps useful for corrosive acid and alkali liquids, and similar hazardous materials. Useful for chemical processing and pollution control. Sethco Mfg. Corp. **159**

Gas flow measurement. Bulletin B-58 discusses a mass flowmeter that measures corrosive and non-corrosive gases with ±1% full scale linearity and ±0.2% repeatability. Applications include air pollution and emission control. Emerson Electric Canada Ltd. **160**

Detector cells. Bulletin SB-10 describes thermal conductivity detector cells for gas chromatography, and discusses theory and circuitry. GOW-MAC Instrument Co. **161**

Dust collector. Bulletin 4000 discusses the Series 2000 collector, which offers improvement in bag cleaning effectiveness and aerodynamic design. Collector size and costs are reduced. Dustex, American Precision Industries, Inc. **162**

Chemical products. Catalog lists chemical products, including distilled diffusion pump fluids, leak sealants, vacuum greases, and lubricants. CVC Products, Inc. **163**

Water treatment. Bulletin 52-101 describes the ACTASOL water treatment system for improved coagulation with substantial savings in clarification of potable water and industrial and municipal raw and wastewater treatment. Philadelphia Quartz Co. **164**

Radioassay. Brochure describes minisystem that acts as a manual gamma well counter/calculator and performs other useful functions in assessing radioactivity level. Packard Instrument Co., Inc. **165**

Air quality services. Literature pack describes company capabilities in meteorology, air quality, air physics, aerosol physics, and environmental and energy-related services. Meteorology Research, Inc. **166**

Clarification improvement. Bulletin 146B tells how the Graver Floc Barrier doubles clarifier capacity and reduces settling costs, which improve effluent quality. Ecodyne Graver Water Division **167**

Iron removal. Bulletin PE-004 explains how the Ferrofilter System with its reaction-driven Rotary Aerator removes iron from water by oxidation. Iron can be reduced to 0.1–0.3 ppm. Keene Corp. **168**

Tanks. Brochure describes welded tanks and pressure vessels fabricated to American Society of Mechanical Engineers, Underwriters Laboratories, and other rigid specifications. Airmark Corp. **169**

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.

Flow monitoring. Product catalog describes the company's line of unique flow and level monitoring devices. Useful for caustics, since sensor cannot corrode. Sensor Products Division of Wesmar **170**

Advanced sewage treatment. Brochure describes new lagoon system with two very advanced features for treatment in lagoons or ponds, or with activated sludge. Aeration efficiencies exceed 50%, and oxygenation efficiencies exceed 80%. TII Corp. **171**

Automated analysis. New guide describes modular instrumentation and accessories for automating laboratory analytical procedure. Included are spectrophotometry, titration, pH measurement, and automatic weighing. Arthur H. Thomas Co. **172**

Nuclear insurance. Brochure and papers describe the Nuclear Energy Liability-Property Insurance Association (NEL-PIA), how it works, and the nature and costs of nuclear insurance. NEL-PIA **173**

Wastewater treatment. Folder details wastewater treatment systems in steel or prestressed concrete for field construction. They are capable of up to 2 mgd of domestic wastewater. Pollution Control, Inc. **174**

Metering pumps. FMI Catalog RP 401-SAN lists complete line of metering pumps designed especially for sanitary service. All conform to milk ordinance code recommended by the U.S. Public Health Service. Fluid Metering, Inc. **175**

Obstruction removal. Brochure describes the "Delumper," which can chop, shred, accelerate flow, or condition oversize materials in sanitary chutes, pipes, and ducts. Cross contamination is prevented, as are bridging problems. Franklin Miller, Inc. **176**

Worker protection. Data sheet describes the MIRAN-201 multi-point ambient air monitor, which can measure any one of over 300 types of toxic vapors for the purpose of worker protection in keeping with OSHA rules. Wilks Scientific Corp. **177**

pH meters. Catalog GLP SI-20-3 lists and specifies pH meter models, electrodes, and pH accessories. Meters and electrodes are guaranteed. Corning Glass Works 178

Sewage pumping. Bulletin 840-1 describes the company's completely packaged sewage lift stations that use dual submersible pumps. Full descriptions and many applications are listed. Enpo-Cornell Pump Co. 179

Microporous filters. Brochures describe new line of precision-calibrated microporous filters for all applications requiring assured retention of bacteria and other particulates. Pore diameters are as low as 0.2-0.45 μ. Amicon Corp. 180

Chlorination. Bulletin 1840-1 describes a new line of gas chlorinators that meter exact amounts of chlorine in water and wastewater treatment to avoid inadequate or excessive dosages. Capital Controls Co. 181

Laboratory glassware. New 1976 catalog with 1372 pages lists glassware and other apparatus and supplies for laboratory use. SGA Scientific 182

Chemical lab services. Brochure describes services from an independent analytical laboratory (Calif.) for the industrial, educational, legal, and professional communities. West Coast Technical Service, Inc. 183

Flameless AA. Report No. 59 discusses use of flameless atomic absorption (AA) for analysis in connection with pollution, natural materials, petroleum products, and other applications. Instrumentation Laboratory Inc. 184

Grease filtering. Form GF-1898 Revised covers recommended steps in designing a grease filter-equipped kitchen exhaust system. Engineering data are included, along with sample calculation sheets. Research Products Corp. 185

Water treatment screens. Booklet WW1175 describes and illustrates the various applications for screens in a number of water and wastewater treatment processes. Johnson Division, UOP Inc. 186

Filtration systems. Bulletin F-10 describes filtration systems that offer ease-of-prime pumping, chemical mixing, and chemical addition. Nonmetallic polyethylene tanks are used. Liquids can be lifted from depths of over 20 ft. SERFILCO 187

Metric glassware. Brochure covers metric glassware that meets "specs" in National Bureau of Standards Handbook 105-2 for official weights and measures use. SGA Scientific 188

Trickle irrigation. Booklet, "A Full Line of Trickle Irrigation Products", covers agricultural, turf, and landscape applications. Rain Bird 189

Incineration. Bulletin No. 120 describes equipment for pollution-free incineration of solid wastes, as well as drying calcining, heating, and cooling. C-E Process Equipment 190

Water cleaning. Brochure, "Keeping pace with oxygen demand, filtration and water sterilization," lists aeration systems, diatomaceous earth (DE) filters, and ultraviolet water sterilizers. XODAR Corp. 191

Solar collectors. Technical booklet, "PPG Standard Solar Collector," describes company's latest equipment in the field. Lawrence P. Galanter, PPG Industries, 10 North, One Gateway Center, Pittsburgh, PA 15222 (write direct).

Texas water resources. Report 199 is an annotated bibliography of Texas water resources reports. Texas Water Development Board, P.O. Box 13087, Austin, TX 78711 (write direct).

Atmospheric hydrocarbons. Report 3/76 outlines methods for determining hydrocarbons in the atmosphere. C. W. van Gelder, Stichting CONCAWE, 60 Van Hogenhoucklaan, The Hague 2018, The Netherlands (write direct).

Stratosphere hazards. Report considers six potential stratospheric ozone hazards other than chlorofluorocarbons. Warren Muir, Council on Environmental Quality, 722 Jackson Place, N.W., Washington, DC 20006 (write direct).

Science publications. Listing includes environmental issues. Date: January 1, 1976. Printing and Publishing Office, National Academy of Sciences, Washington, DC 20418 (write direct).

Toxic substances. Report list as of October 1975. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, DC 20460 (write direct).

Recycling. *Progress Report on Recycling* tells of advances in materials and energy recovery from solid waste. Steel Products News Bureau, 633 Third Ave., New York, NY 10017 (write direct).

Breeder project. *Breeder Briefs* describes progress on the breeder reactor project. Mike Butler, Information Office, Clinch River Breeder Reactor Plant Project Office, P.O. Box U, Oak Ridge, TN 37830 (write direct).

Solar heat. Navy has published "Solar Heating of Buildings and Domestic Hot Water" (Technical Report R835) for home and business applications. Public Affairs Office, U.S. Naval Civil Engineering Laboratory, Naval Construction Battalion Center, Port Hueneme, CA 93043 (write direct).

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1976, 752 pp., $39.50/£21.70 ISBN: 0-12-666601-6

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VOLUME 5/1975, 267 pp., 90 figures, 61 tables,
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BOOKS

Proceedings of the Fourth Annual Industrial Pollution Conference of WWEMA. 63 papers and abstracts. Water and Wastewater Equipment Manufacturers Association, 7900 Westpark Drive, Suite 304, McLean, VA 22101. 1976. $25, paper.

These proceedings contain papers and abstracts from the pollution conference held at Houston, Tex., in March, and includes contributions from experts in the industrial and municipal wastewater communities. While many topics of vital concern are included, the emphasis is on water and resource recovery, which is of increasing importance in the light of present and projected water and materials shortages.

How to Save Gasoline. Public Policy Alternatives for the Automobile. Sorrell Wildhorn, et al. xv + 324 pages. Ballinger Publishing Co., 17 Dunster St., Cambridge, MA 02138. 1975. $17.50, hard cover.

This study evaluates public policies for conserving energy used by automobiles, and reports on the public dialogue concerning possible enactment of the various policies. Evaluation of energy conservation policies for private cars and policy alternatives are discussed. The book is part of The Evaluation of Measures to Conserve Energy, a continuing Rand Corp. program, and it compares alternatives of improving fuel economy through price rises as against regulatory means.

Strip Mining of Coal: Environmental Solutions. William S. Doyle. xi + 307 pages. Noyes Data Corp., Mill Road at Grand Ave., Park Ridge, NJ 07656. 1976. $32, hard cover.

The most immediately available energy source could be strip-mined coal, but the environmental problems involved could be staggering. This work provides comprehensive coverage of surface mining methods and land use; land reclamation; revegetation; acid mine drainage (AMD) and AMD control; and other very pertinent topics, including examples, case histories, and dollars involved. State agency contacts are also given.

Behavioral Toxicology. Bernard Weisse and Victor G. Laties, Eds. xxi + 469 pages. Plenum Publishing Corp., 227 W. 17th St., New York, NY 10011. 1975. $39.50, hard cover.

Are there changes in behavior when humans and animals are exposed to carbon monoxide, methylmercury, and other toxic substances? Possible answers to this and similar questions are given by experts who furnished contributions and discussions to this book; these experts are widely recognized in the field of effects on behavior and performance by drugs and pollutants. Teratological effects are also discussed.

Environmental Quality—1975: The Sixth Annual Report of the Council on Environmental Quality. xxxv + 763 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. 1975. $6.60, paper.

One emphasis is on carcinogens in the environment, a topic that has generated much interest of late. Perspectives and trends in water, air, solid wastes, hazardous materials, and noise are covered, as are related matters. The global environment, population, and endangered animal and plant species are also discussed.

The Genesis Strategy: Climate and Global Survival. Stephen H. Schneider with Lynne E. Mesirow. xxi + 419 pages. Plenum Publishing Corp., 227 W. 17th St., New York, NY 10011. 1976. $14.95, hard cover.

The weather is no longer a subject for small talk. Natural climatic changes could have beneficial or adverse effects, but the implications of climatic modification—quite possibly very adverse—need to be considered carefully. This book discusses these and other pertinent matters, explains why the world is generally unprepared for severe climatic changes—some caused by man's imprudence—and proposes possible ways out of the predicament.

Manual for Environmental Impact Evaluation. Sherman J. Rosen. viii + 232 pages. Prentice-Hall, Inc., Englewood Cliffs, NJ 07632. 1976. $12.95, hard cover.

Mandated by NEPA, the environmental impact statement is a fact of daily life. This book explains the environmental impact evaluation, how it is prepared, what goes into it, and the rationale behind the requirement for such an evaluation.

Polluted Groundwater. David Keith Todd and Daniel E. Orren McNulty. 179 pages. Water Information Center, Inc., 14 Vanderventer Ave., Port Washington, NY 11050. 1976. $16, hard cover.

This book reviews the literature on groundwater pollution brought about by man's activities. It discusses causes, monitoring methods, and control procedures. Among topics covered are pollution from wells, salt water and surface water, urban pollution, and industrial and agricultural pollution. Rather than prepare an annotated bibliography, the authors review groundwater pollution literature in essay form on a subject basis.

Analysis of Air Pollutants. Peter O. Warner. xi + 329 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, NY 10016. 1976. $24, hard cover.

This book offers a comprehensive discussion and how-to-do-it material concerning detection and quantitative determination of air pollutants. Many different analytical methods are discussed, as is determination of trace quantities of pollutants. Also considered is proper calibration of air sampling equipment.

Crisis in the Workplace: Occupational Disease and Injury. Nicholas A. Ashford. 589 pages. The MIT Press, 28 Carleton St., Cambridge, MA 02142. 1976. $16.95, hard cover.

The Occupational Safety and Health Act of 1970 implementation is not at all adequate to prevent occupational dangers, according to the author. He proposes that environmental priorities be redirected so that more emphasis is placed on the workplace environment where essentially all pollution begins. Also addressed are economic issues, federal regulations, and the ineffectualness of voluntary compliance. The author holds a doctorate in chemistry and a degree in law.

SO_x and NO_x Removal Technology in Japan—1976. 61 pages. Japan Management Association, Kyoritsu Building, 3-1-22 Shiba Park, Minato-ku, Tokyo, Japan. 1976. $36, including air mail postage.

This work contains material concerning latest Japanese contributions to SO_x and NO_x control technology.

Air Pollution Control in the Steel Industry. H. M. Englund and W. T. Berry, Eds. 58 pages. Publications Department, Air Pollution Control Association, 4400 Fifth Ave., Pittsburgh, PA 15213. 1976. $6 ($4.50 to APCA members), paper.

This book is one of the APCA reprint series that features what APCA considers to be outstanding papers from its Journal. Coke oven emission controls are discussed, as are acid gases, Claus plant operations, coke oven gas sulfur removal, occupational hazards of exposure to coal tar pitch volatiles, energy consumption, and other related topics.

Light Metals 1976, Volume 2. S. R. Leavitt, Ed. 631 pages. Metallurgical Society of AIME, 345 E. 47th St., New York, NY 10017. 1976. $26 ($16 to AIME members), paper.

This illustrated book contains papers presented at the 105th AIME Annual Meeting held at Las Vegas, Nev., this year. It covers alumina and bauxite production, cast shop technology, and environmental control. Among environmental topics is baghouse use, particulate emission control, dry scrubbing of pot gas, anodizing waste treatment, and wastewater disposal.

Solar Age. Periodical. SolarVision, Inc., Box 288, Vernon, NJ 07462. 1976. $20/yr; $30/2 yrs.

Many aspects of solar energy use are covered. Among them are solar-heated schools in operation, solar cooling, photovoltaics, biofuels, and ocean thermal gradients. Collectors and cells are and will be discussed, as well as storage batteries, financing, building design and orientation, and wind energy technology. Many acknowledged experts in the field are contributing to this publication.

Toward A National Ocean Policy: 1976 and Beyond. Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. 1976. $2.60. Stock No. 038-000-00263-5.

This report analyzes results of the 1975 Law of the Sea Conference held at Geneva, Switzerland. It presents treaty alternatives in future negotiations; outlines options in policy for fisheries, national security, the marine environment, navigation, resources, and research; and stresses the national and international need for a comprehensive management approach to ocean use.

Occupational Monitoring for Genetic Hazards. Marvin S. Legator and Alexander Hollaender, Eds. The New York Academy of Sciences, P.O. Box 5075, F.D.R. Station, New York, NY 10022. 1975. $8, plus $1 for mailing and handling.

Published last December 31, this work, Volume 269 of the Annals, marks the first attempt to focus on concerns and problems of the occupational environment as related to mutagenic compounds. Of special concern are existing and proposed screening techniques, relations of cellular studies to possible mutagenicity, identification of mutagenic compounds, and labor and management efforts for long-term testing.

Deserts of the World. M. P. Petrov; R. Lavoot, translator. 435 pages. Halsted Press, 605 Third Ave., New York, NY 10016. 1976. $47.50.

Originally written in Russian, this book describes and discusses many aspects of deserts. Included are studies of environmental conditions, geomorphology, natural resources, animal and plant life, and adaptation to unfavorable habitats. Deserts on all the continents are dealt with.

Introduction to Pulping Technology. 12 cassette tapes and 20-chapter study guide. Publications Order Department, Technical Association of the Pulp and Paper Industry, One Dunwoody Park, Atlanta, GA 30341. 1976. $195 ($165 to TAPPI members).

This home study course covers every facet of pulping technology from wood structure and anatomy to end products. Among topics of environmental interest are acid recovery and by-products, paper and board recycling, and pollution problems and abatement.

MEETING GUIDE

June 20–22 Portland, Me.
The Future of Wood as an Energy Source. Gorham International Inc.
Write: Andrew C. Nyce or Alvin G. Keene, Gorham International Inc., Gorham, Me. 04038

June 20–25 Blacksburg, Va.
Second International Conference on Numerical Methods of Geomechanics. Engineering Foundation
Among the topics to be discussed are waste disposal and environmental engineering. *Write:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

June 20–25 New Orleans, La.
96th Annual Conference. American Water Works Association (AWWA)
Theme is "Water: Spirit of '76." *Write:* Jerry Righthouse, Meetings Manager, AWWA, 6666 W. Quincy Ave., Denver, Colo. 80235

June 24–25 Los Angeles, Calif.
Stack Sampling Seminar. Research Appliance Co. (RAC)
Write: Ralph J. Bulger, Vice President, Marketing, RAC, Route 8, Gibsonia, Pa. 15044

June 24–27 Amherst, Mass.
Toward Tomorrow in Bicentennial America. The University of Massachusetts and the New England Solar Energy Association
Alternative technological and life-style issues will be discussed. *Write:* Fran Koster, Bicentennial Coordinator, University of Massachusetts, Amherst, Mass. 01002

June 25 Houston, Tex.
Marine/Offshore Industry Outlook Conference. Texas A&M University's Sea Grant Program and the Industrial Economics Research Division as well as the Marine Services Association of Texas
Write: Dewayne Hollin, 1200 South Post Oak Road, Suite 422, Houston, Tex. 77027

June 27–30 Cincinnati, Ohio
Third National Conference on Complete WateReuse: Symbiosis as a Means of Abatement for Multi-Media Pollution. American Institute of Chemical Engineers (AIChE) and EPA: Technology Transfer
Write: Lawrence K. Cecil, Consulting Chemical Engineer, 418 Lincoln Building, 44 Main St., Champaign, Ill. 61820

June 27–30 Lincoln, Neb.
1976 Summer Meeting. American Society of Agricultural Engineers (ASAE)
Environmental topics will be discussed. *Write:* Roger R. Castenson, ASAE, 2950 Niles Road, St. Joseph, Mich. 49085

June 27–July 1 Portland, Ore.
69th Annual Conference & Exhibition. Air Pollution Control Association (APCA)
Write: Public Relations Dept., APCA, 4400 Fifth Ave., Pittsburgh, Pa. 15213

June 27–July 1 Boulder, Colo.
Fifth International CODATA Conference. CODATA
Write: Numerical Data Advisory Board, National Research Council, 2101 Constitution Ave., N.W., Washington, D.C. 20418

June 27–July 2 San Francisco, Calif.
Health Physics Society and the Radiation Research Society Meeting. Health Physics Society and the Radiation Research Society
Write: Richard J. Burk, Jr., executive director, 4720 Montgomery Lane, Suite 506, Bethesda, Md. 20014

June 28–July 2 Andover, N.H.
Environmental Sciences: Water. Gordon Research Conferences
Write: Alexander M. Cruickshank, director, Gordon Research Conferences, Colby-Sawyer College, New London, N.H. 03257

July 4–9 Henniker, N.H.
Assessment of Environmental Standards. Engineering Foundation
Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

July 5–9 Johnson, Vt.
Occupational and Industrial Health. Committee D-22 on Methods of Sampling and Analysis of Atmospheres of the American Society for Testing and Materials (ASTM)
Write: Steven S. Ross, MBA Communications, Inc., 555 Madison Ave., New York, N.Y. 10022

July 6–9 West Lafayette, Ind.
Third Purdue Compressor Technology Conference. Purdue University
Write: Division of Conferences, Purdue University, Stewart Center, West Lafayette, Ind.

July 11–16 Henniker, N.H.
Conference on Wind Energy Conversion. Engineering Foundation
Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

July 12–15 San Diego, Calif.
Sixth Annual Intersociety Conference on Environmental Systems. American Society of Mechanical Engineers (ASME)
Write: Gail Jannon, Meetings Dept., ASME, 345 E. 47th St., New York, N.Y. 10017

July 13–14 Kingston, R.I.
Annual North Eastern Regional Antipollution Conference (ANERAC-1976). University of Rhode Island
Theme is "Assessing the Environmental Impact of the Petroleum Industry in the Northeast." *Write:* Prof. Donald Sussman, Department of Civil and Environmental Engineering or Prof. Stanley Barnett, Department of Chemical Engineering, University of Rhode Island, Kingston, R.I. 02881

July 18–21 Denver, Colo.
Land Use and Nuclear Facility Siting: Current Issues. Atomic Industrial Forum, Inc. (AIF)
Write: Conference Department, AIF, 7101 Wisconsin Ave., N.W., Washington, D.C. 20014

July 18–23 Los Angeles, Calif.
1976 Intersociety Conference and Exposition on Transportation. American Society of Mechanical Engineers (ASME), American Economic Association and others
Write: Gail Jannon, ASME, 345 E. 47th St., New York, N.Y.

July 25–30 Rindge, N.H.
Recycling Implementation—Engineering and Economics. The Engineering Foundation
Write: Engineering Foundation Conferences, 345 E. 47th St., New York, N.Y. 10017

July 25–30 Geneva, N.Y.
35th Research Conference on Instrumentation Science. Instrument Society of America (ISA)
Environmental topics will be included. *Write:* ISA, 400 Stanwix St., Pittsburgh, Pa. 15222

Courses

June 14–18 Washington, D.C.
Solar Heating and Cooling—Residential and Commercial Applications. George Washington University
Fee: $435. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

June 14–18 Hartford, Conn.
Solar Energy for Buildings. The Hartford Graduate Center
Fee: $250. *Write:* Donald B. Florek, Program Manager, The Hartford Graduate Center, 275 Windsor St., Hartford, Conn. 06120

June 14–18 Atlantic City, N.J.
12th Institute on Noise Reduction. Institute on Noise Control
Fee: $400. *Write:* James. H. Botsford, Director, Institute on Noise Control, Inc., 3456 Altonah Rd., Bethlehem, Pa. 13017

June 15–17 Albuquerque, N.M.
8th Annual Heat Pipe Technology. University of New Mexico
Fee: $275. *Write:* Doyle L. Caton, Technology Application Center, University of New Mexico, Albuquerque, N.Mex. 87131

(continued on page 614)

June 20–25 Fort Collins, Colo.
A Series of Short Courses: Atomic Absorption Spectroscopy, Water Chemistry and Introduction to Electroanalytical Chemistry. Colorado State University/Dept. of Chemistry

Fee: $200. *Write:* Anthony P. Schmitt, Dept. of Chemistry, Colorado State University, Fort Collins, Colo. 80523

June 20–25 Fort Collins, Colo.
A Series of Short Courses: Standard Methods of Water Analysis, Ion Selective Electrodes and Optical Emission Spectroscopy. Colorado State University/Dept. of Chemistry

Fee: $200. *Write:* Anthony P. Schmitt, Dept. of Chemistry, Colorado State University, Fort Collins, Colo. 80523

June 21–24 Dallas, Tex.
Atmospheric Sampling, Course No. 435. Air Pollution Training Institute

Fee: $200. *Write:* Registrar, Air Pollution Training Institute, MD-17, National Environmental Research Center, Research Triangle Park, N.C. 27711

June 21–25 Philadelphia, Pa.
Air Pollution Meteorology, Course No. 411. Air Pollution Training Institute

Fee: $135. *Write:* Registrar, Air Pollution Training Institute, MD-17, National Environmental Research Center, Research Triangle Park, N.C. 27711

June 21–25 Philadelphia, Pa.
Principles and Practice of Air Pollution Control. Air Pollution Training Institute

Fee: $135. *Write:* Registrar, Air Pollution Training Institute, MD-17, National Environmental Research Center, Research Triangle Park, N.C. 27711

June 22–24 Philadelphia, Pa.
Air Pollution Administration III, Course No. 460. Air Pollution Training Institute

Fee: $90. *Write:* Registrar, Air Pollution Training Institute, MD-17, National Environmental Research Center, Research Triangle Park, N.C. 27711

June 21–25 Region IV
Surveillance and Monitoring of Estuaries, Course No. 161.3. U.S. Environmental Protection Agency (EPA)

Fee: $110. *Write:* Training, U.S. EPA, Region IV, Environmental Research Lab, College Station Road, Athens, Ga. 30601

June 28–July 2 Cincinnati, Ohio
Effluent Monitoring Procedures: Nutrients, Course No. 164.3. U.S. Environmental Protection Agency (EPA)

Fee: $175. *Write:* Registrar, National Training Center, MPOD, OWPO, WHM, U.S. EPA, Cincinnati, Ohio 45268

July 7–9 East Brunswick, N.J.
Pesticide Residue Analysis. The Center for Professional Advancement

Fee: $325. *Write:* Mrs. Edith Webb, Registrar, The Center for Professional Advancement, P.O. Box 997, Somerville, N.J. 08876

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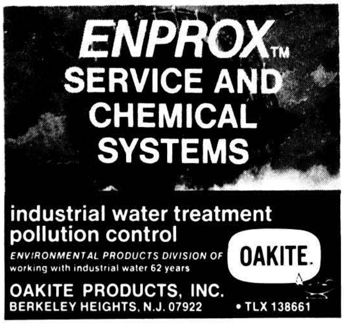

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Westinghouse International School for Environmental Management. Westinghouse Electric Co.
Fee: $2900. *Write:* James H. Wright, general manager, WESD, P.O. Box 1899, Pittsburgh, Pa. 15230

July 12 Chicago, Ill.
Microscopial Identification of Asbestos, Course No. 508. McCrone Research Institute
Fee: $400. *Write:* Registrar, McCrone Research Institute, 2820 S. Michigan Ave., Chicago, Ill. 60616

July 12–16 Schenectady, N.Y.
Seventh Annual Industrial and Product Noise Control Institute. Union College/Graduate Studies and Continuing Education
Fee: $475. *Write:* Sabina Lawrence, Institute Secretary, Union College, Graduate Studies and Special Programs, Schenectady, N.Y. 12308

July 12–August 20 Boston, Mass.
18th Annual Graduate Summer Session of Statistics in the Health Sciences. Harvard University/School of Public Health
Fee: $110. *Write:* Jane Worcester, Dept. of Biostatistics, Harvard School of Public Health, 677 Huntington Ave., Boston, Mass. 02115

July 14–16 Berkeley, Calif.
Blue-Green Algal Ecology and Management. University of California at Berkeley/University Extension
Advance enrollment is required. Fee: $150. *Write:* Continuing Education in Engineering, University of California Extension, 2223 Fulton St., Berkeley, Calif. 94720

July 14–16 Cambridge, Mass.
The Design of the Industrial Workplace. Harvard Graduate School of Design
Fee: $250. *Write:* Patricia L. McManus, Harvard Graduate School of Design, Gund Hall, L-37, Cambridge, Mass. 02138

July 19–23 Madison, Wis.
Water Distribution Plant Design. The University of Wisconsin–Extension
Fee: $350. *Write:* John T. Quigley, program director, Dept. of Engineering, University of Wisconsin–Extension, 432 N. Lake St., Madison, Wis. 53706

July 19–31 Davis, Calif.
Man, Energy and the Environment. University of California Extension
Fee: $225. *Write:* University Extension, University of California, Davis, Calif. 95616

July 26–30 Madison, Wis.
Renewable and Non-Renewable Resources. The University of Wisconsin–Extension
Fee: $300. *Write:* Charles E. Dorgan, program director, Dept. of Engineering, University of Wisconsin–Extension, 432 N. Lake St., Madison, Wis. 53706

July 26–30 Nashville, Tenn.
Pollution Control: Meeting OSHA Standards Through Infrared Spectroscopic and Gas Chromatographic Techniques. Fisk Institute
Fee: $225. *Write:* Director, Fisk Institute, Box 8, Fisk University, Nashville, Tenn. 37203

July 26–30 Richmond, Va.
Application and Practice of Gas Chromatography. Hewlett-Packard
Fee: $275. *Write:* Hewlett-Packard, 1501 Page Mill Rd., Palo Alto, Calif. 94304 or any sales office.

July 26–30 Golden, Colo.
Shale Oil—Its Production, Properties, and Utilization. Colorado School of Mines
Fee: $350. *Write:* P. F. Dickson, professor and head, Chemical and Petroleum-Refining Engineering, Colorado School of Mines, Golden, Colo. 80401

July 29–31 Houston, Tex.
Simplex Optimization in Research and Development. University of Houston/Dept. of Chemistry
Course material finds application in process engineering and chromatography. Fee: $250. *Write:* S. N. Deming, Simplex Optimization in Research and Development, Dept. of Chemistry, University of Houston, Houston, Tex. 77004

Call for Papers

June 7 deadline
Sixteenth Annual Hanford Biology Symposium. U.S. Energy Research and Development Administration and Battelle Memorial Institute/Pacific Northwest Laboratories
Conference will be held on September 27–29 at Richland, Wash. The symposium is entitled "Pulmonary Macrophage and Epithelial Cells." *Write:* Mrs. Judith A. Rising, Symposium Secretary, Biology Dept., Battelle-Northwest, Richland, Wash. 99352

June 15 deadline
Fibrous Structures in Gas and Liquid Filtration. Fiber Society Symposium
Conference will be held on November 9–10 at Princeton, N.J. *Write:* Dr. George Lamb, Senior Scientist, Textile Research Institute, Princeton, N.J. 08540

July 1 deadline
33rd Annual Meeting of the East Central Section of the Air Pollution Control Association (APCA).
Conference will be held September 8–10 in Indianapolis, Ind. *Write:* John M. Sell, 5205 Lancelot Dr., Indianapolis, Ind. 46208

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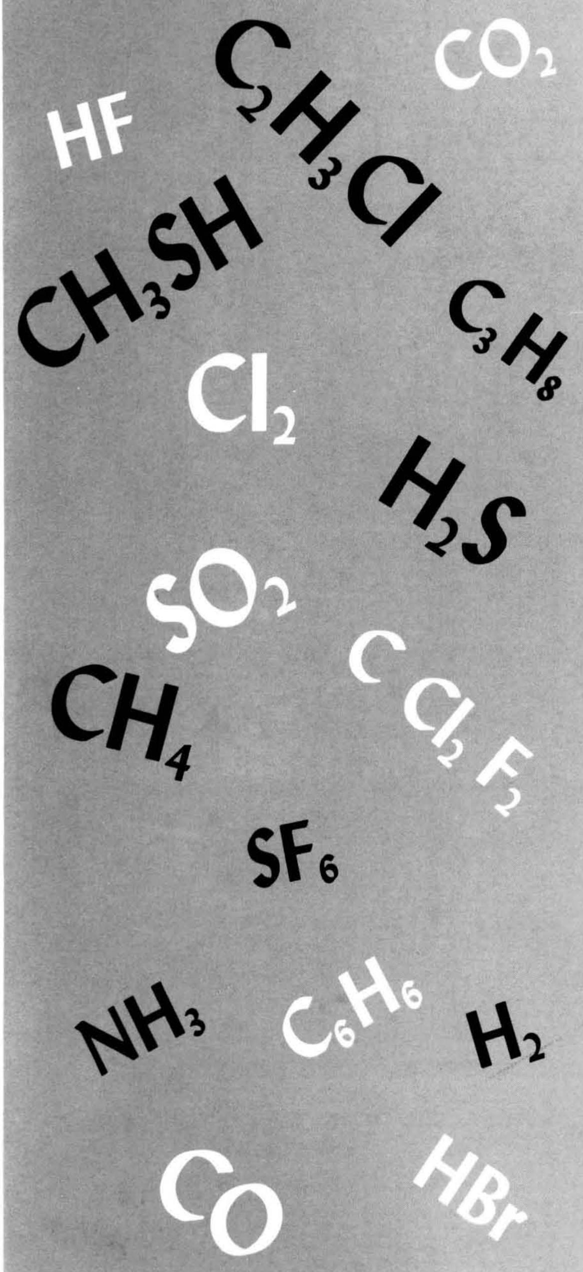

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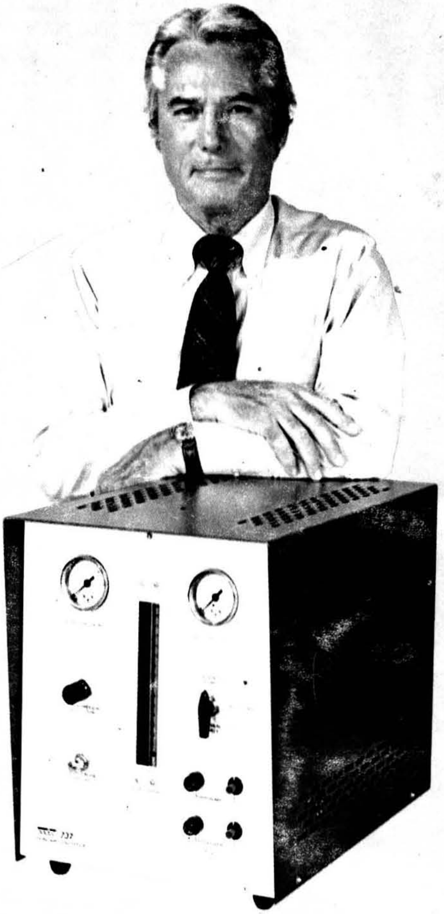

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