

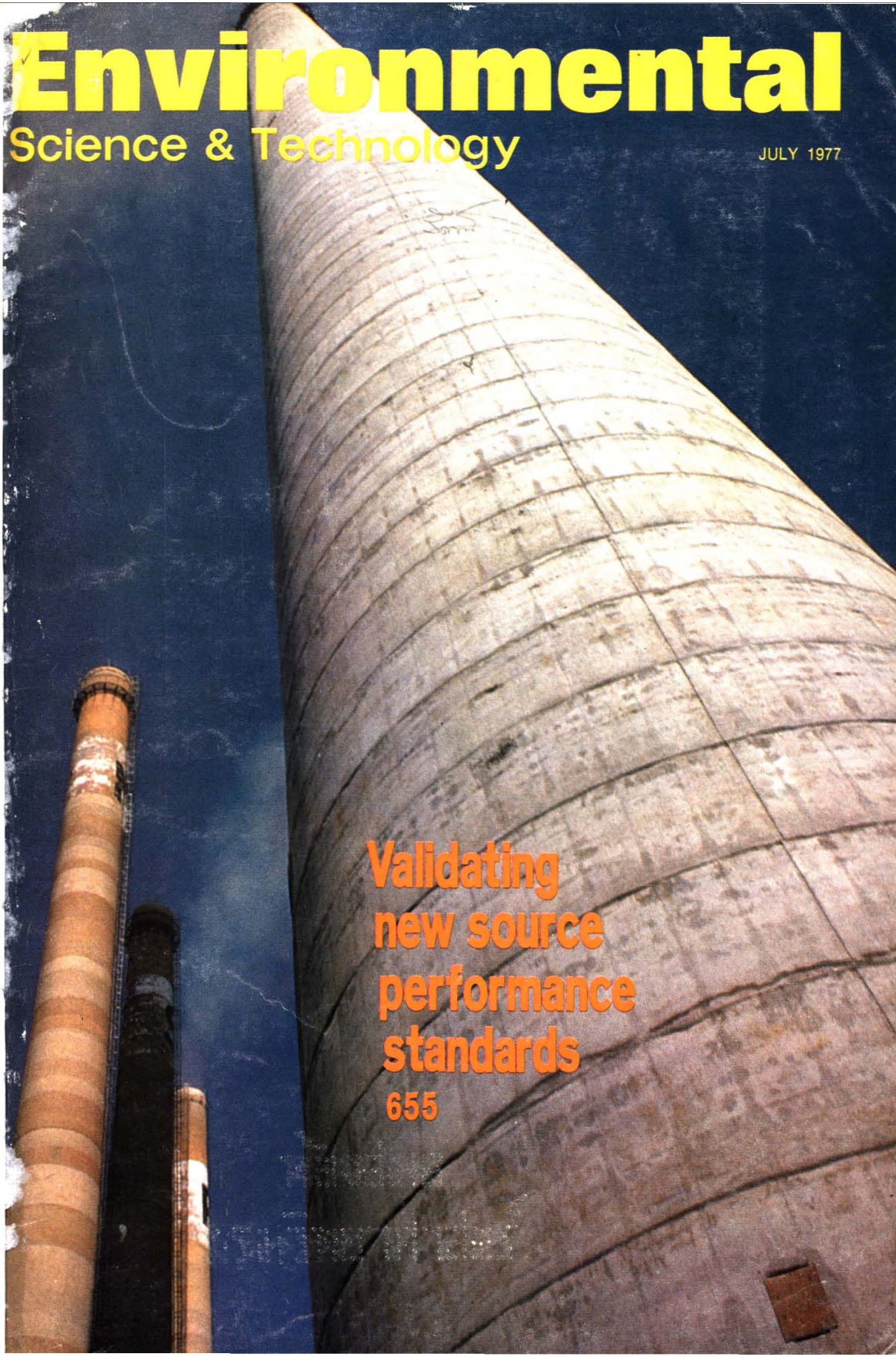
Environmental

Science & Technology

JULY 1977

**Validating
new source
performance
standards**

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For automatic, cyclical sampling of particulates, H₂S gas, and fluorides in ambient air...

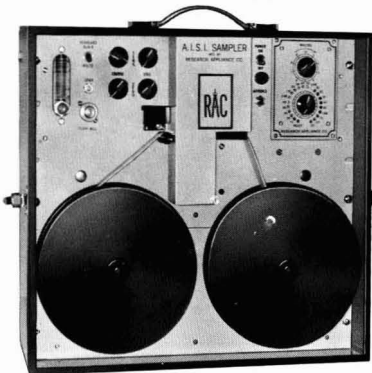
specify RAC filter tape instruments



RAC Model G2 SER Monitor

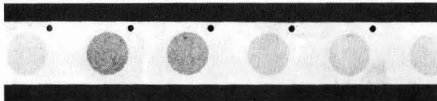


RAC Model G2DT Fluoride Sampler



RAC Model G2-T-600 Monitor

Section of filter tape showing typical 1" dia sample spots.



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For details on *dual-tape fluoride sampler*, send for **BULLETIN 2356**.

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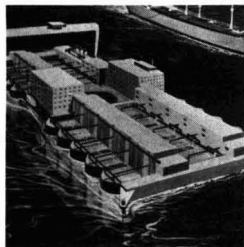
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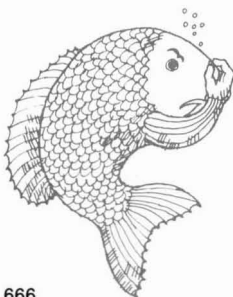
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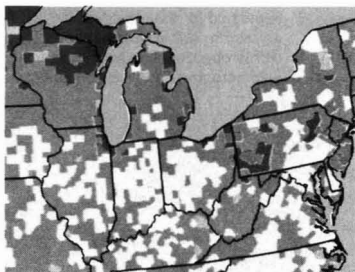
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For author's guide and editorial policy, see June
1977 issue, page 575, or write Katherine I. Biggs,
Manuscript Reviewing Office ES&T

Occasionally *ES&T* conducts a survey of its subscribers for the purpose of evaluating their attitudes toward the editorial content of the Journal. The most recent survey was conducted during the fall of 1976 and attempted to define the readership attitude among the academic, industrial, government and engineering segments of the total circulation. I am pleased to summarize for your information some of the major findings.

Apparently the vast majority of our subscribers look at every issue and about 35% read at least half of each issue. These figures are significantly higher than comparable reader-involvement percentages for sister journals. In terms of the usefulness of publications, *ES&T* appears to be doing a creditable job on an overall basis, but scored lower than sister publications (*Analytical Chemistry*, *Limnology and Oceanography*, *Journal of the Water Pollution Control Federation*, and *Journal of the Air Pollution Control Association*) in the utility of coverage in special interest subjects.

A characteristic of *ES&T* has always been its diverse readership and it is not surprising, therefore, that significant differences arise in the expressed interest of academic recipients (research and engineering), industrial recipients (air and industrial water pollution), and government recipients (instrumentation monitoring and industrial water pollution). Those whose interest in a particular subject is high tended to rate *ES&T* coverage in that area as very good. Exceptions were noted with respect to health-related coverage in which above-average interest exists, but present coverage scores below average. On the other hand, we may be covering solid waste, noise pollution, remote sensing and transportation more heavily than readership interest supports.

ES&T is strongly perceived as unique among other environmental publications because of its breadth of scope, balance between technical information and news, and for its factual format. Nearly all readers enjoy both the Feature/Outlooks section as well as the research papers, although differences exist with regard to individual preferences.

Basically the survey results constitute a vote of confidence for *ES&T* from its readers. If you would like to discuss any particular deficiency in *ES&T*'s present coverage, I would welcome an opportunity to hear from you. Since our data indicate that nearly 60% of all readers read this column, I look forward to receiving some letters.



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WIND ALARM.

A black and white photograph showing several large tower cranes silhouetted against a bright sky. The cranes are positioned on a construction site, with their complex lattice structures and long jibs clearly visible. The foreground shows the dark, silhouetted framework of the building under construction.

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cranes keep their sea legs.

CURRENTS

INTERNATIONAL

About 32 mi² of West Germany known as the Hambach Forest will be strip-mined for lignite coal beginning late next year. By the year 2030, 2.4 billion tons of lignite coal is expected to be mined, and in the process, four villages will be razed, and 3000–10 000 inhabitants will be displaced. Lich-Steintrausse, 25 mi west of Cologne, will be the first village to disappear, followed by Etzweiler, Manheim and Morschenich. Combustion of lignite supplies 33% of the country's electricity needs. On another energy matter, the Workshop on Alternative Energy Strategies, comprised of 35 men from 15 countries, released its report "Energy: Global Prospects 1985–2000." In doomsayer fashion, the report concludes that despite conservation efforts and shifts to other fuels, the non-Communist world will be faced with an oil shortage, perhaps as early as 1981, depending on the vagaries of Saudi Arabia.

WASHINGTON

In his environmental message, President Jimmy Carter stressed the enforcement of laws already on the books. In the first such message to be sent to Congress since 1973, Carter said "... that the primary need today is not for new comprehensive statutes but for sensitive administration and energetic enforcement of the ones we have." Carter endorsed strict clean air and water regulations and more parklands and wilderness areas. His message stressed reforms to eliminate hazards of the workplace, and the need



President Carter

for a government study on global environmental trends. CEQ was directed to take the lead in an interagency effort to coordinate research and collect data to eliminate the problems of toxic substances. EPA was asked to work with Congress to amend the pesticide laws.

EPA published a candidate list of toxic chemicals, revealed increased power industry commitment to scrubbers, and unveiled a new SO₂ control system for power plants. More than 30 000 chemicals that may be subject to the reporting requirements of the Toxic Substances Control Act were published in the *Federal Register* of March 9. In a "Summary Report—Flue Gas Desulfurization Systems—Nov.–Dec. 1976," EPA revealed that nearly three times more scrubbers (122) are being operated, built or planned by power companies than in 1973. On the subject of SO₂ control, EPA stated that a new system using a dual alkali process is entering the second phase of a demonstration project in Louisville, Ky.

The record of the Depts. of HEW and Labor in setting workplace standards for toxic substances, including carcinogens, under the 1970 Occupational Safety and Health Act, is bleak. While HEW has cited thousands of substances as being dangerous, Labor has set standards for only 15, according to a recent General Accounting Office report. Among the recommendations made by GAO was one that stated that if additional funds can be used effectively, Labor should allocate these to developing health standards, and information, education and training activities. OSHA assistant secretary Eula Bingham recently promised "to refocus . . . inspection efforts on the most serious workplace health and safety problems," and to "revise and simplify necessary regulations that are needlessly detailed, complicated or unclear."

The FDA, EPA and the Consumer Product Safety Commission have proposed banning chlorofluorocarbons by 1979. While all nonessential uses of the aerosol spray would be phased out, certain products for which adequate

substitute propellants are not available would be exempted. These include: sprays used by asthma patients, a mine safety warning device, release agents for some plastic molds and some insecticides sprayed from aircraft. The first step in the proposal, which halts the manufacture of these propellants for nonessential uses, would take effect Oct. 15, 1978. On Dec. 15, 1978, all companies would have to cease using existing supplies of these compounds in the manufacture of nonessential items. The third step would halt interstate shipment of these products.

The first loan guaranty for a commercial geothermal energy project was approved by ERDA. The \$9 million guaranty to Republic Geothermal, Inc. (Santa Fe Springs, Calif.) will be used to drill and develop 11 new production and four reinjection wells in the East Mesa area of Imperial Valley, Calif. The drilling project's total cost is estimated at \$12 million, 75% of which is covered by the federal loan. Republic has indicated that it will build an electric power plant that would generate more than 36 MW of electricity; this plant could be operational in the early part of the next decade. The ERDA loan, which covers only the drilling and developing of the geothermal wells, was authorized under the Geothermal Research, Development and Demonstration Act of 1974.

STATES

Vermont now has a law regulating the storage of atomic wastes that is believed to be one of the strongest such laws in the nation. Signed into law as Act No. 77 by Governor Richard Snelling on April 26, the law is designed to prevent the siting of a nuclear waste storage facility in the state, one of 30 sites under consideration by ERDA. Under the law, the Vermont General Assembly would have to agree that such a plant would promote the general welfare and would not adversely affect health or the environment. In another matter, the governor recently approved a bill prohibiting the sale of detergents containing phosphate compounds in



Vermont governor Snelling

greater than trace amounts after April 1, 1978. The law, Act No. 39, became effective in April.

Northern Virginia's treated drinking water contains levels of chloroform that exceed EPA's suggested maximum of 100 ppb. Recent tests of potable water from the Occoquan Reservoir, the region's primary source of drinking water, revealed levels of chloroform of 232.6 ppb. A \$80 million advanced sewage treatment plant is scheduled to begin operation next year. But, according to engineer Clifford W. Randall, this plant won't correct the problem of chloroform formation since 80% of the organic pollution in the reservoir comes from urban and agricultural runoff. Chlorine used to disinfect the raw water reacts with organic matter to form chloroform. As steps to correct the problem, the Fairfax County Water Authority proposed to reduce the quantity of chlorine used in treatment, and Fairfax supervisors passed a motion saying "urban runoff must be reduced."

Connecticut's DEP plan calling for installation of gasoline vapor recovery devices at 80% of the service stations in the state was turned down by the state regulation review committee for the fourth straight time. The Dept. of Environmental Protection had estimated the average cost to service stations to be \$2400/station, which the station could recoup from motorists. This proposed regulation was submitted to EPA as part of Connecticut's transportation control plan. Because the state failed to agree on the installation of these devices, the federal EPA intends to require 95% of the service stations in the state to install vapor controls by 1978. To date, EPA has required 17 states to adopt vapor recovery systems.

New rules and regulations governing solid waste disposal facilities in New York go into effect next month. Designed to reduce the environmental damage resulting from the operation of disposal facilities, the regulations set minimum standards that affect 642 municipal and private landfills, 41 municipal incinerators and 100 refuse

transfer stations and recycling facilities. The cost of these regulations should encourage consolidation of services, which in turn makes resource recovery and recycling systems more feasible, according to Commissioner of Environmental Conservation Peter Berle. Among the new regulations are the requirement that operators of sanitary landfills and incinerators complete a course in solid waste management, and that facilities be permitted by February 1978 or 1979, depending on when they began operation.

Allegheny County, Pa., is the site of an energy conservation and development program that enlists the efforts of citizens of the county in voluntarily conserving energy. Called project "Pacesetter," the program is sponsored by the nonprofit organization, Americans for Energy Independence. Phase one was simply an organization and enlistment program. Phase two began this June and will be completed in the spring of 1978. The recommendations of task forces composed of 400 community leaders were presented in June during Energy Week; public support was then elicited to make the county energy self-sufficient. A recently released report of the Northeastern Illinois Planning Commission found that the six counties of northeastern Illinois used 58% of the energy consumed in the state, but less per capita than any other region.

MONITORING

Instrumental analytical programs support water management, according to Perkin-Elmer (Norwalk, Conn.). As an example, for checking on corrosion control, solids separation, organic/inorganic dissolved solids and toxic materials removal, and other municipal/industrial monitoring needs, a whole battery of sophisticated analytical instruments helps Calgon Corp., for example, to conduct a smooth and very effective water management program for numerous customers. Perkin-Elmer also says that this instrumentation will be vital to keeping tabs on emissions from the burning of coal. For instance, knowledge of carbon, hydrogen, nitrogen, sulfur, and trace element contents, especially when gained through non-destructive testing, can go a long way to improve coal cleaning and burning strategies aimed at minimizing pollution.

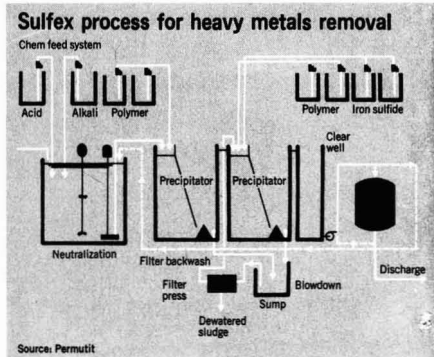
One way to measure water quality continuously is with the NASA (Houston, Tex.) automated, on-line Water Monitor System (WMS), whose modular components were developed for NASA by Boeing, TRW, and other

contractors, (ES&T, April 1975, p 294). Among the many parameters that can be measured are chemiluminescence/bacteria, coliform, bioluminescence, total oxygen demand, nitrate/nitrite, pH, chloride, and total organic carbon. The idea of the WMS is to provide data in real time, or as close to real time as possible, so that standards for high-quality effluent can be achieved, and potential for reclamation/reuse of water can be enhanced. A WMS installation is at Houston's Southwest Treatment Facility.

TECHNOLOGY

For drying agricultural products, heat from a coal-oil slurry mixture could be an alternative to oil alone, when immediate replacement of oil-burning equipment is uneconomical. Acurex Corp. (Mountain View, Calif.) is to demonstrate this concept for tobacco drying at the Lorillard Division of Loews (Danville, Va.). The Acurex concept involves burning pulverized coal, held in liquid suspension and mixed with oil, in boiler equipment designed to burn oil. To put the idea to work, the firm has a \$2 million ERDA contract. Acurex views slurry technology as "near-term," meaning that only minor problems need to be solved to make it cost-competitive with oil burning systems.

Removing heavy metals from wastewaters by precipitation as sulfides is practical, according to new process technology of the Permutit Co. At this year's Purdue Industrial Waste Conference, Murray Scott said that the company's Sulfex process removes most chelated metals and simultaneously reduces hexavalent chromium as the other heavy metals are precipitated as sulfides. For best results, two precipitators are used. A large part of the metals are removed by hydroxide precipitation in a first unit. Residual metals in the effluent of the first unit are then polished by sulfide



precipitation in the second unit. Permutit will have two 40 gpm plants, using the process, in operation before the end of the year.

A pollutant turned into an anti-pollution chemical? Yes, according to Rhône Poulenc S.A. (Paris, France).

Previously, iron (II) sulfate (FeSO_4) of high grade, a titanium ore beneficiation by-product, was diluted and discharged out to sea. However, Rhône Poulenc found that FeSO_4 , converted to iron (II) chlorosulfate, becomes a very effective flocculant. This flocculant can tie up heavy metals and phosphates, and settle them out of water, the company says. There are plans to use the flocculant, marketed as "CLAIRTAN", to protect Lake Zurich (Switzerland), and to process drinking water for Paris with a pilot unit at Choisy-le-Roi. Meanwhile, "CLAIRTAN" is being used to supply water (up to 150 000 m^3/d) to the industrial area of Le Havre, France.

One use for waste cellulose fiber is to make energy-saving insulating board.

The Ontario Research Foundation (ORF, Mississauga, Ont., Canada) developed a way to combine the fiber with a certain resin, and create an excellent insulating material. The material will retain its shape, and be immune from settling. It can be produced in a variety of shapes—for instance, to insulate pipes—and can be laminated with vapor-barrier paper or heat-reflecting aluminum foil. The material can be made flame retardant. The ORC has also developed a new method to determine pesticide residue on vegetables, to meet Canada's pesticide registration regulations.

Where might heavy metals in the aquatic environment end up? They could be taken up by water plants. A.

Mudroch of the Canada Center for Inland waters told the Second American Chemical Society/Chemical Institute of Canada Joint Conference (Montreal, May-June). For example, certain *Typhae* species' roots take up chromium, copper, lead, nickel, and zinc. A water lily might absorb chromium, copper, and nickel, while submerged *Myriophyllum* was high in chromium, cobalt, copper, and lead. Plant studies were made in an artificial marsh in Lake St. Clair, mainly from April-November 1976, normally in water in depths of 0-50 cm. Metals were in ppm ranges; mostly in plants and sediments, and much less in the water. Water pH varied 7-8, depending on the month.

One approach to disposal of radioactive waste involves

"glassified" technique. Glass beads so small that they are almost powder could be treated with a chemical that will

react with radioactives such as plutonium, and strontium and cesium isotopes, and bind these "hot" materials to the glass. The task of finding the optimum binding chemical that will also remove radioactives is being handled by John Geldard of Clemson University (S.C.). Once the "hots" are so bound to the commercially available glass beads that they cannot be scraped off, effluent is safe for discharge, and the beads, now radioactive, could be melted and molded into bricks, and buried with no danger of leaching out and entering the groundwater supply. Geldard has \$150 000 of ERDA support to develop the concept.

INDUSTRY

Clean air rules require particulate suppression, and create a need for electric precipitators (ep) to do the job. To enhance performance,

Research-Cottrell has been building $1/16$ -scale models of every utility ep ordered (*ES&T*, January 1977, p 24). This procedure often helped to identify and remove "bugs" before they could cause serious down time in a full-scale system. This "debugging" is further enhanced by a full-size model—minus ash hopper or gas flow—aimed at optimizing the reliability of every one of the thousands of hardware components comprising an ep. Every part and mechanical function is "shaken down," and the company expects to shorten lead time from inception to a new "nuts and bolts" idea to incorporation in a working ep by a factor of 10.

Composting may be the name of the garbage game in Hong Kong, and

Nissho-Iwai Co., Ltd. (Tokyo, Japan) will help to set up a plant to mix Hong Kong's garbage after it is crushed and mixed with manure. The Nissho-Iwai approach will convert even the highly moisture-laden garbage into compost at the rate of 240 tpd over an 8-h day. The Japanese firm also will help to do a study concerning the solvent refining of brown coal from the Latrobe Valley, Australia. The idea is to determine feasibility of refining this brown coal to a high-grade char for metallurgical use. In Japan, Nissho-Iwai is known as *sogo shosha*, or company that "meets challenges of building new environments for living."

"Technology exists not only to control waste . . . but to recover and recycle the valuable raw materials," Lars

Olsson, president of SF Air Control, Inc. (Old Greenwich, Conn.), a part of AB Svenska Fläktfabriken (Fläkt) (Sweden), said. However, he noted that "we must make better use of the systems that have been developed." One key to

better use that Olsson suggested is the Fläkt-RRR system with which a 120-tpd demonstration plant is working near Stockholm. It handles unsorted municipal solid waste from which steel, glass, paper, and plastics are separated for eventual reuse. The remainder, mostly organic materials, can be converted into fuel. Olsson believes that a recovery plant can economically reduce initial quantities of refuse by 90%.



SF Air Control pres. Olsson

By 1985, meeting just three water, air, and noise regulations will cost Du Pont

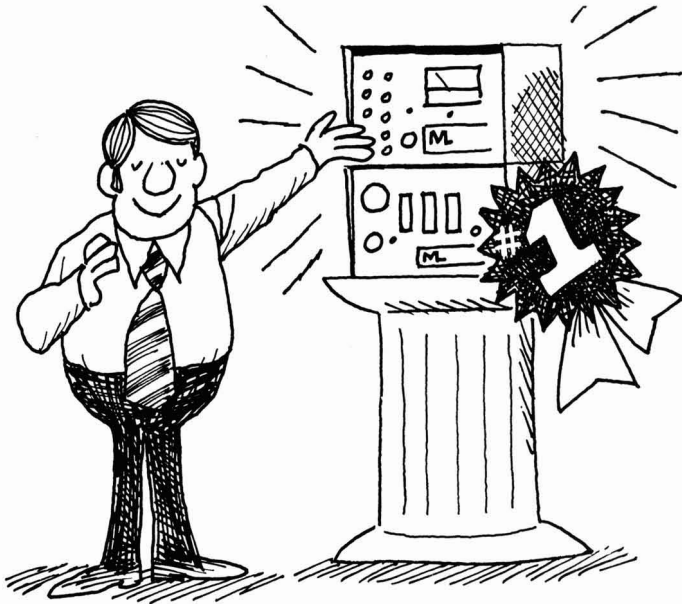
\$3 billion, or more, Irving Shapiro, the company's chairman, said. One point he complained strongly about was water; he noted that in many places, this year's cleanup standards will make water fishable-swimmable. Why then, Shapiro asked, require addition of 1983 "best available" technology in cases in which goals have already been met? As an example, he cited Du Pont's Sabine River (Tex.) plant, at which a \$15 million investment to date achieved or exceeded "fishable-swimmable".

Additional technology for 1983 would run \$10-15 million, plus \$5 million/y operating costs. Shapiro said that the \$3 billion spent on productive capacity could provide more than 15 000 jobs, and suggested that the government look into "zero-based regulation," as well as budgeting.

Possible help for the California drought: recycling of as much as 80% of industrial effluent is possible with

currently available technology, Thomas McConomy (*ES&T*, October 1976, p 974), general manager of Calgon Corp.'s Environmental Systems Division, said. That technology consists of granular-activated carbon (GAC), whose granules are very porous, and are each about the size of freeze-dried coffee particles. The pores trap contaminants, and allow water to pass through. Most of the used GAC can be thermally reactivated. McConomy noted that water recycling could allow industries in California to keep operating; otherwise, because there is insufficient new water to meet industries' needs, plants would have to close down, and jobs would be lost.

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*Federal Register Vol. 41, No. 232, pg. 52686-95, Dec. 1, 1976.

CIRCLE 14 ON READER SERVICE CARD

Removing SO₂ in heating plant boilers

Research-Cottrell, the U.S. licensee of the Swedish process of A. B. Bahco, cleans up emissions from coal-fired boilers; the process is useful on small installations of the 100 MW size—small boilers, industrial boilers, and small power plant boilers

Historians may remember 1977 as the year of the coal lump instead of the snake. The energy crunch hit hard for millions who still face the prospects of dwindling natural gas supplies and soaring electrical costs.

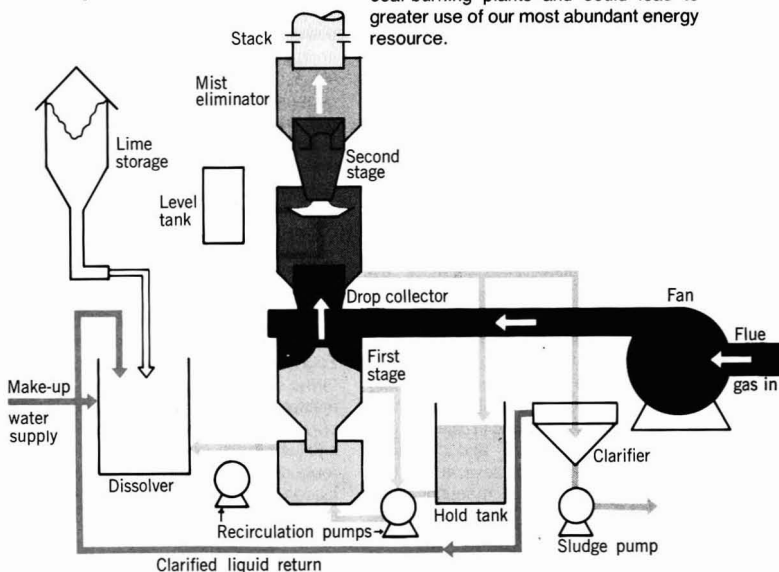
Experts say that the U.S. has an unlimited coal resource within its continental borders that could generate our electrical and heating requirements for the next 500 years. But what about the pollution problem?

Near Columbus, Ohio, is Strategic Air Command, Rickenbacker Air Force Base. The field was built in 1942 and was designed to be heated with coal. The plant houses eight boilers and an impressive number of smoke stacks. It operates much to the dismay of local residents, around the clock, 365 days a year. Only 12 months ago the plant was the source of a 12-mile-long smoke screen.

Civil engineer Jim Rasor, said, "Rickenbacker had plans to convert to oil in 1973. At the time bids were being sent out for the job, the Pentagon was looking at Research-Cottrell and the Swedish Bahco scrubber. R-C obtained a license to use the technology in the U.S. and Rickenbacker AFB is where it went."

The Air Force experimental pollution abatement system with the Bahco scrubber is one of a kind in the U.S. and has been in operation for almost a year. Because of the importance of coal as an alternate fuel, Rickenbacker has become a common name in environmental circles.

SO₂ removal: How the Bahco process works



Civil engineer Rasor
"AF experiment is doing the job"

How it works

In back of the heating plant is a silo filled with lime. The game plan calls for the smoke to be blown into the scrubber, which contains two venturis. The bottom of the scrubber is filled with a lime solution; another pump with lime solution is located halfway up the chimney-shaped tower. Large pumps churn the liquid.

The smoke is forced through the lower venturi into the churning lime, which sponges up harmful sulphur oxides. The process is again repeated through the upper venturi, with the gases passing through a fan that spins them upward like a tornado. The remaining suspended particles are spun out of the updraft, strike the inner walls of the chamber, and fall harmlessly to the bottom of the tank. The sanitized gases then leave the scrubber stack in the form of harmless steam.

"The system is not without its drawbacks," Rasor continues. "There is a sludge by-product, calcium sulfate. This thick black liquid is pumped into a nearby rubber-lined lagoon. The pool will take 5 years worth of sludge. The Japanese have a Bahco system similar to ours and have been adding chemicals to the by-product to make gypsum wall board."

Since the Rickenbacker scrubber is the only one in the U.S., the Environmental Protection Agency keeps close tabs on the operation. The scrubber has far surpassed present EPA emission standards for this type of system, which means that the Air Force experiment is doing the job.

The project at the AF base has been saving money by burning a cheaper, locally available, high-sulphur coal, and even with the added cost of the lime they are still operating below the price of fuel oil. The Rickenbacker project may become a blueprint for future American coal-burning plants and could lead to greater use of our most abundant energy resource.

It has been said over and over again since the oil embargo of 1973, and *ES&T* will repeat it: the U.S. depends upon fossil fuels, and its needs must be met increasingly by coal if severe economic dislocations are not to occur. Environmental problems of coal mining and use have also been, and will continue to be, discussed at almost interminable length. Nevertheless, as last year was drawing to a close, some choices concerning the U.S. turn to coal became clear. Industry and environmentalist groups:

- could be at constant loggerheads, contending with each other (and both with government agencies) in the courts, and provide large amounts of work and financial gain to various lawyers and law firms
- could sit down and talk calmly and rationally with each other, and try to hammer out a workable, environmentally acceptable approach to coal mining/use, and, as an added benefit, divert time, effort, and money that would otherwise be expended for disputation and litigation to much more useful purposes.

"Come, let us reason together"

This plea has been heard since Biblical times, and one person who believed that it would not fall on deaf ears when coal was to be discussed was Gerald Decker, corporate energy manager for The Dow Chemical Co. (Midland, Mich.). He proposed the idea of reason instead of rancor to Laurence Moss, former president of the Sierra Club. Subsequently, an initial meeting between industry people and leading environmentalists held in Virginia last July, persuaded both sides that a "meeting of the minds" on many topics was a distinct possibility. Thus, the National Coal Policy Project was born, and is now headquartered at the Center for Strategic and International Studies, Georgetown University, Washington, D.C.

However, in order that all sides truly "reason together," certain ground rules had to be established. Essentially, those concerned had to agree:

- to share all pertinent facts
- to avoid dogmatism
- to simplify complex concepts for communication to lay people
- to identify and isolate subjective considerations
- to distinguish between facts and value judgments
- not to mislead with unfair tricks
- not to impugn each other's motives lightly.

To keep the reasoning process moving at a useful pace, the Project's plenary group had its first meeting in January, and the next in early April, and continues meeting at intervals of several months. Between plenary group meetings, task forces, which do the substantive work, meet frequently. These task forces obtain, analyze, and evaluate facts and data, de-

OUTLOOK



Toward a consensus on coal

The National Coal Policy Project aims to show how environmentalists and industry can work together, rather than fight each other all the time

velop alternatives, and make recommendations regarding specific issues. Generally, these issues comprise mining; transportation of coal; air pollution; industrial fuel utilization/conservation; and energy pricing. Approximately 100 people are associated with the Project in some capacity, with about 24 composing the plenary group. In addition to the plenary group that oversees task force studies, and determines Project positions by consensus, and the task forces, there are a technical staff, and planning and budget committees.

A one-year effort

Basically, the Project consists of an environmental caucus and an industrial caucus; as a Project spokesman told *ES&T*, the list of participants reads like a "Who's Who in Energy." The environmental side is represented by people who play leading roles in coal-related issues, and who have been involved in grass-roots environmentalist organizations, litigation, and in some cases, legislation aimed at reducing adverse environmental impacts of coal production/use.

By comparison, the industrial caucus

is made up of representatives of major coal-using industries, such as cement, chemicals, electric power, glass, iron/steel, and paper. While the coal-producing industry contributes technical expertise and personnel to the task forces, present and prospective coal users dominate the industrial component of the Project.

The Project is expected to take about one year from its formal start. It is to be not just another study culminating in a report, but a vehicle for reconciliation of environmentalist and industry leaders who have large followings. Its budget is \$675 000, provided by foundations, government agencies, and industry. Expenses for environmentalists' participation are paid exclusively from non-industry sources, so that even an appearance of conflict of interest is avoided.

Pending completion of the Project, those involved in it are committed to let their conclusions be known through publication of reports and summaries. In addition, they hold seminars for federal officials, trade associations, and the press. The first Project communications concerning areas of industry-environmental consensus are slated to be made public

in September after a plenary group meeting.

A first-hand look

Perhaps the effort to reconcile environmentalist and industrial views on coal receives a "boost" when those involved can visit sites at which coal is, or will be, mined and used, Dow's Decker, and former Sierra Club president Moss told *ES&T*. For this reason, where possible, some of the task force meetings are held at these sites. Task force members can get a first-hand look at various mining, use, pollution, and land reclamation problems by talking with design and operations people, and familiarizing themselves with various coal sites and regions, and differences between these sites and regions.

For example, one such meeting was held at Big Brown Lake mine and power plant, located in the lignite fields of Texas. A second such field trip and meeting was held in Wyoming and Montana; others are planned for southern Illinois and Appalachia.

One fact of which the task force members quickly became aware, through these meetings in the field, is the great extent to which problems can vary from region to region, or even from site to site.



Dow's Decker
proposed that reason prevail

For instance, in the northeastern Texas lignite fields, surface-mined land has a good potential for reclamation, because of adequate rainfall and favorable overburden characteristics. However, farther to the southwest, lower precipitation creates more difficult conditions for re-vegetation of mine spoils.

On the other hand, geological and climatic conditions in West Virginia or Montana would present other sets of advantages and difficulties in solving rec-

lamation, air/water pollution, and other problems.

Thus, perhaps, acid mine drainage may be much more of a consideration in Pennsylvania than it is in Texas, or land restoration and revegetation may be somewhat easier in parts of southern Illinois, say, than in Wyoming. For these and numerous other reasons, those working on the Project may propose a regional, or, in some cases, local strategy, rather than an across-the-board national approach to environmentally acceptable development and use of U.S. coal resources.

Values

Perhaps much of the discord between environmentalists, industry people, and regulators may be ascribed to different sets of philosophical values, or, if one wishes, world views held and shared by members of these different groups. One



Laurence Moss
agreed to parley

of the Project's main aims is to determine whether, and to what extent, these values or world views can be reconciled. Another is to find out how much disagreement stems from lack of technical communication.

But neither values nor technical points of view stand a chance of being reconciled if people on different sides of an issue have made up their minds in such a way that they do not wish to be confused with facts. That is why the Project's ground rules entail those previously mentioned, which comprise the "Rule of Reason." When those rules are applied in letter and spirit, all concerned begin to learn how many areas of consensus and agreement there are, after all. It is such fairly achieved agreement that enhances human progress—not only with respect to acceptable coal development, but to many other areas as well. JJ

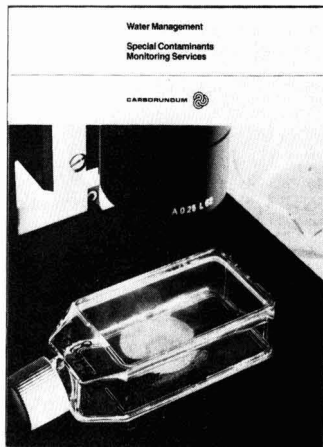
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CIRCLE 4 ON READER SERVICE CARD

Volume 11, Number 7, July 1977 647

Air pollutants and health: an epidemiologic approach

A 10-year effort in six cities is surveying children and adults for health effects and simultaneously monitoring the ambient environment at three different levels

They ride the soft summer breezes and the blustery gusts of winter. They waft through the air of homes, schools and workplaces. They recognize no age, sex or race barriers when they harm their victims' health. They have been legislated, monitored, measured, characterized and traced through environments. And still we know little of how they affect health. They are air pollutants.

In 1970, Congress passed the Clean Air Act. In 1971, the EPA, under its mandate, set national ambient air quality standards for six criteria pollutants based on the best data then available. Since 1971, scientists and regulators have debated the adequacy of these standards in protecting public health. Although many studies have attempted to test their adequacy, none has succeeded in producing more than provocative grist for future study mills.

Genesis of a program

Until 1974 the most comprehensive environmental health study in the U.S. was EPA's Community Health and Environmental Surveillance System (CHESS) (*ES&T*, March 1973, p 204). And this study died in a blaze of criticism and controversy.

Despite the fact that the CHESS study raised more questions than it answered, it was a pathfinder. And, in phoenix-like fashion, from its ashes has come an elegantly designed, one-of-a-kind project that approaches the study of the health effects of air pollutants from an epidemiologic standpoint.

This unique 10-year effort, begun in 1974, is a two-pronged study designed to measure the levels of air pollution—especially sulfur dioxide (SO₂), sulfates and respirable particulates—and to assess the effects of pollutant levels on the health of children and adults. It brings together the knowledge, talent and ingenuity of Benjamin Ferris, Frank Speizer, Yvonne Bishop, John Spengler, Mikhail Wolfson, Douglas Dockery, and Steven

Colome—medical and environmental scientists from the Harvard School of Public Health, plus a host of trained interviewers.

The National Institute of Environmental Health Sciences is supporting this study with \$3.5 million committed to the project through 1979. At that time, additional funds will be requested to carry the project through to 1983, 10 years after its inception. In April of this year, the Electric Power Research Institute bought "a piece of the action"; EPRI awarded Harvard \$378 000 through 1979.

In announcing EPRI's support of a role for the electric utility industry in this epidemiologic study, James McCarroll, manager of the institute's Health Effects Program, described the effort as "probably the most important on-going environmental health study in the U.S. today."

Indeed, the Harvard study is constructed to relate the effects of known exposure levels of air pollutants in the general (as opposed to occupational) environment to chronic respiratory symptoms and changes in pulmonary function. To be able to make these correlations, the scientists are simultaneously taking measurements of pollutants in the

ambient environment, and assessing health effects by using questionnaires on respiratory symptoms and performing lung function tests.

Although the Harvard team recognizes that its study may suffer from lack of knowing the best measures of pollutant exposure and health effects, the scientists nevertheless feel that their prospective epidemiologic study will properly test some of the issues raised by CHESS. In particular, the issues of threshold level of exposure below which no effect is detectable, and the role of sulfates in the environment will be addressed and, hopefully, answered. Sheer economics dictated that this study approach ozone only as a species of oxidants, that carbon monoxide (CO) be measured in scant detail and that the issue of hydrocarbons (HC) be skirted entirely.

An elaborate scheme

Even discounting ozone, CO and HC measurements, the enormity of the task the scientists set for themselves is readily apparent from these statistics:

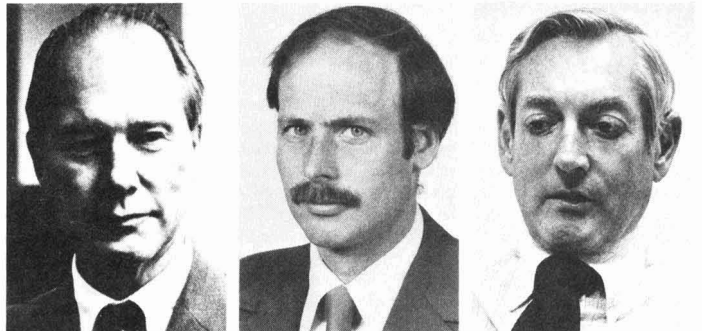
- The six communities being studied are thousands of miles apart. They run the gamut from rural and relatively pristine Portage, Wis., to industrial and relatively polluted Steubenville, Ohio, based on their annual averages of SO₂, total suspended particulates (TSP) and sulfate levels.

- In each of these cities, between 1400–1800 adults aged 25–74 are surveyed for respiratory symptoms and lung function every three years, and all children, approximately 1600–2400, in the first four school grades are surveyed annually.

- Among the cooperating institutions are the U.S. EPA; state, city and local environmental agencies and health departments; local school boards or boards of education; universities; and utilities.

- There is one fixed-monitoring site, at least 10 indoor/outdoor sites and several dozen personal samplers generating data 24 hours every day, 24 hours every sixth day and 12 hours every other day for 15 days during a six-week period in the summer and winter, respectively.

- At the central station and the in-



Harvard's Ferris and Spengler; EPRI's McCarroll

door/outdoor sites, four or five pollutants and five physical factors are being monitored; with the personal samplers, two pollutants and, selectively, 20 trace elements are being measured.

Monitoring the general environment

Environmental exposure is being monitored at three levels, each of increasing refinement: central station monitoring, indoor/outdoor monitoring and personal monitoring.

Central station monitoring—the historical and, even today, typical approach to air quality measurement—tracks the pollutants of concern on a continuous basis. But the site is fixed and may not be representative of actual individual exposure.

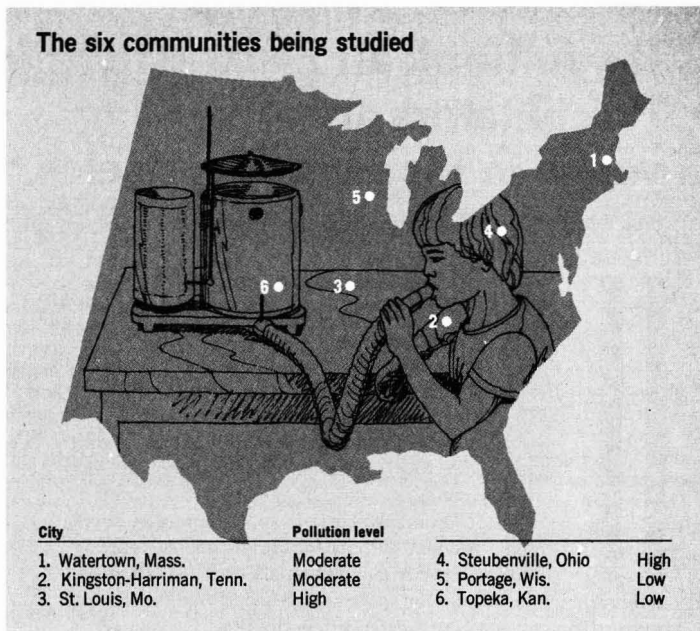
The indoor/outdoor measurements taken at selected homes scattered throughout the community permit a better assessment of how well the central station describes the pollution level of a community.

But the ultimate measurement refinement is, of course, the personal samplers that travel continuously with selected individuals. In addition to the portable monitor worn by the subject, a second, identical sampler is left at the subject's home. Initially, these portable units were purchased commercially. But the study team has substantially modified the samplers and now intends to "manufacture" the units in-house.

While the personal samplers allow comparison of exposures at home to those levels encountered by the individual during his normal day's activities, they also offer another refinement. The data collected from the samplers can also be compared to data collected from the fixed station so that the representativeness of that fixed station for individuals who move about the community can be ascertained.

At each central station, SO₂, TSP, mass respirable particulates (MRP)—particles with a mass mean diameter of 3.5 μ—NO₂ and ozone are the pollutants being monitored continuously the year round. In addition, wind speed and direction, temperature, relative humidity and precipitation are also measured.

The instrumentation at this fixed site is a mixture of sophisticated electronic devices and less exotic samplers for historic comparison. TSP samples are taken with hi-vol and low-vol samplers; MRP samples are taken with low-vol samplers with cyclone presamplers; and 24-hour samples of NO₂ and SO₂ are taken with bubblers. Additionally, NO₂ and SO₂ are monitored continuously: NO₂ by chemiluminescent reactions and SO₂ by flame photometry. This summer, in an effort to field test the devices, the EPA is placing a dichotomous sampler at the fixed site in each of the six cities. This sampler separates particulates 3.5–20 μ in diameter from those 3.5 μ and below. Samples collected every other day



will be analyzed by the EPA, and the data will be made available to the Harvard study.

The data collected at the fixed sites offer a means of gross comparison of pollution levels among the six cities. The central location also serves as a reference point for the SO₂ bubblers and the MRP and TSP samplers located throughout the communities.

When fixed sites already exist that are representative for residential outdoor exposure, the data collected from these sites are used in the Harvard study. In St. Louis, for example, data from the Regional Air Monitoring Station (RAMS) and from a city-operated station are being used. In Kingston-Harriman, the state of Tennessee and the TVA are making their data available to the study team. And in Steubenville, Ohio, the Northern Ohio Valley Air Authority is operating the team's instruments at already established central sites.

Refined monitoring

At the indoor/outdoor monitoring sites, the pollutants being measured are: SO₂, MRP, NO₂ and particulate sulfates. The five physical factors measured at the central station are also monitored at these scattered sites. The indoor samples are taken in a room most frequently used by the family, but kitchens, bathrooms and bedrooms are excluded.

The personal sampler worn by the selected individual, and a duplicate of that instrument left at the subject's home, measure for respirable particulates. The collected samples are analyzed for MRP and water-soluble sulfates, the latter by a

technique developed by Mikhail Wolfson. Some samples, on a selected basis, are analyzed for trace elements by the more esoteric techniques of atomic absorption, neutron activation and electron spectroscopy.

A diary kept by the subject in which he notes his activities for the day allows a comparison to be made between home exposure and exposure during a normal day's activities.

This intricate, tri-level monitoring scheme generates an enormous volume of data that are all retained. Data retention is necessary because there is presently no certain knowledge which measure best reflects exposure.

Health effects assessment

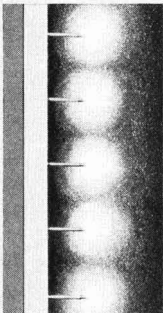
Gauging the health of adults and children in the six communities is accomplished by using questionnaires to document respiratory symptoms and by performing simple pulmonary function tests.

In addition to asking for chronic respiratory symptoms, the adult questionnaire surveys smoking habits and residential and occupational history. This standard questionnaire is designed to control for factors other than air pollutants that can influence lung diseases. Among these factors are smoking, obviously, but occupational exposure, age, lung size, heredity and the less-obvious socioeconomic forces play a role.

For children, the questionnaire, completed by a parent or guardian, asks about previous respiratory illnesses; living conditions including the type of fuel and heating system used in the home; and the

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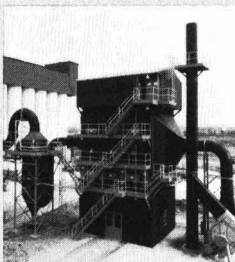


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occupation and smoking habits of the parents or guardians.

Lung-function measurements of adults and children are made on spirometers—low-resistance, low-inertia, water-filled instruments. Spirometer tracings of forced expiratory volume in one second and forced vital capacity in six seconds are converted to properly corrected values that the Harvard scientists feel are significant indicators for the presence of pulmonary disease.

In the scheme of the study, the children are surveyed annually, and adult groups in two of the six cities are studied each year and are resurveyed every three years thereafter. The Harvard team is returning to Watertown, Mass., and Kingston-Harriman, Tenn., this fall to resurvey the first two adult groups monitored.

The health assessment scheme will allow the scientists to correlate levels of air pollution with the observed rate of decrease in lung function in adults and increase in lung function in children. The prospective study of adults will permit an evaluation of changes over a 10-year period in persons who maintain constant smoking habits and occupational exposures. In children, the study will allow an evaluation of changes in lung function in the absence of such obscuring factors as smoking and occupational exposure.

It is from children, in fact, that the most valuable information may come, since the true effects of air pollution should not, theoretically, be masked by other environmental factors.

Preliminary findings

The study has been under way since the winter of 1974. The volume of accumulated data is so enormous that the analysis of this information is still in the preliminary stage. In general, and not too surprisingly, the Harvard scientists have found more respiratory symptoms and more changes in pulmonary function in the dirty cities. However, when the data were corrected for age and lung size, but not for smoking habits, the smoking effect so overwhelmed the data that the effects of air pollutants on health could not be discerned. Further refinement of the data will hopefully permit the scientists to dissect the influence of air pollutants on health from other environmental factors.

With the passage of the Clean Air Act, Congress erected a tenuous legislative shield between air pollutants and public health. The adequacy of the standards promulgated under this law depends on the data base used to develop them. Today the data base is woefully incomplete and present standards may be too weak to protect health, or so stringent as to inhibit economic growth. Either way, the work of the Harvard scientists should fortify that data base and, in the process, go a long way toward improving the standards

LRE

How hot is solar energy?

Today, not as hot as some think,
but ocean thermal is heating up

Everyone want solar energy? Yes. Why do we want it? To help with the energy crunch. Right. How many will pay for it? Well . . . Let's get industry to spend money for it! Great. Let's get the federal government to help too! Good idea.

OTEC, ocean thermal energy conversion, is one of six solar energy technology options that constituted the original U.S. solar energy plan. Today, it is the hottest one in the federal solar funding shop. More than twice as much money will be spent in OTEC development in fiscal year 1978, beginning this October 1, than the previous year. But, according to many, that still is far from enough. Federal funding for OTEC is still very small compared to coal and nuclear R&D.

OTEC is the only nonnuclear, nonfossil fuel baseload energy option available to the U.S. that does not use some form of energy storage. The six solar technologies were selected by the RANN project of the NSF. When ERDA was formed January 19, 1975, the lead role in solar energy was transferred to the new agency.

OTEC is unique. Other solar technologies attempt to make direct use of the sun's radiation to produce energy in a form suitable for human purposes. These include photovoltaic, solar thermal conversion to electricity, solar heating and cooling, and photochemical process such as biomass conversion. Others include waves, currents, tides, salinity gradients, and hydropower. But OTEC uses the oceans—an intermediate media—as its direct source of energy.

The real advantage of OTEC, which is not shared with the other forms of solar energy, is that it can operate 24 hours a day without the use of an auxiliary storage medium. The other forms of terrestrial solar energy conversion are limited to use only during daylight hours, or otherwise have time varying levels of output (wind energy), unless some auxiliary energy storage method is used.

OTEC, a solar concept to harness the thermal energy stored in the oceans (*ES&T*, February 1975, p 104), is now moving into the hardware development phase. OTEC plants operate on the temperature difference (ΔT) between warm surface water and cold deep water. The ΔT runs a heat engine. The warm ocean surface water vaporizes a working fluid; the vapor drives a turbine, and is subsequently condensed by the cold ocean

water brought up from the depths of a half mile below the surface. The cycle is continuous, and the turbines produce electricity.

Worldwide, there are 40 sites with sufficient thermal gradients. Since the OTEC plant efficiency increases with approximately the square of the ΔT available, the best sites are in the tropical oceans within 8–10° latitude of the equator. The appeal of OTEC is considerable, realizing that certain resource-poor and less developed nations with such gradients have an untapped energy resource that could be used when OTEC plants are built.

There are no major technical mysteries to OTEC. It's all economics. Like other new energy technologies, it is capital-intensive, but less so than others. It is said to offer production costs for electricity, ammonia, aluminum, and other energy-intensive products that will be competitive in 6 to 8 years (or as soon as these OTEC plants can be developed and built) with plants using fossil fuel or nuclear power. Another point is that the thermal gradient is almost two orders of magnitude smaller than that used in conventional energy plants.

The final configuration for an OTEC plant is a complete tradeoff in engineering parameters. With a given temperature gradient, the pumps, heat exchangers, and turbine would have to be a certain

size. With a lesser temperature gradient, these equipment items, and hence the whole plant, will have to be bigger.

If the OTEC plant is placed in strong currents, the plant will have to be moored at the bottom. On the other hand, if the plant grazes with the currents, the plant design does not incur some of the site-specific penalties. In the "doldrums" near the equator, where currents are small, a floating plant-ship can use a propulsion systems to "graze" at $\frac{1}{2}$ -knot speed to seek out the highest ΔT year round.

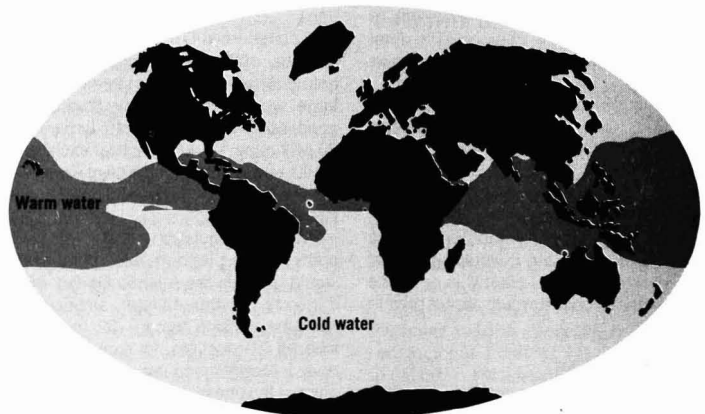
The choices

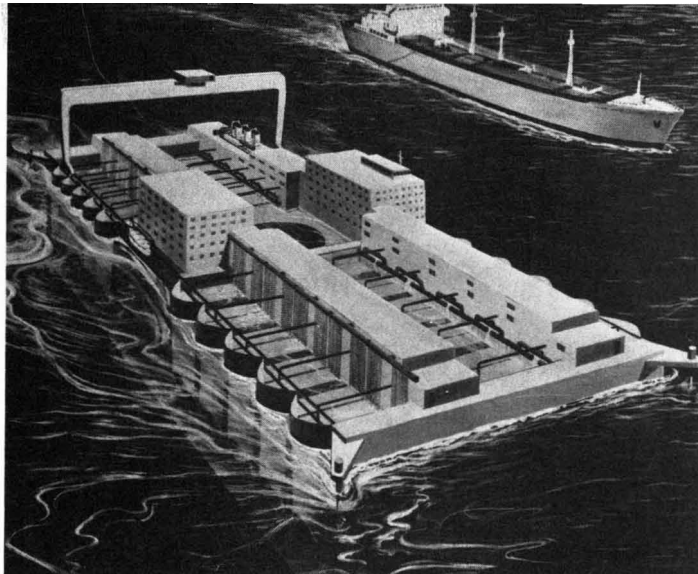
One of the major hurdles for the OTEC is that the plant must be economically competitive with land-based alternatives. It's a high hurdle.

Some of the technical teams in this warm cold water contest include the Applied Physics Laboratory (Laurel, Md.), Lockheed Ocean Systems Division (Sunnyvale, Calif.), TRW (Redondo Beach, Calif.), and Sea Solar Power, Inc. To date, these teams are all pulling for the same national goal of development of OTEC as an energy alternative for the U.S. But the Japanese and French are also getting active in OTEC.

There are several design concepts. The APL scientists conceive of a roving vessel that would ply the warm water of the ocean and would graze for energy. An OTEC plant-ship designed to produce 1000 metric tons per day of ammonia might run between \$240–325 million. (APL estimates \$325 million for the first one and \$240 million for the ninth). The Lockheed group came up with a submerged spar buoy OTEC plant, for the Gulf of Mexico, perhaps. Why submerged? An OTEC plant in that area would be subject to hurricanes. By submerging, the plant is protected.

Whether the OTEC plant is moored at one site or roving is a hotly contested





APL design. It's a roving platform of reinforced concrete, 476 ft long, 196 ft wide and 70 ft deep. Concept is to graze for energy on the warm equatorial ocean waters, and to make ammonia and help conserve NG

design decision. That decision gets into the specific use that is to be made of the electricity. According to the mission analysis of the incentives for the commercialization of OTEC by the University of Southern California scientists B. J. Washom and J. M. Nilles, in a report that became available this January, the site-specific plant would transmit the electricity shoreside where it might be used. The roving vessel would use the electricity, in the first commercial application, to make ammonia.

Once this mission decision is made, the heat exchanger design can be optimized for the chosen use. With the fixed site, the delta T might not remain optimum under all seasons; for example, at a fixed site in the Gulf of Mexico, the seasonal variation in ΔT may be 10 to 13 °F (e.g., from 31 °F in winter to 44 °F in summer). The roving plant can keep the ΔT variation down to a few degrees.

At best, there is a suggestion and counter suggestion to nearly every one of the many technical choices. The final engineering parameters have not yet been specified.

There are different schools of thought on OTEC. One calls for putting a platform in the water, building the heat exchangers, and making a complete OTEC system work. The other favors more experimentation and exploration of all operating engineering parameters before putting any unit in the water. It would seem that the earlier the OTEC plant is in or on the water, the sooner it would attract private capital.

The APL concept

If the building of a 5-MW plant gets underway in 1978, then the platform would be operational by 1980. APL sci-

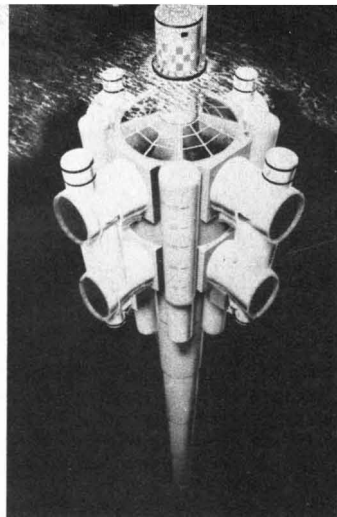
entist William Avery pointed out that the objective of the floating platform plant was to reduce risk before commercialization of OTEC plants. This roving plant would:

- accumulate data on performance
- accumulate data on cost
- accumulate data on scheduling.

Avery and other APL scientists explain that their design for a 100-MW OTEC plant would have 20 identical modules of 5-MW each. The 5-MW pilot plant would use the full 100-MW demonstration-size platform and 60-ft diameter cold water pipe. This arrangement will produce realistic plant motions and provide room for expansion of the heat engine and for subsequent onboard demonstrations of the ammonia process and/or refining of aluminum or other metals such as nickel and chromium. This APL pilot plant would cost \$45 million, including the 5-MW power module and all the ancillary equipment necessary to the heat engine and platform operations.

A commercial OTEC plant designed to produce 1000 metric tons per day of ammonia would be about three times as large with 64 each of evaporator and condenser modules and 16 turbines of 20-MW each. Thus, if one heat exchanger module was shut down the plant would still deliver 98.5% of the design power; with two down, 97%.

With a propulsive thruster at each corner of the platform, this "plant-ship" would graze in the Atlantic Ocean about 5° south of the equator seeking the warmest surface water—82 to 86 °F. Infrared (IR) satellites, for example, would relay information on the surface temperature of the ocean, indicating zones where the warmest surface area could be used; hence, grazing would be optimized.



Lockheed design. It's a submerged spar buoy, 250-ft diameter, 2545-ft high, including the cold water pipe, weighing 300 000 tons. Concept is to send 265 MW of power ashore for the needs of 160 000 residents

The cold water would come to the plant from a depth of 2500–3000 ft through the large diameter pipe. The pipe ratio of length to diameter would be 30 to 40:1, about the same as a milkshake straw. The platform would roll and pitch only about one-tenth of a degree in 20-ft-high waves. This OTEC plant might ply the waters at a speed up to 12 miles per day, keeping close to the ΔT specified in the heat exchanger design.

Besides the large Atlantic Ocean siting regions that are roughly midway between Brazil and Africa, where there is little or no shipping to contend with, there are suitable sites in the Pacific. They would not be near the U.S. west coast because the surface water is not warm enough, but they could be west of Mexico or several hundred miles south of Hawaii.

The ERDA plan

Meanwhile, ERDA plans to spend \$26 million on OTEC in fiscal year 1978, starting October 1. A 1-MW heat exchanger unit will be evaluated on OTEC-1, formerly the Hughes Mining Barge, now docked in Oakland, Calif.

Ultimately, ERDA plans to build an off-shore moored platform that would generate electricity for shoreside use. Such platforms would be close to the U.S., both in the Gulf of Mexico—at such sites as New Orleans, La., Brownsville, Tex., and Key West, Fla.—and off the U.S. mainland, such as Hawaii, Puerto Rico, and the Virgin Islands. Of course, some sites in the Gulf are in the area of hurricanes. Thus, the design must meet hurricane conditions.

When ERDA was formed, its components included a group from the AEC, and hence, proponents of nuclear energy; a group from the Department of the Interior,

and hence, proponents of coal gasification projects; and a group, small in comparison with the others, from the NSF, and hence, proponents of solar energy.

H. H. Marvin, director of the ERDA solar energy division, became the director in the summer of 1975. This solar energy division is part of the office of the assistant administrator for Solar Geothermal and Advanced Energy Systems (ASGA). It's one of six main offices in the ERDA. Earlier, Pezdirtz, of the energy storage branch in the Office of Conservation, told *ES&T* readers about flywheels (*ES&T*, July 1976, p 636).

Marvin says that the fiscal year funding request for his division is \$305 million, \$26 million of which goes to OTEC. The number of personnel for 1978 is 113, a modest increase from less than 100 people the previous year, with a \$290 million budget. During that year, OTEC funding was \$13.5 million. ERDA has chosen TRW (Redondo Beach, Calif.) to design and fabricate the 1-MW heat exchanger for the first ocean test in early 1979 on the converted Hughes Mining Barge, OTEC-1.

Once outfitted, OTEC-1 will be sent to an ocean site for evaluation of the TRW heat exchanger. The site may be in the Gulf of Mexico, where the surface water temperature varies 10 °F or more, winter to summer, or along the coast of Mexico, where the ΔT is greater and less variable. Or again, it may be tested at the Palmyra Islands, between Tahiti and Hawaii, suggested by William Heronemus, one of the first OTEC proponents.

A second step, for which RFP's (request for proposal) are imminent, involves operating a complete 5-MW OTEC prototype system. The projected completion date is 1981. Then, by 1984, an OTEC demonstration plant including 25-MW heat exchangers could be built. This power unit would be modular; it would be used to constitute OTEC plants of 100 MW or larger.

The contrast

The heat exchanger is the critical item in the whole plan. The question becomes: whether to construct it of titanium or aluminum? Whether to go with the low-cost, 5-MW APL design or a more expensive shell-and-tube type at 25-MW size?

The ERDA plans to proceed with early ocean testing utilizing the OTEC-1. The former Hughes mining barge is regarded by some as a platform of convenience. It would have a 2500-ft long scaled-down cold water pipe, about nine ft in diameter.

By 1980, the ERDA plan will not have answered the go, no-go question for the future commercialization of OTEC. The design proposed by Lockheed, submerged and hurricane proof, would be considerably more expensive than the roving platform design. Also, it's a new type of structure, not a near-term-type venture,

and probably would not be built before 1990.

On the other hand, the APL design, a roving platform of reinforced concrete construction, is more in line with current shipbuilding techniques. There are more than 20 shipyards in the U.S. today with space available and facilities to build this platform.

This reinforced concrete technology was used to build over 100 concrete ships during World War II, some of which were recently inspected and found to be in excellent condition. The new construction-barge-type pilot plant proposed by APL would be very similar to the 461-ft by 136-ft by 56-ft deep ARCO barge delivered by Concrete Technology Inc. of Tacoma, Wash., in April 1976, just 27 months after contract, including all the



ERDA's Marvin
heads the solar energy division

preliminary and final design work. In comparison, the proposed APL platform would be 476 ft by 196 ft by 70 ft deep, and the preliminary engineering design is to begin this fall. It could be in the water in 1980 if the funding is provided, APL claims.

The heat exchangers, too, are the real cost item. Using the APL platform and aluminum heat exchangers, 33% of the OTEC/ammonia plant-ship cost (\$80 million of \$240 million) for the ninth 325-MW plant, or \$246/kW is in the heat exchangers. In the Lockheed approach with titanium shell-and-tube heat exchangers, 49% of the cost (\$221 million of \$450 million) for the 25th 265-MW plant, or \$834/kW, is in the heat exchangers. It is generally agreed that titanium heat exchangers will cost two to three times as much as aluminum ones for any given plant design and mission.

Marvin says that the difference between the Lockheed and APL cost figures are traceable to their assumptions re-

garding the technologies used in the heat exchangers. Lockheed also recognizes the cost advantage of aluminum and has done an extensive ERDA-funded study of the producibility of both titanium and aluminum shell-and-tube heat exchangers. The main difference in heat exchanger costs between Lockheed and APL, if both were aluminum, is due to the fact that the APL heat exchangers have no shells. They simply are fitted into rectangular openings in the concrete platform, so that the seawater can flow down over the tubes by gravity (the ammonia working fluid is inside the tubes).

The 3.5-inch-thick, welded spherical aluminum shells proposed by Lockheed account for one-third of their cost. Although titanium is more corrosion resistant than aluminum, the APL scientists say that aluminum corrosion will be small enough to have little effect on design for the intended 20-year life. Also, with the APL modular approach, if a few modules should require repair or replacement in less than 20 years, this can be done with minimal affect on operating cost estimates.

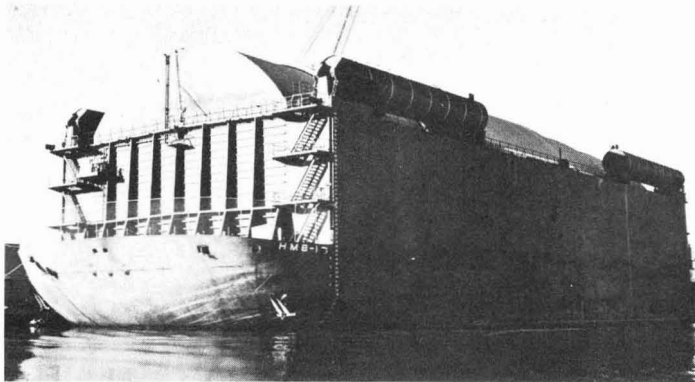
The evaporators, whether aluminum or titanium, will be fouled gradually by microorganisms in the warm seawater. Some experiments by J. G. Fetkovich of Carnegie-Mellon University in the Pacific Ocean just off Keahole Point, Hawaii, have indicated that the fouling buildup will be very slight in the first two to four weeks after each cleaning. Additional tests by APL and the Natural Energy Laboratory of Hawaii are now starting at Keahole Point, using a full-scale section of the APL heat exchanger.

In a shell-and-tube heat exchanger, which puts the seawater inside the tubes, TRW and Lockheed have proposed to shoot abrasive-coated rubber balls through the tubes to clean them. (Hydro-nautics Inc., studying cleaning methods for ERDA says the system may not be practical.) The APL concept is to use moving water jets to clean the outside (seawater side) of their tubes. Both methods remain to be demonstrated on the specific heat exchanger designs in 1977 or possibly early 1978. The water-jet method is used successfully in shipyards to clean very heavily fouled ship hulls.

Biofouling may or may not occur in the condensers from the cold, deep water. But pumping is not a problem. One spokesman at the 4th OTEC conference (New Orleans, La.) this spring, Dr. O. Roels, mentioned that cold water from 875-m depth had been pumped continuously for the past five years at a site off St. Croix, Virgin Islands.

The big decision is how fast to get to the actual use of the thermal gradient. APL recommends a 5-MW module in addition to the 5-MW system ERDA claims will be operating in 1980.

A basic requirement for OTEC is the adequacy of the thermal gradient. This is



OTEC-1. ERDA will outfit the barge with a state-of-the-art heat exchanger; early ocean tests are planned for 1979

fundamental for the heat exchanger design and determines where commercial OTEC plants can be sited. For example, if the heat exchanger is designed for one delta T and operates at a smaller delta T , the operating efficiency would be decreased.

The energy savings

One might wonder how an OTEC plant in the ocean, making ammonia, would help with the U.S. energy situation. APL's E. J. Francis explains. Today, about 3% of the natural gas supply in the U.S. goes for the production of ammonia. In the past two years, the price of natural gas has increased about 660%. By 1985, about 7-8% of the "lower 48" states' natural gas supply will be used to make ammonia, 75% of which would be used in fertilizer, principally for corn and wheat production.

How this ammonia production relates to the OTEC funding picture is quite vivid. Before the natural gas price escalation, the number of OTEC plants required to be built before a return on investment could be realized was six or seven. With the price escalation, only two or three OTEC plants for ammonia production may have to be built, with partial government support, before a return on investment adequate to attract full private funding can be attained for subsequent plants.

On an OTEC plant, all raw materials for ammonia production are available. Hydrogen would be obtained from the electrolysis of fresh water made from seawater. Nitrogen would be obtained by air liquefaction.

Further, with ammonia production there is no major problem with logistics. Nor is there the problem of transmitting the electricity shoreside. The ammonia would be generated on the OTEC and then shipped to the U.S. in refrigerated tankers such as already exist.

The transmission of electricity from a submerged OTEC plant to the shore faces the hostile environment of 2500-4000-ft depths. Pressures are roughly equivalent

to about 1100-1800 psia. Conventional alternating current line losses include radiated power, high voltage corona leaks, and resistance losses. If the OTEC plant generates high voltage direct current, there are primarily just corona and resistive losses. For this reason, the electricity generated by an OTEC plant at a specific offshore site probably would be sent ashore as high voltage direct current. Once ashore, it would go through an inverter, to change to alternating current usable in the U.S. power grid.

For the roving, tropical, OTEC/ammonia plant another aspect is to reduce the cost of the electrolysis operation, obtaining hydrogen gas from seawater. In Avery's view, the cost is 1.7 times higher than it need be. The cost might be cut in half in six or seven years.

An electrolytic process of General Electric would be used, which involves a solid-polymer electrolyte cell. The seawater is on one side of a solid membrane, and hydrogen gas comes off the other side of the membrane. The solid polymer electrolyte (SPE) is Teflon with SO_3 groups. This membrane is impervious to everything, with the exception of hydrogen ions (H^+).

Some 45 000 hours, spanning four years of operating experience, have been logged with such cells. The SPE film, made by Du Pont, is protected by patent. To date, it has only been made in pilot batches; its cost is about \$20/ft². In recent tests, GE has been using an alternative material that may prove lower in cost.

Go Hawaii

In its first annual report (1975), the Natural Energy Laboratory of Hawaii said that Hawaii is in a position to move ahead in ocean and solar energy research and development as the federal energy program crystallizes.

Former ERDA administrator Robert Seamans compared this energy research organization in Hawaii with the U.S. space program, which he organized in the early

60's. In his view, this new laboratory will be as crucial to the ERDA as the Kennedy Space Center was to the space program. Other contenders for energy labs include Florida, Louisiana, and Puerto Rico.

An Hawaiian site is natural. "Almost all of the energy in Hawaii derives from oil, and all, of necessity, is imported by sea," Governor George R. Ariyoshi said. During 1972, only 22 days with significant amounts of cloud cover were reported from the relatively new Keahole airport. The port of Kawaihae, 23 miles northeast of Keahole Point, is a commercial deep-water harbor.

This site, on Keahole Point, fulfills the requirements for an ocean-related natural energy research lab. A land parcel of approximately 140 acres along the shoreline has already been designated. Aside from tourism, a preferred new industry on the Big Island (Hawaii), as in the state as a whole, is research and development. The west coast of the Big Island offers excellent potential. Research vessels can easily moor at the deepwater port at Kawaihae.

Prognosis

It has been said that the developing nations of the world with thermal gradients now have an untapped resource. But how, under the sun, are they going to be able to finance high technology? Unless, of course, the U.S. develops it and gives it away in the form of aid!

A difficult obstacle confronting OTEC, or any federal program for that matter, is the new federal exercise of zero-base budgeting. Coming down to the bottom line, at least in the mission analysis report, under the "worse" conditions the price of OTEC electricity is 2.5 times as expensive as conventional electricity. The capital intensiveness is a fundamental problem that is delaying the widespread use of any solar energy technologies, or other new nonsolar energy technologies.

The market for OTEC plants within the continental U.S. is relatively limited and restricted to the Southeast states and Hawaii. In the absence of private capital, the federal government appears to be the only potential source of funding for the necessary R&D and initial construction. So, the federal government and your tax dollar must come forth to catalyze development of this solar resource. Meanwhile, the more the prices of coal, oil, nuclear fuels escalate, the more economically viable OTEC becomes.

EPRI, the official research arm of the electric utilities, has no plans, as yet, for a R&D effort in the OTEC area. Neither does the Fertilizer Institute of America, nor the chemical industries represented by the Manufacturing Chemists Association. One glaring omission in the President's budget request for fiscal year 1978, and his energy concerns, is a national mandate for priority demonstration of OTEC plants. SSM



FEATURE

How EPA validates NSPS methodology

Under the authority of Section 111 of the Clean Air Act, as amended, the U.S. Environmental Protection Agency (EPA), on December 23, 1971, promulgated its first group of new source performance standards (NSPS), which placed restrictions on the allowable emissions from new plants in five industrial categories. These were followed in 1974 by standards for seven additional industries, and standards covering several others have now either been promulgated or are in varying stages of development. Moreover, four substances (asbestos, beryllium, mercury, and vinyl chloride) have been designated as hazardous air pollutants, and emission standards for the first three were promulgated in 1973 under Section 112 of the Clean Air Act.

Of fundamental importance to enforcement of the above standards is the measurement process. At the time that the initial NSPS were established, many of the measurement methods used to determine compliance with these standards had not been fully evaluated, nor had their precision, accuracy, and general reliability in the hands of typical users been determined. It is for this reason that the Quality Assurance Branch, Environmental Monitoring and Support Laboratory, EPA, has for the past three years been engaged in a systematic program to standardize or validate those source test methods that will be used to determine compliance with these federal emission standards.

Collaborative tests have been, and are being developed to establish monitoring procedures for keeping tabs on Clean Air Act compliance

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Traditionally, the within-laboratory and between-laboratory precision of test methods is determined through collaborative testing (round-robin testing). The collaborative test is designed so that each participant makes one or more measurements on identical samples by use of the same test method. Then, from a statistical analysis of the results, an estimate is made of the within-laboratory and between-laboratory precision of the test method. This general technique has been used very widely for the validation of methods for the analysis of such materials as water, drugs, food and agricultural products, fertilizers, coal, and ores.

Experience has shown that before a stationary source test method can be successfully collaboratively tested, it must be described in sufficient detail to ensure that each collaborator uses exactly the same sampling and analysis procedures. Further, it must give repeatable results when one laboratory analyzes the same sample several times. This repeatability can be assured only through intensive method evaluation, which now constitutes a large portion of the total program. This evaluation, followed by collaborative testing, is resulting in more fully described methods of known precision and accuracy, and of proven reliability.

The standardization process

The validation of source test methodology is a complex, lengthy, and costly process, but years of experience have indicated the need for a complete and systematic examination even for those methods and measurement principles with fairly extensive histories of usage. Basically, this examination consists of the following steps:

- The method is examined for technical accuracy, clarity, and completeness of detail.

- The method is subjected to a thorough and rigorous laboratory evaluation, which may include investigations of sample collection efficiency, applicable concentration range, mode of calibration, and effects of interferences.

- The method receives field evaluation at an applicable test site; statistically designed experiments, with novel and original evaluation techniques to determine its performance under typical field conditions, are often performed.

- Finally, the method is submitted to an interlaboratory collaborative test at an appropriate test site. Qualified participants determine its precision, accuracy, and field reliability. Based on the test results and other information gained from the test, a final draft of the method is prepared and recommendation is made for its adoption by the agency.

Collaborative test design

For collaborative tests of a stationary source emission method, both the sampling and the analytical procedures must be evaluated, usually at a real source representative of those where the method will be used. All participants must have access to the same pollutant concentration in the stack, for, if they cannot obtain identical samples, they surely will not get reproducible results. For gaseous pollutants, this can frequently be accomplished by extracting a side stream from the stack and piping it to ground level, where it is delivered through a manifold to the collaborators who simultaneously sample the gaseous pollutant.

Collaborative testing of methods for pollutants that exist in particulate form is complicated by the requirement that all test teams sample the material isokinetically directly from the stack. Here the problem becomes one of the simultaneous extraction of representative samples from the stack by each of the collaborative test teams. Since spatial and temporal variations may constantly be occurring in both the velocity profile and the pollutant profile, an attempt must be made to compensate for this so that each participant has access to statistically identical or equivalent samples.

Because they could not ensure for statistically identical or equivalent samples, previous test designs were considered imperfect, and often included source variability in the precision estimates. Thus, a different approach was sought for collaborative testing methods for pollutants that exist in particulate form. The result was a new test design that uses paired sampling trains in which two probe-pitot tube assemblies could simultaneously sample at very nearly the same point in the stack. Since the paired probe tips sample in rather close proximity, the effects of spatial and temporal stack variation on the samples collected by the adjacent probes are greatly minimized. This test design employed six independent test teams operating separate trains in three of the paired train systems for the entire duration of the test. Both trains in the remaining pair were operated by a single team, with one operator running both meter boxes. Since all equipment in each train in this pair was virtually identical, had been carefully calibrated, and was operated by the same individual, the sample pair collected during any given run could be considered replicates.

Estimates of the variability within a laboratory were based upon the differences in concentration reported by the paired-train laboratory for the replicate samples on each determination or run. Differences among laboratories were estimated by contrasts between paired trains that were operated by the six single-train laboratories.

Data analysis

Prior to evaluation of the precision of a method, the determinations are tested for equality of variance by means of Bartlett's test for homogeneity of variances. In addition, the determinations are passed through either of two common-variance stabilizing transformations; the logarithmic or the square root, and Bartlett's test is again applied. The use of transformations serves two purposes. First of all, it can put the data into an acceptable form for an analysis of variance; and secondly, it can

provide information concerning the true nature of the distribution of sample points. The transformation that provides the highest degree of run equality of variance is accepted and used for deriving the precision estimates.

When the distributional nature of the data is such that its original or linear form provides the highest degree of equality of variance, a constant variance that is independent of the mean level is implied. In this case, the variances are estimated by a pooled analysis of variance on the original data.



Probe. A technician takes samples from stack gases; another records the data from the instrumentation

In order to provide the maximum useful information, the test must be designed, and the data analyzed in such a fashion that the precision estimates for a determination can be partitioned into their respective variance components. The variance components of interest are:

- the within-laboratory standard deviation, σ , which measures the dispersion in replicate single determinations made by one laboratory team sampling the same concentration level

- the between-laboratory standard deviation, σ_b , which measures the total variability in a determination caused by simultaneous determinations by different laboratories sampling the same true-stack concentration

- the laboratory bias standard deviation, $\sigma_L = \sqrt{\sigma_b^2 - \sigma^2}$, which is that portion of the total variability that can be ascribed to differences in the field operators, analysts, and the instrumentation, and to different manners of performance of procedural details left unspecified in the method.

With respect to the accuracy of a method, an attempt is made to define its absolute accuracy; this is, how well the measure-

ment value agrees with the actual or true value. Estimates of method accuracy must frequently be based on the analysis of standard cylinder gases. One approach is to have each collaborator measure the concentration of the cylinder gas (or other material), after which a mean and a standard deviation are calculated for the group of collaborators. A 95% confidence interval is then calculated around this mean. If the true concentration of the cylinder gas lies within this 95% confidence interval, then the method is said to be unbiased and accurate within the limits of its precision.

A more common means of stating method accuracy consists of averaging the respective biases of all collaborators and expressing this average as a percentage (either positive or negative) of the overall mean, or of the true value, when known. Both approaches to stating method accuracy will be found in the various collaborative test reports.

Since the initiation of the program in August 1972, evaluations and collaborative studies have been done on a number of methods. Table 1 lists those methods for which some collaborative testing has already been completed, and a discussion of the results of these investigations will now follow. Those readers interested in a more detailed discussion and interpretation of these results are referred to the review by Midgett, and to the individual collaborative test reports.

Velocity

For example, collaborative tests of the Type S Pitot Tube Method for stack gas velocity and volumetric flow rate (EPA Method 2) were conducted at a Portland cement plant, a coal-fired power plant, and two different municipal incinerators. The precision components were shown to be proportional to the mean of the determinations and are expressed as percentages of the true mean in Table 2 for both the velocity and the volumetric flow rate determinations.

Based upon the results of these tests, the precision of the volumetric flow-rate determination seems adequate for use with other test methods in determining pollutant emission rates. A

TABLE 2

Estimates of precision (standard deviation proportional to mean value)

Method no.	Parameter, units	Standard deviations, percent of mean value (δ) ^a		
		σ	σ_b	σ_L
2	Velocity, ft/s	3.9	5.0	3.2
2	Volumetric flow rate, ft ³ /h	5.5	5.6	1.1
5	Particulate matter, mg/m ³	10.4	12.1	6.1
6	SO ₂ , mg/m ³	4.0	5.8	4.2
7 ^b	NO _x , mg/m ³	6.6	9.5	6.9
7 ^c	NO _x , mg/m ³	14.9	18.5	10.5
8	H ₂ SO ₄ mist (including SO ₃), mg/m ³	58.5	66.1	30.8

^a σ = within-laboratory deviation; σ_b = between-laboratory deviation; σ_L = laboratory bias. ^b Pooled power plant/pilot combustion plant data. ^c Nitric acid plant data.

previous single-laboratory study indicated that for nonturbulent streams, Method 2 provides an accurate estimate of the true stack gas velocity at velocities of 55–60 ft/s.

Gas analysis

Several collaborative tests of the Orsat methodology for the determination of carbon dioxide (CO₂), excess air, and stack gas molecular weight (EPA Method 3) have been conducted to investigate various aspects of the method's performance. The most recent collaborative field test, by use of a revised version of Method 3, was conducted at a municipal incinerator. Estimates of precision for the various parameters are summarized in terms of standard deviation in Table 3.

Based upon the results of all studies completed, it is concluded that:

- The Orsat method is tedious and requires great attention to detail and technique.
- The original EPA Method 3 operator performance criterion (three consecutive analyses that vary no more than 0.2% by volume) is not easily met in the field, and even meeting this criterion does not ensure that highly reproducible and accurate results will be obtained.
- The use of Orsat data to convert particulate catches to such

TABLE 1

Methods collaboratively tested

Parameter	Method of determination	EPA Method no.
Stack gas velocity and volumetric flow rate	S-type pitot tube	2
Stack gas molecular weight, CO ₂ , O ₂	Orsat	3
Stack gas moisture content	Condensation and volumetric measurement	5
Particulates	Dry filtration and gravimetric determination	5
Sulfur dioxide	Selective absorption and barium thiorin titration	6
Nitrogen oxides	Phenol disulfonic acid	7
Sulfuric acid mist/sulfur dioxide	Selective absorption and barium thiorin titration	8
Opacity of stack	Visual estimation of percent opacity	9
Carbon monoxide	Nondispersive infrared absorption	10

TABLE 3

Precision estimates (standard deviation independent of mean value)

Method no.	Parameter, units	Standard deviations, parameter units ^a		
		σ	σ_b	σ_L
3	CO ₂ , %	0.20	0.40	0.35
3	O ₂ , %	0.32	0.61	0.52
3	Dry mol wt, g/g-mol	0.035	0.048	0.033
5	Moisture fraction	0.009	0.012	0.008
8	SO ₂ , mg/m ³	123	115	99
9	Opacity, %	2.05	2.42	1.29
10	CO, mg/m ³	14.3	32.3	29.0

^a σ = within-laboratory deviation; σ_b = between-laboratory deviation; σ_L = laboratory bias.

reference conditions as 12% CO₂ and 50% excess air can introduce significant errors into the corrected particulate loading.

- The Orsat method is, however, quite satisfactory for use in determining stack gas molecular weights.

Particulates

Collaborative tests of EPA Method 5 for determination of particulate matter emissions were done at a coal-fired power plant, a Portland cement plant, and a municipal incinerator, with the early test design that has subsequently been abandoned. Although attempts were made to find the best test sites available at the time, the power plant testing was conducted at a far less-than-desirable sampling location. Also, the cement plant was subject to extreme load variation over the duration of the test. For the purpose of statistical treatment, the determinations were grouped into blocks by means of the most appropriate blocking criteria that could be devised for each test. A coefficient of variation approach was then used to calculate a within-laboratory, between-laboratory, and laboratory bias component for each test. These ranged from 25.3–31.1%, 36.7–58.4%, 19.6–51.0%, respectively, for the three tests.

Because of problems and uncertainties in the original test designs, as well as difficulties with the test sites, a fourth collaborative test of Method 5, using the paired sampling train test design previously discussed, was undertaken. The test, conducted at a municipal incinerator in September 1975, used a revised and more detailed version of Method 5, since the original method write-up was considered deficient.

Data analysis produced the precision estimates shown in Table 2. (See also Table 3 for the moisture fraction results.) These test results show the precision capabilities of Method 5 to be considerably greater than had been previously thought, and this improvement may be due in part to better test design. There was no feasible way that the accuracy of the method could be estimated under field conditions. Those readers seeking a complete discussion of the probable reasons for the poor precision obtained on the earlier tests are referred to the review by Midgett.

SO₂/NO_x

EPA Method 6 for SO₂ was evaluated, and then was collaboratively tested at two different sites—a 140-megawatt coal-fired electric generating plant, and an oil-fired pilot combustion plant. Analysis of the data by means of a coefficient-of-variation approach provided estimates of the precision components listed in Table 2. From these values, it is evident that Method 6 is capable of good precision when used by competent personnel. Analysis of standard sulfate solutions indicated that most of the precision variation is found in the field-sampling phase of Method 6, as opposed to the analytical phase.

A gas cylinder accuracy test first showed Method 6 to be accurate at SO₂ concentrations of up to about 480 mg/m³, but indicated that it acquires a significant negative bias above the range of about 480–800 mg/m³. However, more recent work within EPA has indicated that this conclusion was in error, and the method is unbiased up to SO₂ concentrations of at least 5000 mg/m³.

EPA Method 7 for NO_x was evaluated for interference effects in the laboratory, and then subjected to collaborative testing at the same two sites used for the Method 6 tests described above. A third test was conducted at a nitric acid plant. The data from the first two tests were pooled to provide a larger data base, and then analyzed with a coefficient-of-variation approach. A similar analysis was performed on the nitric acid plant data. The resulting precision estimates are presented in Table 2, first for the pooled power plant/pilot combustion plant data, and then for the nitric acid plant data.

Because of the larger data base resulting from the pooling of the data from the first two tests, and because of the frequently unstable conditions encountered at the nitric acid plant, it is felt that more reliance may be placed on the precision estimates

obtained from the former tests. Analysis of a standard test atmosphere established that Method 7 is unbiased and accurate within the limits of its precision.

Sulfuric acid mist

EPA Method 8 for the measurement of sulfuric acid (H₂SO₄) mist (including any free SO₃) and SO₂ was collaboratively tested at a dual-absorption contact process sulfuric acid plant. Simultaneous samples were collected by four collaborative test teams in a manner analogous to that previously described for the earlier Method 5 tests.

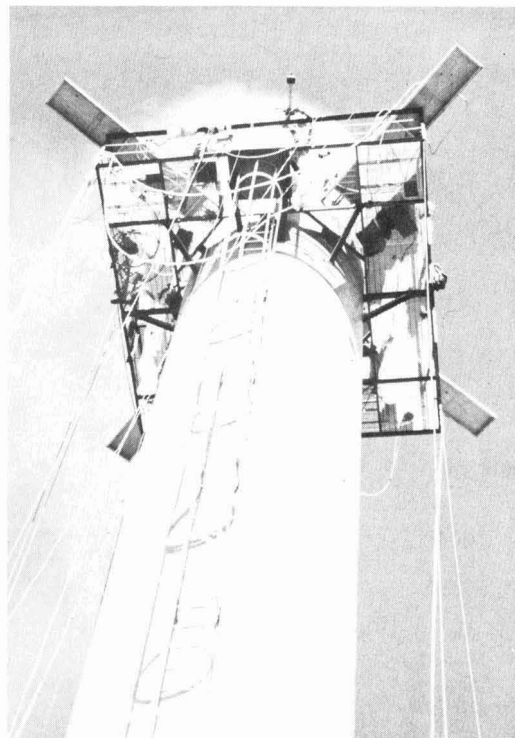
Inspection of the data revealed that H₂SO₄ mist concentrations varied by as much as an order of magnitude between collaborators within single runs, with several very high values occurring. SO₂ determinations varied by as much as a factor of two, and showed a significant negative correlation with the variation in the H₂SO₄ mist values.

The precision components shown in Table 2 for H₂SO₄ mist, and in Table 3 for SO₂, were developed after six extraordinarily high acid mist values were excluded from the data set. Thus, the precision of the acid mist determination was extremely poor in this test and the SO₂ determination, while better than that of the acid mist, was not highly precise either. However, the analytical phase was found to be precise and accurate.

Because of the significant negative correlation between the H₂SO₄ mist determinations and the SO₂ determinations, one is immediately led to suspect some intrinsic problem in the method. But at this time, it is impossible to say whether the imprecision observed is due to a real deficiency in the method, some phenomenon peculiar to the test site, or other unknown factors.

Opacity

Collaborative testing of EPA Method 9 for visual determination of opacity of emissions from stationary sources was conducted by certified observers at three collaborative test sites: a training smoke generator, a sulfuric acid plant, and a fossil fuel-fired



Stack. Particulate matter test is being validated here

steam generator. The initial test on the training smoke generator was conducted to provide background information on the use of the method, while the test at the sulfuric acid plant and the fossil fuel-fired steam generator was conducted to obtain information on the use of the method on applicable sources under field conditions.

Composite precision estimates based upon the results of all the tests were derived, and these are shown in Table 3. With data from the training generator and from Test 3 at the steam station, a composite estimate of the accuracy of Method 9 was derived for ideal (clear sky) conditions. This estimate compares the expected deviation of the observer from the average metered opacity, and is given by the equation, $\text{deviation} = 3.13 - 0.31$ (meter average), for the range from 5–35%, average opacity.

Where Methods are defined

Methods 1–9: *Federal Register*, **36** (247), 24876–24895 (1971)

Methods 10–11: *Federal Register*, **39** (47), 9308–9323 (1974)

Method 9 (revised): *Federal Register*, **39** (219), 39872–39876 (1974)

Methods 1–8 (proposed revisions): *Federal Register*, **41** (111), 23060–23090 (1976)

With respect to the other experimental factors and variables studied, it was concluded from the clear-sky data of Test 3 that:

- The angle of observation does affect the observer's determinations, and, in this study, the most accurate readings were made when the group was at an approximately 45-degree angle to the sun.
 - The experienced observers were able to read average opacity more accurately than the inexperienced observers, but the difference occurred mainly in the high opacity range ($\geq 25\%$).
 - Attempts at reading opacity in increments of 1% produced greater within-observer variability and was less accurate than reading in 5% increments.
 - Averaging the results of two observers yielded increased accuracy over the result of a single observer.
- Based partly on the results of these studies, Method 9 was revised and improved and has now been repromulgated to replace the original method of 1971.

Carbon monoxide

A collaborative test of EPA Method 10 for carbon monoxide (CO) was done at a petroleum refinery, where seven collaborators sampled the emissions from the CO boiler downstream of the fluid catalytic cracking unit catalyst regenerator. An indirect approach based upon the pairing of runs of similar concentration was used to estimate the precision components of the method shown in Table 3. From an analysis of cylinder gases supplied by the National Bureau of Standards (NBS), a somewhat similar between-laboratory term was calculated (26 mg/m^3 as compared to the 32 mg/m^3 shown in Table 3 for the field data). However, the standards data showed about a threefold improvement in the within-laboratory standard deviation over the field data (5.2 mg/m^3 vs. 14 mg/m^3), and this is probably due to the presence of some source variability in the field estimates.

As done in this study, Method 10 produced results with only moderate accuracy of $\pm 101 \text{ mg/m}^3$ (2σ level), on the average, over the concentration range of $277\text{--}1048 \text{ mg/m}^3$ of CO. One factor that adversely affected the accuracy of Method 10 was the failure of many of the collaborators to correct adequately

for the nonlinearity response characteristics of their instruments.

Another factor was the calibration gases themselves, some of which were in error by as much as 30%, when compared with the NBS standard gases.

Future plans

Results obtained thus far from the methods standardization program indicate that the program has been successful for the most part, although questions concerning the performance of some of the methods tested still remain. It has been shown that the methods for stack gas velocity and volumetric flow rate, particulates, sulfur dioxide, nitrogen oxides, and plume opacity (Methods 2, 5, 6, 7, 9) are indeed reliable if used properly under the conditions for which they were designed. The Orsat procedure (Method 3) is generally satisfactory, provided that its limitations are recognized, and that its limits of precision can be accepted. The method for carbon monoxide (Method 10) is thought to be capable of good accuracy and precision, but it appears that the suppliers of standard gases need to improve the state of their technology. The collaborative test also indicates that some users of nondispersive infrared (NDIR) instrumentation need further training in correcting for the nonlinear response characteristics of their instruments.

Results of the tests of the sulfuric acid mist/sulfur dioxide method (Method 8) indicate that either this method suffers from extremely poor precision, or that the test design was incapable of compensating for the normal range of concentration and velocity variation in time and space at the selected test site. The cause of this poor precision has been investigated, and another collaborative test of the method, using paired sampling trains, has recently been completed. The results of this test are not yet available.

It should be pointed out that EPA Methods 1 through 8 have recently been revised (1976), and that many of these revisions reflect refinements and improvements brought about through the methods standardization program. While the basic chemistry and procedures of these methods remain unchanged, the revisions supply much needed detail, and correct other deficiencies of the original versions. They are due for promulgation in a forthcoming issue of the *Federal Register*.

Several other test methods are now in various stages of the standardization process. These include methods for mercury, vinyl chloride, hydrogen sulfide, fluorides, polychlorinated biphenyls, lead, and arsenic.

The hydrogen sulfide method (Method 11) was evaluated in the laboratory and found to suffer a major interference from thiols, which are common constituents of such gas streams. A modified method, which is designed to eliminate this interference problem, was therefore developed, and this method has now been collaboratively tested. A report on the work is in progress. Field investigations of the fluoride method (Method 13) are complete and a collaborative test has recently been conducted. A report on this work will also be forthcoming.

Additional reading

"National Emission Standards for Hazardous Air Pollutants," U.S. Environmental Protection Agency, *Federal Register*, **38** (66), 8820–8850 (1973).

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Coordinated by JJ



Drinking water quality and chronic disease

Poorly designed studies and poorly generated data have made the job of relating trace elements in water to disease very difficult; some recommendations to ease the situation are offered

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Clean drinking water, free of disease-causing agents, has long been taken for granted in the U.S. However, the public's confidence was shaken when a series of drinking water samples from several major U.S. cities was analyzed last year and found to contain possible disease-causing agents.

With the discovery of these potentially dangerous substances, came the question of the relationship between many chronic diseases and the chemical composition of treated water. This question was discussed at a workshop held under the auspices of the National Academy of Sciences Subcommittee on the Geochemical Environment in Relation to Health and Disease (GERHD) at Captive Island, during the fall of 1974. This paper summarizes the major findings of the workshop: the health effects of trace elements in drinking water, their sources and distribution, and the effects of water treatment. The workshop pointed up the need for more reliable data.

Although the true incidence of acute water-borne disease is difficult to estimate, documented outbreaks caused by chemical poisoning in the U.S. during the period 1946-1972 numbered 19, which involved 279 cases of illness. This chemical contamination of drinking water resulted both from man's activities and from natural geochemical sources.

The influence of chemical constituents of water on the development of certain chronic disease, however, still remains controversial and unresolved. Many studies have shown a relation between water hardness and certain cardiovascular diseases. Data have also been presented that suggest a link between selected trace elements and certain cancers, and between calcium and magnesium and urolithiasis. These data however, are not unequivocal. A further study of these relationships is desirable from a public-health standpoint. Attempts to relate problems of health and disease to specific element concentrations in water or to a broad population base are meaningful only if the source and the effects of treatment and delivery of that water are considered. Comprehensive and reliable chemical data (especially trace elements) of finished water supplies in the U.S. are badly needed.

Intake of trace metals

While water seems to offer the most direct means of studying the relationships between trace metal intake and human health, food is man's major source of trace metals. It is possible that the physiological availability of metals in food and water may be different. If water is to provide a significant contribution to the body burden of trace metals, the metal must be more readily available in water than in food.

The community Water Supply Survey, which covered 969 water systems in nine geographic areas around the country, collected water samples at the consumer's tap. It was not a totally representative sample of the U.S., but its wide coverage provides an estimate of the metal intake from potable water (Table 1).

The importance of chemical speciation of metals on body assimilation has been demonstrated by comparative studies that have shown high uptake of methyl and dimethyl mercury but not inorganic mercury from the intestinal tract. In addition, numerous studies have been conducted that document variations in the availability of trace metals in water as a function of other dietary components such as phytates, hemicelluloses, and amino acid-carbohydrate complexes.

The chemical form of substances in natural water or in water entering a treatment plant affects the efficiency of their removal. For example, stable, water-soluble complexes of metals with either organic or inorganic ligands can pass through a treatment plant unaffected. Sand filters are generally less effective for

metal removal than treatment involving coagulation. Chlorination of water following treatment will often degrade organic complexes of metals.

As water leaves the plant and enters the distribution system, it is again subject to concentration and species variation through interaction with other warm constituents and reactions with elements of the distribution system. Calcium and magnesium salts associated with water hardness are excellent coprecipitators of divalent ions such as zinc, cadmium, and lead, and often accumulate on the wall of pipes in the distribution system.

Investigations have found a relationship between cadmium and hypertension, and an inhibition of the cadmium effect by water hardness. The effect of water hardness on cadmium availability can logically be attributed to the tendency of carbonate and phosphate—the anions often associated with water hardness—to precipitate cadmium, thus either effectively removing it or converting it to an unavailable chemical form.

Reliable techniques are not available for identifying such species in water at present. However, computer models are available for calculating most probable species by using available information on formation constants of the various metal inorganic and organic complexes that could occur in such systems.

Work reported by several investigators has also indicated that the amount of hardness in surface or groundwater supplies has a buffering effect that decreases the toxicity of certain trace substances and influences the growth of aquatic life. The general trend that the toxic effects of metals decrease with increased water hardness has been noted by investigators working with water-pollution problems in the metal-mining industries. This apparent buffering effect of water hardness may play an important role in protecting livestock.

On the other hand, there is a good correlation between cerebrovascular mortality and the acidity (softness) of water supplies. Investigators are attempting more clearly to define the role of drinking water in cardiovascular diseases.

With few exceptions, relatively little is known about the quality of water in individual water wells. It is, therefore, difficult to equate health problems with the quality of water in the rural areas of the U.S.

Reviews of water-borne diseases found that over 92% of the cases involving public systems were associated with the water

TABLE 1

Average intake of metals via water

Metal	Community water supplies		
	Average concn, mg/L	Microgram intake at 2 L/day	Percentage of samples with mg/L or more
Cadmium	1.3	3	63
Chromium	2.3	5	11
Cobalt	2.2	4	62
Copper	134.5	270	99
Iron	166.5	440	99
Lead	13.1	26	74
Manganese	22.2	44	78
Nickel	4.8	10	78
Silver	0.8	2	23
Zinc	193.8	390	100

source and treatment deficiencies. However, most disease outbreaks associated with private water systems resulted primarily from the use of untreated groundwater.

Metal contamination in drinking-water supply systems in rural areas utilizing individual water sources will continue to be a problem to the epidemiologist. Many incidences of metal toxicity have been reported connected with the pH of the water supply and the type of storage or distribution system utilized.

Sources and treatment

To conduct meaningful studies in this area, one must be cognizant of the mechanics of drinking-water delivery systems in the U.S. Water used for drinking is essentially a local product. That is, it is normally consumed within a reasonable distance of its source.

A distinction needs to be made between raw and finished (treated) water and between community and individual water systems. Data must be obtained on raw-water sources, the treatment of water, the chemical composition of water as it comes from the tap, and the nature of the chemical species present.

In most metropolitan areas, water is generally treated before it is consumed. However, the degree and effectiveness of treatment may vary dramatically from one water district to another. Attention paid to natural surface-water or groundwater composition may be misleading if one ignores the changes effected by treatment on the chemistry of a particular water source.

Trace-element chemistry of surface water varies greatly in composition on a seasonal basis. Groundwater from a given source or aquifer, however, tends to be of reasonably constant composition over time. Iron, nickel, cobalt, cadmium, lead, zinc, and copper are most likely to be removed by the lime-softening process, while lithium, selenium, molybdenum, and arsenic are most likely to pass into the delivery system (pipes) relatively unchanged. However, water as it emerges from a tap may have been changed considerably from what entered the delivery system.

that picked up trace metals was: cadmium, 15; chromium, 17; cobalt, 10; copper, 28; iron, 39; lead, 20; manganese, 32; nickel, 34; silver, 15; and zinc, 67. When corrosive water is distributed, metal contamination can be even more serious.

Distribution studies conducted in Seattle and Boston (Table 2) illustrate the effect of corrosive water on tap-water quality. Both Boston and Seattle use impounded surface water, and chlorination is the only disinfection treatment. The hardness and alkalinity of these waters are remarkably low and the pH is on the acidic side. The dissolved oxygen content of Seattle's water approaches saturation; this makes Seattle waters excellent solvents that exhibit aggressive corrosion tendencies.

The difference in metal pickup between these systems is probably related to the type of plumbing material and service lines in use. In Boston a high percentage of homes sampled had lead service pipes, whereas in Seattle copper and galvanized iron were more commonly used. No lead pipes were reported in Seattle and the source of lead in this case was probably from the solder used to join the copper piping.

Until recently, few states had minimum standards governing the employment of treatment-plant operators, but the situation is rapidly changing. Currently 36 states have some type of program that requires mandatory certification of operators. The quality of these programs varies from stringent examination to adherence to general formalities. The trend, however, is toward the examination procedure.

There is a shortage of private and public funds for training professional and technical personnel in the water-treatment field. A major problem exists in drinking-water research because of this lack of training.

Quality of drinking water

Except for those health studies conducted after-the-fact, when pollution of water sources has been suspected, virtually no nationwide data exist on the quality of the water as it comes from users' taps. The EPA's Interstate Carrier Water Supply study unfortunately covered a large population but a small geographic area. These data, however, are primarily from treatment plant taps (finished water sources).

Although water-plant analyses may be well performed, little is known about the changes in the chemical quality of the water as it moves through the distribution system. Many large cities probably possess such data in unpublished form, and these data would be valuable to epidemiologists who could use them to facilitate study of urban populations large enough for reliable statistical analysis. Funds for this purpose have, in fact, declined decidedly in the last 5 years, and the money available for research in water treatment and quality has decreased to the extent that more is known about wastewater than about drinking water.

Sampling, laboratory methods, data

Samples are generally collected at an operator's convenience and not according to some reliable procedure. This practice maximizes the condition for data variance. It is particularly important to establish a range of values for surface-water supplies, because water quality varies considerably. A literature search indicates no uniform sampling or sample storage procedures used prior to analysis by all health research groups. This deficiency leads to collection procedures that are redundant or incompatible to the point of being almost useless.

Good sampling, storage, and preservation procedures used on a nationwide basis are badly needed, and additional studies on this subject should be made at the earliest possible time. In a survey conducted by the Trace Elements and Toxicity Subcommittee of the Committee on Water Quality, Environmental Engineering Division, American Society of Civil Engineers (ASCE), the data indicate that only four of the 50 states and four possessions of the U.S. have criteria for evaluating or accrediting their testing laboratories. Virtually no programs exist for sample exchange and for analytical cross-checking in any state.

Only the largest cities can afford their own analytical facilities.

TABLE 2

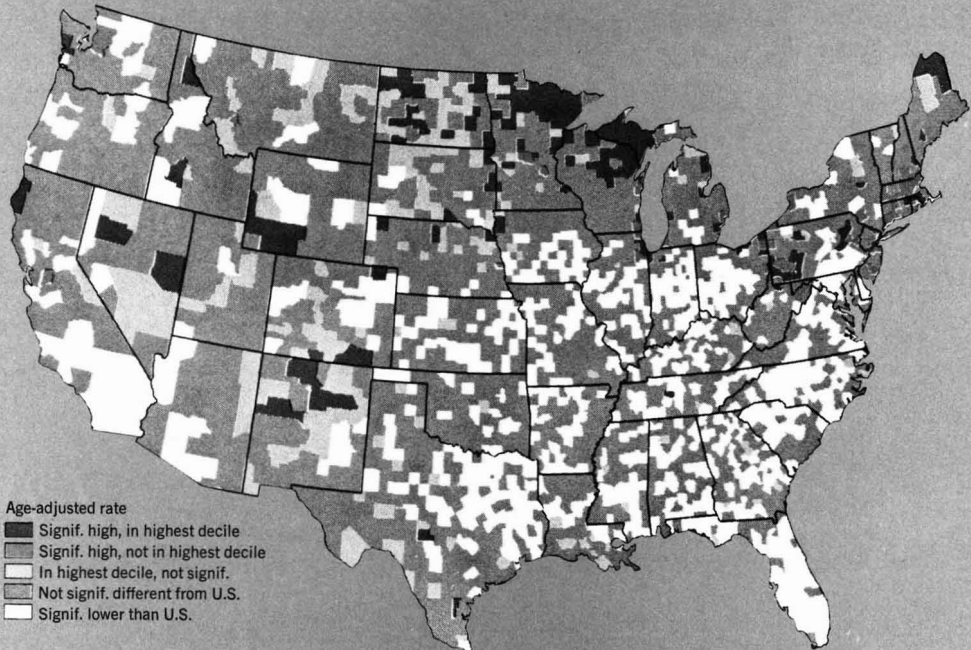
Percentage of homes with a sample exceeding drinking water standards

Metal	Boston	Seattle
Cd	0	7
Cr	0	—
Cu	19	24
Fe	9	76
Pb	65	24
Mn	0	5
Zn	0	10

A major source of metal contamination of drinking water is the water supply itself. This contamination begins with the chemicals used during treatment. Copper is often added for algae control in reservoirs. Treatment chemicals contain trace metals and may (and undoubtedly do) contribute to trace-metal concentration levels found in water. Corrosion of the distribution system and household plumbing add to the metal content of drinking water.

An industrial health survey was conducted in Chicago in 1968. Water samples collected as part of this survey provided an opportunity to determine the metal content of a large number of samples from a single system. Composite samples were collected at the treatment plants, and these results were compared with 550 grab samples collected from the distribution system to give an indication of metal pickup. The percentage of samples

Stomach cancer mortality in white males^a



^a Mason, T.J. and McKay, F.W., 1976. Cancer Mortality by County, 1950-1969. NCI, Washington, D.C.

Most small systems must use commercial laboratories, a practice that immediately raises problems, not only of laboratory quality but of sample collection, and of the effectiveness, length, and conditions of storage.

The research scientist must have confidence in the reliability of the data he is using if studies relating water chemistry to health and disease are to have meaning. Two important aspects of the reliability of water-quality data are: the ability of the analytical method or technique to generate valid data; and the capability of the analyst to produce data in which a high degree of confidence can be placed.

It is obvious that to produce reliable data, the laboratory must use methods of proven adequacy for the purpose intended. Compendia of acceptable methods are available.

Any methods proposed as a standard acceptable method for water analysis should, as a minimum requirement, be accompanied by a statement giving the accuracy and precision of the method. This precision statement expresses the degree of reliability of the analysis, provided that the method is used by an experienced analyst working in a properly equipped laboratory. Such a statement assures the data user that the data have at least this degree of reliability. In spite of the use of standard analytical methods, data may be unacceptable because the analyses were performed in a careless manner, or in an improperly equipped or managed laboratory.

Concentrations of trace or minor constituents frequently are so low that they approach the limit of detection of the analytical method. Moreover, values of this small magnitude are often of significance when the data are examined and related to their effects on health and disease. When it is determined that such very low concentrations are significant, special analytical techniques must be used, the analytical costs increase appreciably, and the accumulation of sufficient data that can lead to valid statistical treatment is severely limited. Most often a

compromise must be achieved whereby a statistically significant amount of data must be obtained at a reasonable cost, usually with more sacrifice of data reliability.

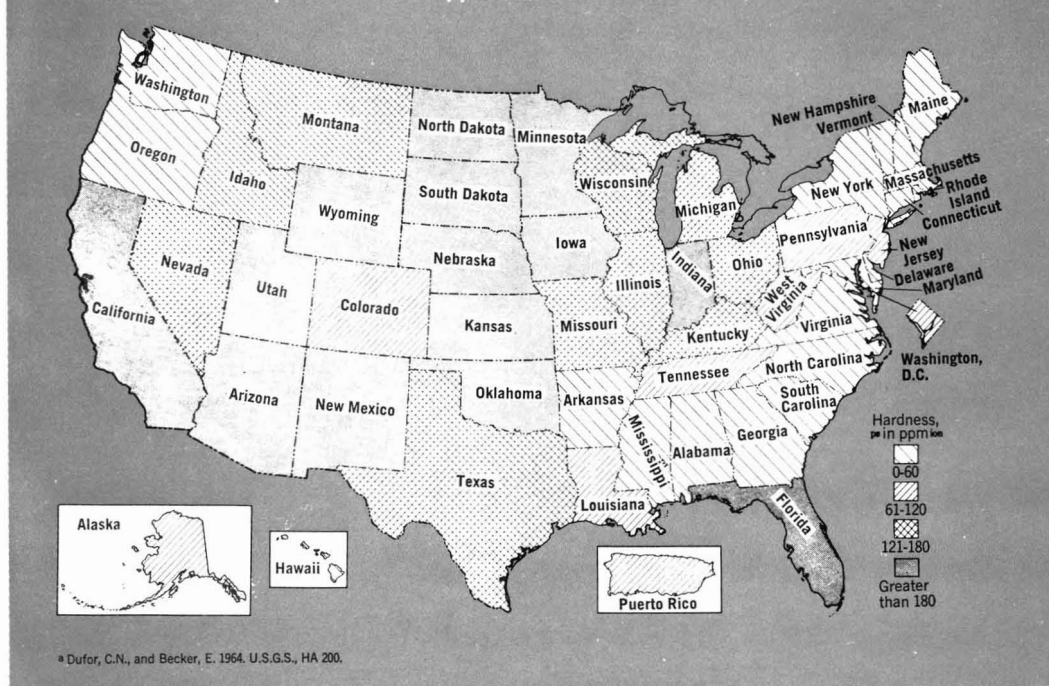
Water quality is a constantly changing factor, especially in the case of surface waters. Consequently, reliance on a single analysis is risky. Samples should be collected over a sufficient period of time to identify the ranges of concentration that may be expected for the several constituents of interest. Data reporting the mean concentration over a period of time will be more significant than data based on the analysis of a single sample.

In practice, the frequency of reporting is erratic. More important, the only information sought is whether or not certain constituents exceed state or federal standards. As a result, the bulk of data is being reported as a value of "less than" that required for a particular standard and does not provide usable information for the researcher. Another and perhaps equally important factor is that few states require or request information on elements other than those for which there are specific limitations or standards. Consequently, relatively little information is available on those trace elements for which there are currently no standards, and little information is accessible on anions at all, except for chlorides, nitrates, sulfates, bicarbonates and, possibly, phosphates.

Predictive mapping

Numerous problems are associated with producing reliable nationwide maps representing water-quality parameters. Among these are the availability and quality of the data, relevance of the data to the purpose at hand, and the representation of the three-dimensional aspect of water sources on a two-dimensional map. For many trace elements of interest, the availability and quality of the data are the most important constraints on map production.

Water hardness of public water supplies^a



Though the amount of trace-element data has increased rapidly in the past several years, there are still large areas in the U.S. with little or no available data. Presently no standard group of trace elements that are routinely determined by all laboratories exists.

Further, most data-storage systems that combine data from numerous sources provide no means of evaluating the quality of the data. When using these data, equal consideration is often given to interpretations based on excellent or poor data.

It should be noted though, that many factors need to be considered when constructing maps of trace-element distribution in water. Water supplies in many areas can be obtained from either streams or subsurface aquifers. Many areas are underlain by ground aquifers, each capable of furnishing adequate water supplies to municipalities. In preparing such maps it is important to note, in fact, that many communities use multiple sources of water supply; thus it is important to define the water used by each population.

To better define the relationship between water hardness and chronic disease, an area taking its water supply from an aquifer whose chemical composition is uniform would be preferable. For example, the Florida hardwater aquifers (Biscayne and Floridan systems) all underlay an area of sufficiently large population to be considered for this purpose. Furthermore, being essentially a pure calcium carbonate system, the input of magnesium would be minimal. This circumstance should, for example, provide a means of studying the effects of calcium as separate from that of magnesium. Such a distinction is of interest to those studying urolithiasis problems.

A population in the upper midwest or along those states bordering the Great Lakes could be selected whose water source is from a dolomitic aquifer. This would make it possible to study the effects of hard water (dolomitic) with a high magnesium content. Maps such as those showing hardness of surface and subsurface waters can be extremely useful in this regard.

Considerable useful geochemical information pertaining to

groundwater quality is also available. It is possible to delineate those areas of the U.S. that should be of concern medically by using hardness maps already available.

A large amount of reliable data on the quality of both surface and groundwater can be obtained from cities, rural water co-operatives, private utilities, state geological surveys, federal agencies, and many other sources. As a result of the problems previously mentioned, the quality of these data must be evaluated on a case-by-case basis.

If all the information could be assembled in central data-storage systems together with information on how, when, and where the samples were collected, stored, and analyzed, this knowledge could be more effectively used by epidemiologists to establish criteria for making judgments. Similarly, if information from physicians were made more readily available, it would be of great value not only to those interested in the geochemical environment and health but also to the professionals in the fields of water treatment and distribution.

Recommendations

One method of expanding the usefulness of existing data on both surface and groundwater chemistry (mostly major element data—calcium, magnesium, sodium, potassium, bicarbonate, and chlorine) would be to have maps of water quality plotted on the basis of drainage basins of low- to medium-order streams. This usefulness would be further refined by developing maps of water-quality data on a distribution-system basis.

Greater emphasis needs to be placed on securing useful information on concentrations of all the trace elements in water.

Water-quality maps that separate concentrations of calcium and magnesium, rather than combining the two in a hardness map, would be of great value. To develop information on trace-element speciation in natural water systems would be of even greater value. The ionic species of an element present in the water will have a great effect on its bioavailability.

A system must be developed for collecting an accurate data base on specific groundwater aquifers, and for determining the quality of the tap water derived from these groundwater sources. Only with the availability of reliable water chemistry data can useful studies be conducted.

There is also a need to develop a data base and analytical procedures on the chemical form of the specific metals associated with disease. In particular, it is necessary to know what anions are associated with the metals in high- and low-risk areas, and whether organic metalics are a major problem. It has been reported that organics materially increase the mobility of metals in an aquatic environment. Perhaps the same phenomenon also makes these metals more available to biological systems.

Long-term multidisciplinary studies should be made of the relation between the geochemical environment and disease, particularly in those areas where the existing data base is reliable. The studies should be of sufficient duration so that meaningful data collection, analysis, and interpretation can be made to protect human health through better technology.

The information for this paper came in part from studies of the National Academy of Sciences. More detailed information will be forthcoming in Volume III of Geochemistry and the Environment. The assistance of G. F. Craun, G. Feder, J. C. Jennett, and M. Skougstad is gratefully acknowledged.

All three authors were members of the National Academy of Sciences Subcommittee on the Geochemical Environment in Relation to Health and Disease at the Captive Island, Fla., workshop when this paper was developed.

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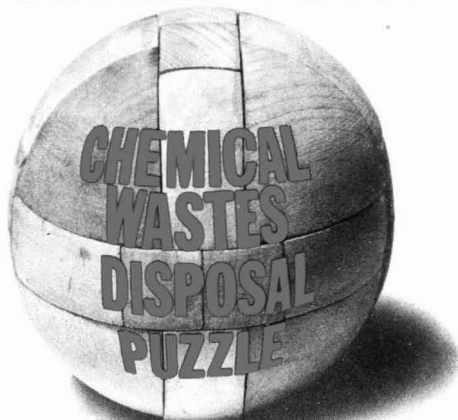
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We'll take care of your problem wastes, usually for less than it costs you to do it yourselves. You'll avoid expenditure for sophisticated equipment, you'll gain the economies of high-volume treatment, you'll reduce your operational hazards, you'll minimize your liability exposure. And if your wastes contain recoverables, you may be able to reduce your disposal costs.

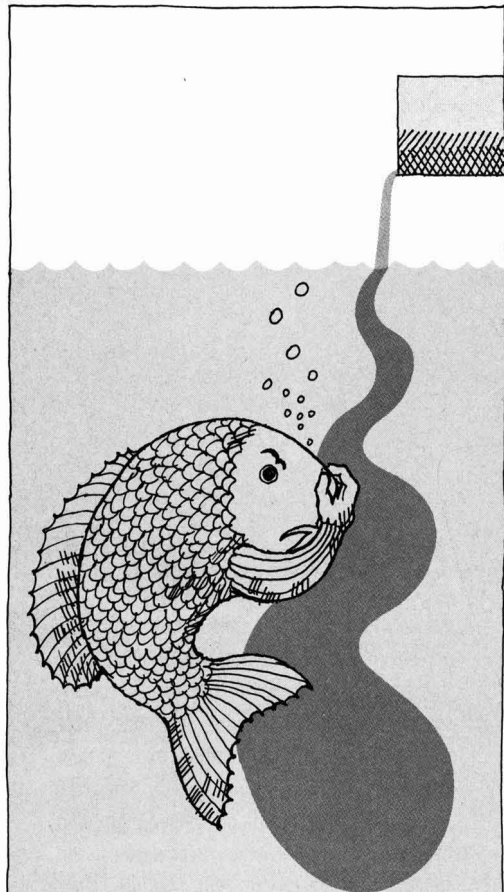
CHEM-TROL POLLUTION SERVICES, INC.
MODEL CITY, NEW YORK 14107
716-754-8231

EARTHLINE COMPANY
GAESS ENVIRONMENTAL SERVICES DIVISION
PASSAIC, NEW JERSEY 07055
201-773-2931

HARTLEY & HARTLEY, INC.
KAWKAWLIN, MICHIGAN 48506
517-684-3960

EARTHLINE DIVISION
WILSONVILLE, ILLINOIS 62093
217-835-2931





Defining a harmful quantity

A proposal for defining such a quantity
for 95% of the nation's waterways
is presented that will aid the EPA
in implementing its mandate
under P.L. 92-500

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The Dow Chemical Company
Midland, Mich. 48640

With the passage of the Federal Water Pollution Control Act of 1972, the Environmental Protection Agency (EPA) received the mandate to restore and maintain the chemical, physical and biological integrity of the nation's waters. A paramount problem then became the definition of just what constitutes a harmful quantity (HQ) of any material alien to natural waters. The difficulty in defining a HQ is compounded by the ambiguity of Section 311 of the law, by the wide variety of substances listed as harmful (some 300 at the date of this writing), and by the ability of the body of water to assimilate the substance.

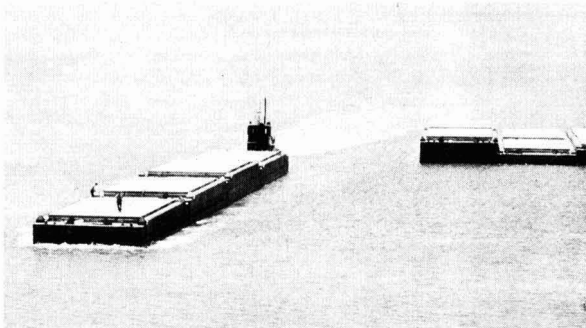
So complex is the problem that four years after the enactment of the amendments final regulations have not yet appeared. An appreciation of the technical difficulty can be seen by examining the photographs, which depict scenes of the Mississippi River (250 000 cfs river), a medium size river (1000 cfs) and a small stream (50-100 cfs). Obviously what is a HQ for a small stream may not be harmful for a large stream. How can this paradox be resolved? The purpose of this paper is to set forth certain parameters, well within the intent of the law, that, if followed, will enable EPA administrators to define HQ.

P.L. 92-500 summarized

P.L. 92-500 requires the EPA administrator to designate those chemicals that, when released into navigable water, constitute a harm to the environment. Section 311 of the Act further requires the administrator to determine the amount of each designated chemical that actually causes the harm. This amount is referred to as harmful quantity (HQ). This determination of HQ has compelled the EPA and its contractors (Battelle) to develop methodologies capable of defining this number. The difficulty may be more fully appreciated by referring to the actual section of the law describing HQ.

Section 311(b)(4) describing the concept of HQ states, "the President shall by regulation, to be issued as soon as possible after the date of enactment of this paragraph, determine for the purposes of this section, those quantities of oil and any hazardous substances the discharge of which, *at such times, locations, circumstances, and conditions* will be harmful . . ." (emphasis added). The President assigned this authority to the EPA administrator. In order to follow the letter of the law, the administrator would have to have complete knowledge of an accident before it occurred in order to take time, location, circumstance and conditions surrounding the discharge (spill) into the determination of a HQ. Obviously, this becomes impossible and it is here that most of the difficulty resides in writing final regulations.

Once established, the HQ value becomes very important, especially when it is remembered that a discharge of this quantity triggers the notification scheme and the calculation of the penalty that will be levied against the discharger. When a person in charge of a vessel or an onshore facility has knowledge of the discharge of a HQ, he is to immediately notify the appropriate agency of the U.S. Government [Section 311(b)(5)]. A penalty will then be assessed by the administrator under Section 311(b)(2)(B)(iii). This penalty will be assessed on those hazardous



Large river. The 250 000 cfs Mississippi River flowing near St. Louis

A proposal for defining a harmful quantity

- HQ should be defined in terms of a quantity of chemical which, when spilled, requires notification
- Under Section 311(b)(2)(B)(iii)(aa), the penalty should be assessed between \$500–5000 depending on the toxicity, degradability and persistence of the chemical
- Under Section 311(b)(2)(B)(iii)(bb) to be used in the case of willful negligence, the penalty should be based on the formula established by EPA in its proposed regulations
- HQ (for notification purposes) for those materials designated to be nonremovable should be defined according to the rationale described below
- HQ (for notification purposes) for removable materials (floaters) should be related to some other parameter besides toxicity. A significant sheen on the surface is one possibility
- Harmful quantities for designated hazardous chemicals should be classified as below:

Nonremovable Category	96-h LC ₅₀	HQ (lb)
A	1 ppm	100
B	1–10	1000
C	10–100	10 000
D	100–500	50 000

Removable materials

(Specific Gravity less than 1.0, and solubility in water 1000 mg/L or less, floaters) HQ will be related to a significant sheen on the surface of the water. A significant sheen is one that is visible on the surface of the water.

materials determined to be nonremovable; the penalty assessment has nothing to do with the HQ designation.

The penalty under Section 311(b)(2)(B)(iii)(aa) is based on the toxicity, degradability and dispersal characteristics of the substance. Under Section 311(b)(2)(B)(iii)(bb), the administrator can, at his discretion, base the penalty on the number of units discharged multiplied by a dollar amount established for each unit. The unit under this penalty clause is a unit of measurement based upon usual trade practice. Usually, the penalty for such a unit is in the range of \$100–\$1000/unit based, once again, on the toxicity, degradability and dispersal characteristics of the substance. This is a rather complicated procedure and may be more easily visualized by means of a flow chart (Figure 1).

Proposed rule-making

The agency in its proposed rule-making under Section 311(1) designated about 300 chemicals as hazardous, based for the most part on 96-h LC₅₀ fish toxicity. They then divided the list into four categories. The most hazardous was designated category A and had toxicity numbers of less than 1 ppm; category

B fell in the range of 1–10 ppm, followed by C at 10–100 ppm and D at 100–500 ppm. Materials with a 96-h LC₅₀ greater than 500 ppm were not considered hazardous. In order to define the unit of measure as described under penalty section (bb), EPA discovered that cyanide, a member of Category A, was shipped in 1 lb containers; hence a unit of measure based on usual trade practice was one pound.

This is all quite reasonable. However, by a quantum leap in logic, the agency arbitrarily equated one pound with a HQ for Category A. The rest was simple; the fish toxicities in each category went up by an order of magnitude, consequently HQ was increased in a similar manner. This resulted in the following table of harmful quantities (Table 1).

The Agency appears to be very comfortable with this rationale. One of the reasons for this is that benzene happens to fall into Category C with a HQ of 100 lb. For some reason, the agency equates a 100-lb spill of benzene with a sheen. A harmful quantity of oil is a sheen on the surface of water. Since benzene is derived from oil, and 100 lb gives a sheen, then quid pro quo.

In summary, the problems with the EPA proposal are:

- The agency has equated the unit of measure with HQ. This has resulted in a very low value for HQ, which in no way is related to harm. Furthermore, the proposed definition of HQ does not even consider the time, locations and circumstances surrounding the spill or discharge of a designated hazardous material.
- According to the law, the unit of measure concept should be applied only to the penalty schedule under 311(b)(2)(B)(iii)(bb) and not to (aa).
- Such a small number for HQ will cause a tremendous amount of reporting or a disregard of the regulation on the part of the offender.

Alternate approach to rule-making

Pending legislative redress of the wording of Section 311(b)(4), there is no way to define HQ according to the letter of the law as it is presently written. To do so would require complete knowledge of the spill before the accident occurred. We agree with EPA that the intent of this clause should be to provide a notification number associated with each chemical and when a quantity is spilled into any public waters, regardless of size, the authorities would be notified. Furthermore, this notification number should be reasonably protective of the navigable water in the nation. We hold no brief with the agency's objective of defining a number that will protect all of the nation's water. Such a goal is as unrealistic as providing 100% safety for all people living in this country.

It is our contention that if a notification quantity can be defined for any designated hazardous chemical to protect 95% of the water, all major streams will be covered. Referring back to the photographs, if a number can be associated with a chemical that will protect the small streams, this will also be protective of the larger rivers on which chemicals are likely to be transported, manufactured or used. A proposal for protecting 95% of the waters of the U.S. is shown in the box.



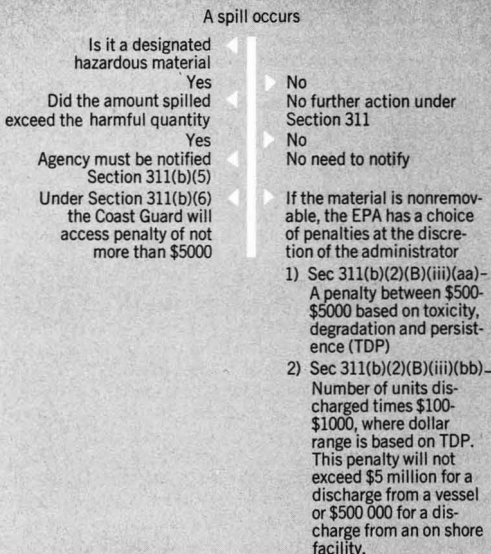
Intermediate river. Recreational activities on this 1000-cfs river



Small river. Peaceful pursuits on a small 50–100 cfs river

FIGURE 1

What happens when a spill occurs



Rationale for proposed HQ

How do we define a harmful quantity? It must be related to both the concentration of the chemical, and the length of time that species are exposed to that concentration. Furthermore, it should be recognized that it is impossible to define a HQ that protects all waters. Clearly, even one gram of a chemical is harmful to some organisms in a very small volume of water.

Consequently, the definition we propose for a HQ is relevant to 95% of all streams in the U.S. Such a definition requires reporting of virtually all of the significant spills that occur. Battelle in its study examined a large number of water sheds. It was concluded that streams of 36 cfs or larger constituted 95% of all the water flowing in the country. Consequently, a HQ for this size stream will cover 95% of all water flowing in rivers. Furthermore, a HQ associated with such a small stream will also be protective of the other major water body types.

The LC₅₀ values that are normally reported for fish are usually of 96-h duration. Applying this to a stream would mean that the resulting concentration would have to be equal to or greater than the LC₅₀ values for at least 96 hours. This is an unreasonable length of time, and is one of the questions that Battelle attempted to answer in its report to EPA.

In analyzing the available data Battelle concluded that six hours was a more suitable length of time. Since most of the available fish toxicity data were on a 96-h basis, it was necessary to convert this to six hours. A reasonable estimation was found possible by dividing the 96-h LC₅₀ by a factor of 0.125. Performing this division, the critical concentrations in Table 1 (di-

viding the midpoint 96-h LC₅₀ of each category) were found to be: A = 4 ppm, B = 40 ppm, C = 400 and D = 2000.

The question that then had to be answered was: How much chemical (hazard rating A) had to be added to a 36-cfs stream to yield a concentration of 4 ppm or greater for a period of at least six hours? From a knowledge of river flow and dispersion studies, this amount turned out to be 500 lb. By applying a safety factor of 5 to allow for a more sensitive species, a HQ of 100 lb for Category A material was calculated. The HQ for the remaining categories was estimated in a similar manner and is shown in the box.

It should be pointed out that these HQ's are *very conservative estimates*. They represent harmful quantities only for those substances that are *completely soluble in water*. It is well known that most organic chemicals, while they are classified as soluble, are in fact only partially soluble. A good example is chloroform, where it was recently shown that only a small portion of the spilled chemical actually went into the wave as it traveled downstream. This would mean that the actual concentration of the chemical in the water as a result of a major spill will be only a small part of what was calculated.

The estimation of harmful quantity was based on the following assumptions:

- Measure of harm is related to the 96-h LC₅₀ on median receptor aquatic species such as fathead minnows or bluegills.
- It is possible to convert a 96-h LC₅₀ to a 6-h LC₅₀ by dividing the 96-h value by a factor of 0.125.
- Hazard will be arbitrarily categorized into four classifications based on fish toxicity. This is similar to the proposal made by EPA in their proposed regulations.
- A 36-cfs stream represents the smallest receiving body of water that is likely to be the recipient of a chemical spill. Acceptance of this assumption implies that if the HQ defined for such a stream is valid, then the HQ will be acceptable for other receiving bodies of water such as lakes, estuaries and coastal zones.
- The underlying assumptions used in developing the mathematical model for chemical spills in rivers are reasonable.
- Reducing the calculated HQ by a factor of five to protect other aquatic organisms.

If these six assumptions can be accepted, then the calculated HQ for each category appears to be reasonable. It is this value that would be used for triggering the reporting and penalty assessment portion of Section 311 of P.L. 92-500.

In summary

EPA was presented with an impossible task in writing regulations to implement Section 311 of P.L. 92-500. Implementation of this section has resulted in a proposed set of regulations that encourage ignoring the law. EPA's rationale for these regulations was not logical, nor did it follow the law (as it probably couldn't). There is need for legislative change.

Additional reading

Federal Register, December 30, 1975, p 59982.

Title 40 Code of Federal Regulations, Part 110.3.

"Determination of Harmful Quantities and Rate of Penalty for Hazardous Substances," EPA-440 19-76-005-6 prepared by Battelle for EPA, October, 1974.

Neely, W. B., Blau, G. E., Alfrey, T., *Environ. Sci. Technol.*, **10**, 72 (1976).

TABLE 1

EPA's proposed classification, HQ and penalty schedule

Category	96-h LC ₅₀	HQ (lb)
A	1 ppm	1
B	1-10 ppm	10
C	10-100 ppm	100
D	100-500 ppm	500

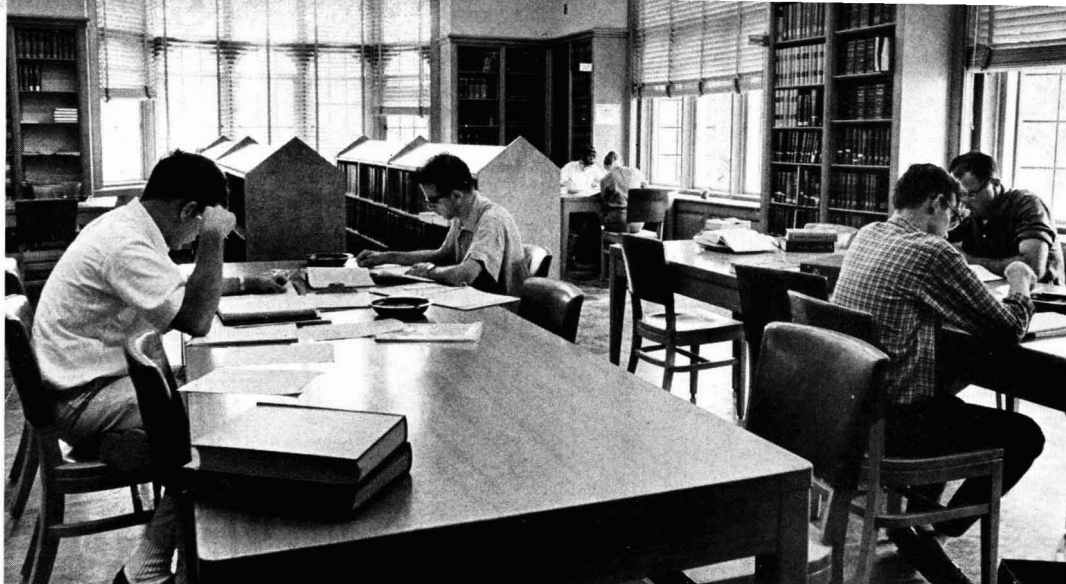
Penalty schedule

1. Under 311(b)(2)(B)(iii)(aa), if a HQ has been discharged, the administrator will set a penalty between \$500-5000.

2. If the spill results from willful negligence on the part of the operator, the penalty will be based on a formula as prescribed in the *Fed. Regist.*, Dec. 31, 1975. The formula: one pound times \$1000 times a factor that scales the range between 1-10.



W. Brock Neely is a technical advisor in Dow's Environmental Science Research Laboratory. Dr. Neely also serves on EPA's Ecology Advisory Committee. Besides these activities, Dr. Neely is writing a book on the transportation and transformation of chemicals in the environment. Coordinated by LRE



Water chemistry: seeking information

Any literature search involves hard, time-consuming work. For one field, at least, here's how such work can be made easier

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Water chemistry is a scientific discipline that originated from a variety of basic and applied science and engineering fields. Among those fields are chemistry, geology, limnology, oceanography, soil science, public health, and civil-environmental (sanitary) engineering. Because of these multidisciplinary roots, water chemistry is a difficult specialty to define. However, an appropriate description has been offered (see box).

Water chemistry education

The education of water chemists in the United States reflects the diverse background of this discipline. Very few university chemistry departments offer more than one or two courses; by comparison, environmental science and engineering programs, schools of public health, and the like, provide the strongest support. However, at least one chemistry department (The University of Maryland, College Park) has made a commitment to the field of environmental chemistry, and offers instruction in water chemistry as well as atmospheric chemistry, geochemistry, and other pertinent subjects. Part of the reluctance of traditional academic chemists to get involved in water chemistry programs is apparently caused by uneven funding patterns, although there are also some significant conceptual difficulties involved.

Among the universities having programs housed in departments of environmental science and engineering and schools of public health that have substantial offerings in water chemistry are the Universities of California, Florida, Michigan, Minnesota, North Carolina, Tennessee, Texas, Washington, and Wisconsin. Similarly strong programs are operating at the California, Illinois, and Massachusetts Institutes of Technology and at Harvard and Rutgers Universities. Other institutions are no doubt involved in

water chemistry education to some degree, but those listed above are particularly known to the author.

The curricula of water chemistry are as diverse as the institutions and professors involved. Nevertheless, they provide the student with a strong background in chemistry and a broad familiarization with the collateral disciplines that were cited in the beginning of this article.

Water chemistry literature

The multidisciplinary roots of water chemistry have resulted in a variety of publication outlets for the research performed in this field. There is no "Journal of Water Chemistry," *per se*, which would be analogous to the *Journal of Organic Chemistry*, or *Inorganic Chemistry*, for example. Also, prior to 1967, there was no American Chemical Society (ACS) journal committed entirely to the chemical aspects of the environment.

The initiation of *Environmental Science & Technology* in 1967 gave water chemists their first formal chemical publishing outlet. To be sure, other ACS journals such as *Analytical Chemistry*, *Industrial & Engineering Chemistry*, and a few others have always published some papers in the field of water chemistry. But in *ES&T* it became possible to have many more articles concerning environmental and multidisciplinary aspects of water chemistry research published.

ES&T, though, is not a surrogate for a "Journal of Water Chemistry." It must serve all environmental chemical disciplines equally, and thus share its space allocations among water, air, and waste chemistry articles and papers. It must also consider the broader policy questions involved in environmental matters.

It is premature to suggest the establishment of a journal de-

voted exclusively to water chemistry. The coverage would necessarily be so broad that it would eventually have to be divided into more specialized journals, thereby defeating its originally intended purpose. Thus, an important question arises: "Where does one find the published information of interest to, and most often needed by, water chemists?" In an effort to answer this question, a survey of the literature available to water chemists was made. The material was initially collated for use in a senior-graduate level course that the author teaches in the Water Chemistry Program at the University of Wisconsin-Madison. The utility of the material to water chemistry students, librarians, and colleagues led to this article.

Texts and reference books

The acceptance of water chemistry as a recognized chemical discipline was enhanced by the publication of one of the few authoritative and comprehensive texts on the subject. Appropriately titled *Aquatic Chemistry* (Wiley-Interscience, 1970), the book was authored by Professors Werner Stumm (the 1976 ACS Monsanto Award winner) and James J. Morgan (*ES&T's* first editor). The text includes examples of recent environmental research applications that illustrate basic aquatic chemical principles. A 1967 reference work, edited by Samuel D. Faust and Joseph V. Hunter, and based on the proceedings of the Fourth Rudolphs Conference, held at Rutgers University (New Brunswick, N.J.), is one of the few other relevant texts that were available to water chemists before the publication of *Aquatic Chemistry*.

There are also a number of reference books available that deal with specific aspects of water chemistry. Many of these are based on papers presented at scientific meetings, or are collections of topically-related articles assembled by editors. Readers are referred to the catalogs of publishing houses or to the most current *Books in Print* (R.R. Bowker Co., New York, N.Y.) for listings of these works.

A number of analytical reference books for use by water chemists-analysts are also available. These are published by governmental agencies, professional organizations, and others, and include such well-used works as *Standard Methods for the Examination of Water and Wastewater* (APHA et al.).

Bibliographic resources

The literature of water chemistry, and of chemistry in general, is expanding rapidly. The annual volume of newly published chemical and chemical engineering literature is doubling approximately every nine years. It is almost impossible for water chemists to go to a single library (except, perhaps, the Library of Congress) and expect to find all of the journals that they might need in a broad-based research program. Even if all of those journals were locally available, few individuals have the time to scan each and every one. Therefore, one solution is to utilize some of the current awareness (tables of contents or titles) services that are available. A few of these are listed in Table 1. By selecting an appropriate combination of current awareness services, water chemists can optimize the time and expense of their coverage of the current literature.

In addition to the current awareness services, water chemists can subscribe to the *Automatic Subject Citation Alert* (ASCA) provided by the Institute of Scientific Information. This is a subscriber-specific service that is tailored to an individual's own interest areas. The ASCA system is not available in libraries but its data base, that is, the *Science Citation Index* (SCI), is available in many locations. By utilizing the SCI data base, water chemists can make their literature-reviewing activities more efficient, since SCI is well suited to multidisciplinary research topics. An advantage of SCI is that every paper published in the journals covered by the data base is indexed and cross-referenced.

In contrast to the above approach, abstracting services (Table 1) provide a more selective review of the literature needs of water chemists. Journals that are surveyed by the abstract services are not given complete coverage, and the papers se-

Water chemistry

"Water chemistry can be best defined as that branch of chemistry dealing with natural and artificial aquatic environments which is concerned with surface water and ground water systems as well as water and waste treatment processes. Such scientific phenomena as chemical equilibrium, thermodynamics and kinetics-dynamics are relied on to explain the reactions and changes occurring in the bulk of a body of water, in its unconsolidated sediments or sludges and at the water-air and water-solid interfaces. Water chemistry is unique in that it deals with viable aquatic systems where principles of other scientific disciplines become relevant."

Source: Hindin, *J. Chem. Educ.*, 52, 599 (1975).

lected depend on the acuity of the abstractors. Nevertheless, the abstract services do provide an additional dimension in information dissemination, since the actual abstracts are published along with citation information. This assists abstract readers in selecting articles that may merit further and more thorough reading.

Journals

Regardless of how comprehensive or encompassing the standard reference texts and the current awareness or abstracting services may be, the real strength of water chemistry is manifested in the primary literature of its published research. Water chemistry research papers are presently published in a wide variety of journals. Many of these journals are assembled in Tables 2 through 7 according to topical categories such as analytical techniques, environmental engineering and science.

The journals in each table are ones that the author has selected as being among the most useful to a wide spectrum of water chemistry practitioners and their diverse research interests. The author recognizes that the lists are not necessarily complete, and that they reflect some of his own interests and biases. The lists are not based on computer analyses of citation frequencies, although such an analysis might serve to confirm or reject some of the selections solely on a numerical basis.

Another factor in the choice of journals was a desire to have each journal covered by at least two of the bibliographic resources discussed earlier (Table 1). This criterion has been satisfied to a large extent, with only a few exceptions.

Tables 2 through 7 should be used by persons seeking to assess the breadth of research in the water chemistry field. By routinely screening the journals in these tables, readers can readily determine the publications that are most useful for their own research area. In time, individual researchers, teachers, and students will be able to reduce their journal screening to a core list that might be substantially smaller than the lists in Tables 2 through 7.

ACS publications

In addition to journals such as *ES&T* and *Analytical Chemistry*, the ACS also publishes books that often include water chemistry topics. These are represented in the *Advances in Chemistry* and *Symposia in Print* series. The ACS frequently updates listings of those titles still in print. Moreover, the ACS Division of Environmental Chemistry publishes preprints (four-page extended abstracts) of papers presented before the Division at the semi-annual ACS National Meetings. These preprints are distributed to about 1500 Division members and are also available in certain libraries. Remaining copies from earlier press runs can be purchased from the Publications Committee of the Division (contact ACS for this information).

Reference materials in both the Government and ACS publications categories are frequently abstracted by some of the

TABLE 1

Bibliographic resources**Current awareness***Titles and Tables of Contents*

- | | |
|---|---|
| • Chemical Titles (American Chemical Society, Columbus, Ohio) | a |
| • Current Contents® (Institute for Scientific Information,® Philadelphia, Pa.)
... Agriculture, Biology & Environmental Sciences | b |
| ... Physical & Chemical Sciences | c |
| • Environmental Periodicals Bibliography (Environmental Studies Institute, Santa Barbara, Calif.) | d |

Abstracts

Selected Abstracts (selections do not necessarily give complete coverage of all papers in each journal issue)

- | | |
|--|---|
| • Chemical Abstracts (American Chemical Society, Columbus, Ohio) | e |
| • Selected Water Resources Abstracts (U.S. Department of the Interior, Washington, D.C.) | f |

Indices*Computer Generated Index*

- | | |
|--|---|
| • Science Citation Index® and Automated Subject Citation Alert (ASCA)® (Institute for Scientific Information, Philadelphia, Pa.) | g |
|--|---|

Other Indices

- | | |
|--|---|
| • Engineering Index (United Engineering Center, New York, N.Y.) Covers various subjects in engineering, technology and applied science. Uses key words such as Water—standards, analysis, filtration, pollution, supply, treatment, etc. Journal coverage substantially less than a through g above. | * |
| • Applied Science & Technology Index (H.W. Wilson Co., Bronx, N.Y.) Uses key words such as Water—wastes, analysis, pollution, purification, standards, etc. Journal coverage also substantially less than a through g above. | * |

* Not included in Tables 2-7

TABLE 2

Analytical techniques

American Laboratory	e, f
Analyst (London)	a, c, e, f, g
Analytica Chimica Acta	a, c, e, f, g
Analytical Chemistry	a, c, e, f, g
Analytical Letters	a, c, e, f, g
Applied Spectroscopy	a, c, e, g
Atomic Absorption Newsletter	f
International Journal of Environmental Analytical Chemistry	b
Journal of the American Oil Chemists Society	b, c, e, g
Journal of the Association of Official Analytical Chemists	a, b, e, g
Journal of Chromatography	a, c, d, e, f, g
Talanta	a, c, e, g

TABLE 3

Geological sciences and soils

American Mineralogist	a, c, e, g
Canadian Journal of Earth Sciences	c, e, g
Chemical Geology	a, c, e, g
Clays and Clay Minerals	a, b, c, e, g
Earth and Planetary Science Letters	a, c, e, g

Environmental Geology	b, c, d, g
Geochimica et Cosmochimica Acta	a, c, e, f, g
Geological Society of America Bulletin	c, e, f, g
Ground Water	b, f, g
Journal of Geology	c, f, g
Journal of Soil Science	a, b, d, e, g
Soil Science	a, b, d, e, f, g
Soil Science Society of America Journal	a, b, d, e, f, g

TABLE 4

Environmental health, environmental toxicology and pesticides

Archives of Environmental Contamination and Toxicology	b, f, g
Archives of Environmental Health	a, b, d, e, f, g
Bulletin of Environmental Contamination and Toxicology	a, b, d, e, f, g
Environmental Health Perspectives	b, d
Journal of Environmental Health	b, d, f
Journal of Environmental Science and Health, Part B	b, d, f, g
Journal of Pesticide Science	b
Journal of Toxicology and Environmental Health	b
Pesticide Science	a, b, d, e, g
Pesticides Monitoring Journal	b, f, g

TABLE 5

Limnology and oceanography

Deep-Sea Research	b, g
Estuarine and Coastal Marine Science	b, f
Freshwater Biology	b, d, f, g
Hydrobiologia	b, f, g
Journal of the Fisheries Research Board of Canada	b, d, e, f, g
Journal of Great Lakes Research	e, g
Journal of the Marine Biological Association of the U.K.	b, g
Journal of Marine Research	b, g
Limnology and Oceanography	b, e, f, g
Marine Biology	b, d, e, f, g
Marine Chemistry	b, f, g
Marine Geology	c, f, g
Netherlands Journal of Sea Research	b
Transactions of the American Fisheries Society	b, d, f, g

TABLE 6

Environmental engineering and science

CRC Critical Reviews in Environmental Control	b, d
Journal of the American Water Works Association	a, d, e, f, g
Journal of Colloid and Interface Science	a, c, e, f, g
Journal of the Environmental Engineering Division, ASCE	b, d, f, g
Journal of Environmental Science and Health, Part A	b, d, f, g
Journal of Hydrology	c, f, g
Journal of the Water Pollution Control Federation	a, b, d, e, f, g
Swiss Journal of Hydrology	b
Water and Pollution Control	f
Water and Sewage Works	d, f
Water and Wastes Engineering	b, d, f, g
Water Research	a, b, c, d, e, f, g
Water Resources Bulletin	b, f, g
Water Resources Research	b, d, f, g

TABLE 7

Multidisciplinary (ecology, policy, regulations, pollution, and related topics)

Ambio	b,d
American Journal of Science	a,c,e,g
American Midland Naturalist	b,d,f,g
American Naturalist	b,d,f,g
Applied Environmental Microbiology	a,b,d,e,f,g
Atmospheric Environment	a,b,c,d,e,f,g
Chemosphere	b,d
Chesapeake Science	b
Ecological Modeling	b
Ecological Monographs	b,d,f,g
Écology	b,d,f,g
Environment	b,d,f,g
Environmental Pollution	b,d,f,g
Environmental Research	d,f,g
Environmental Science & Technology	a,b,d,e,f,g
Federal Register	e,f
Journal of Applied Bacteriology	b,g
Journal of Applied Ecology	b,g
Journal of Bacteriology	a,e,g
Journal of Chemical Ecology	b
Journal of Ecology	b,d,g
Journal of Environmental Management	b,d,g
Journal of Environmental Quality	a,b,d,e,f,g
Nature	a,b,c,e,f,g
Philosophical Transactions of the Royal Society of London, B	b,g
Science	a,c,e,f,g
Science of the Total Environment	b,d,f,g
Water, Air and Soil Pollution	b,c,d,e,f,g

bibliographic resource organizations (Table 1). The coverage is not always complete, however, but at least it provides water chemists with an overview of the materials available.

Proceedings, unpublished articles, and reports

One of the most frustrating aspects of the water chemistry literature is the matter of conference "proceedings" and non-traditionally published articles. How are they generated?

Many conferences of interest to water chemists are held each year. Some of these gatherings result in "proceedings" that are distributed to attendees. Unfortunately, distribution to other interested persons, libraries, and abstracting services is often on a random basis. Consequently, when some of the attendees use these limited distribution "proceedings" as literature citations in their own published papers, others have a difficult task in trying to locate these "proceedings" for further, in-depth reading.

Conference organizers might ensure that widespread distribution of these "proceedings" is provided for in the conference budget. At least, complimentary copies might be made available to libraries of institutions that have large aquatic research programs, and also to the relevant abstracting services, and the Institute for Scientific Information, which is now indexing non-journal publications. Additionally, notice of the existence of the "proceedings" might be made in appropriate journals.

One useful technique in this regard could be the preparation of summary articles that highlight the conferences, and identify authors and their respective research findings. *Chemical & Engineering News* does this on a selective basis for ACS National Meetings, and *ES&T* has published such articles in its "Features" department on a variety of conferences related to the water chemistry field.

The preparation and distribution of mimeographed, photocopied, or otherwise unpublished manuscripts is another feature

Government publications

Publications of the U.S. Government Printing Office (GPO) and the National Technical Information Service (NTIS) are frequently of interest to water chemists. Included in these categories are the reports and Professional Papers of the U.S. Geological Survey, as well as the in-house and contractor reports of the U.S. Environmental Protection Agency and other governmental agencies. Both the GPO and NTIS publish catalogs that list the publications available for purchase, and these should be routinely consulted.

of water chemistry and the environmental science field in general, making literature reviewing difficult. There are many aquatic scientists, research institutes, state and federal agencies, and corporations developing conceptual papers, or generating research and monitoring reports that do not follow the editorial style of established journals. Often, these unpublished manuscripts and reports contain information that is valuable to others, but they never become widely available because of a very limited distribution pattern. Many of those reports contain a considerable amount of environmental data that never reach computer storage and retrieval systems. This has led to the development of an "invisible data bank."

The matter of limited availability of conference "proceedings" and other unpublished materials is an important one that should be addressed by concerned aquatic scientists and information retrieval specialists. It is reasonable to suggest that some of the research efforts presented by these unpublished materials have been duplicated by other researchers who were genuinely unaware of the original work. In this time of stricter cost-accounting of research programs, it is imperative that as many of these unpublished materials as possible be disseminated widely, with appropriate coverage by the various bibliographic resources discussed above.

Many places to look

The literature of water chemistry is extensive; it appears in a wide variety of journals; and it is covered in varying detail by bibliographic resources. Scholars desiring to pursue research in the field of water chemistry should be aware of these facts, in order to utilize the literature in an efficient, systematic, and comprehensive manner.

Some of the journals listed in Tables 2-7 were originally collated by Prof. G. F. Lee as part of unpublished course materials distributed at the University of Wisconsin. Prof. Lee (*ES&T*, April 1976, p 334) is now at the University of Texas-Dallas.

Additional reading

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Coordinated by JJ

CURRENT RESEARCH

Submicron Particle Size and Charge Characteristics of $^{239,240}\text{Pu}$ in Natural Waters

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■ The submicron particle size distribution and charge characteristics of atmospheric fallout $^{239,240}\text{Pu}$ are determined by ultrafiltration and ion-exchange resin techniques at extremely low activities (~ 1 femtocurie/L) in rain, snow, and surface waters of the northcentral and southeastern United States. Results indicate that fallout $^{239,240}\text{Pu}$ exhibits different size and charge characteristics as well as total activities in waters of differing pH and anionic composition. These observations are of importance in attempting to predict the geochemical behavior of plutonium on a wide geographical scale.

The concern over possible environmental contamination by radionuclides has been enhanced by proposals of major increases in the use of nuclear power to ease the demands on petroleum-generated energy. As the supply of uranium is exhausted, plutonium usage will be required for continued nuclear power generation. Therefore, the fate of the isotopes of plutonium in the biogeochemical cycles of the environment is of particular concern, especially since the bioavailability of this element may be affected by its chemical state and size spectrum. Although the chemistry of plutonium is one of the best understood of all elements at the laboratory scale, little is known of the solution chemistry of this element at environmental levels, which are approximately 10 orders of magnitude less than usually observed in laboratory studies.

For several years, Argonne National Laboratory has been studying the distribution of plutonium in the waters, sediments, and biota of the Great Lakes in an effort to derive a predictive capability for this element at concentrations ($\sim 10^{-18}$ M) which are realistic in an environmental framework (1). One phase of this program has been determination of the distribution in the colloidal and subcolloidal size ranges, and the ionic charge of plutonium which has been in the environment for several years. This report presents some of the findings from this study and compares the submicron particle and total charge distribution pattern of $^{239,240}\text{Pu}$ present in precipitation and surface waters from diverse areas of the eastern United States as a result of atmospheric fallout from nuclear testing.

Methods

Water samples from Lake Michigan were taken at a station approximately 13 km southwest of Grand Haven, Mich. (water depth = 67 m), from the University of Michigan research vessel, R/V *Mysis*. Water samples from 3 m were taken using a submersible pump, while those from 60 m depth were taken by repeated lowerings of a 30-L Niskin sampling bottle. Two hundred liters of water were pressure filtered through $3.0\text{-}\mu\text{m}$ and then through $0.45\text{-}\mu\text{m}$ membrane filters (Millipore Corp.). Two 50-L samples of filtered water were immediately spiked with ^{236}Pu (1.2 dpm) as an internal standard, and 100 mL of concentrated HCl which lowered the pH to approximately 2.

A third 50-L filtered water sample was taken for ultrafiltration through a Bio-Fiber 80 Miniplant (Bio-Rad Lab.) which has an approximate size retention of particles greater than 30 000 molecular weight (MW) or about 30 \AA diameter.

The water which passed through the fiber bundle was collected and spiked as above. The fiber bundle was then back-flushed with deionized water which was spiked and retained. The final 50 L of filtered water were passed (1 L/min) through successive ion-exchange resin beds containing $\frac{1}{2}$ lb of anion resin (Dowex 1A $\times 8$, 100–200 mesh, chloride form) and $\frac{1}{2}$ lb of cation resin (Dowex 50W $\times 8$, 100–200 mesh, hydrogen form). The water which passed through these resins was discarded. The fractionation scheme outlined in Figure 1 has also been accomplished by passing water samples through the ultrafiltration fibers prior to ion exchange. Both methods give comparable results. The scheme used here was chosen because of its flexibility aboard a ship.

Snow samples were collected by placing large polyethylene sheets on the ground after the beginning of a snow storm. The snow was then transferred to large (200 L) covered plastic vats and allowed to melt at room temperature (approximately two days), but with gas exchange to the atmosphere. The melt water was then passed through the same fractionation scheme as the Lake Michigan water samples. The pH of the sample was determined with a Beckman pH meter with combination glass electrode.

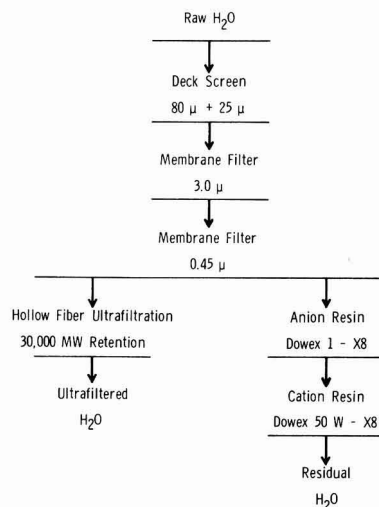


Figure 1. Flow diagram of fractionation scheme employed for $^{239,240}\text{Pu}$ particle size and charge distribution studies of natural water samples

Rain water samples were taken by placing two large boards (1.2 × 2.4 m) covered with polyethylene so that the water falling on them during a rain storm would be funneled and collected in a large plastic vat. The pH of the solutions was determined, and the water collected in this manner was then fractionated as above. Snow and rain samples were collected on the Argonne site.

Water samples from Banks Lake, a small black water lake in south Georgia whose limnological parameters have been previously described (2), and from Okefenokee swamp in Georgia, were obtained by J. E. Schindler, University of Georgia. Water was pumped into large carboys from a depth of 1 m. The samples were immediately air freighted to this laboratory, where they were fractionated within four days of collection. Observations on Lake Michigan waters showed that the distribution of plutonium activity did not change in this period of time in samples stored at a pH of approximately 8. The pH of the samples from Georgia was 4–5, and it is assumed that the observed distributions were not altered significantly during transit and storage.

The various water samples were analyzed for $^{239,240}\text{Pu}$ by the method of Golchert and Sedlet (3). The resins were dried at 110 °C, ashed at 500 °C, dissolved in concentrated nitric acid, spiked with ^{236}Pu (1.2 dpm), evaporated to dryness, dissolved in concentrated HBr to ensure isotopic exchange, evaporated to dryness again, taken up in nitric acid, and then analyzed in the same manner as the water samples. The activity of $^{239,240}\text{Pu}$ was determined by comparing the integrated count under that peak with that in the ^{236}Pu internal standard peak.

Discussion

The results of this investigation are summarized in Table I ($\pm 1 \sigma$ counting error). The concentrations of $^{239,240}\text{Pu}$ in

filtered surface and deep waters from Lake Michigan exhibit the same lower surface values relative to deep waters as previously reported in unfiltered samples taken during a summer season (4). Water samples from lakes in the southeastern United States and of precipitation samples from the Argonne area have significantly higher $^{239,240}\text{Pu}$ activities than filtered water in Lake Michigan. The decrease in $^{239,240}\text{Pu}$ concentration in Banks Lake surface waters between May and December may indicate a seasonal trend similar to that observed in Lake Michigan, but more analyses will have to be undertaken to substantiate these values.

One possible explanation for the increased $^{239,240}\text{Pu}$ activity values observed in lake samples from places other than Lake Michigan may be found in the pH differences observed in these samples. Lake Michigan surface waters during August and September are supersaturated with calcium carbonate (5, 6) and hence have a pH of approximately 8. All samples which are higher in $^{239,240}\text{Pu}$ activity have pH values 3–4 units more acidic than Lake Michigan. It may be postulated that the presence of carbonate, which forms a strong complex with plutonium (7), is the major factor controlling the level of filterable $^{239,240}\text{Pu}$ in waters of high pH. This hypothesis is supported by the fact that surface waters of a southeastern pond from South Carolina, with pH values approximately the same as Lake Michigan, have $^{239,240}\text{Pu}$ activities less than or equal to those of Lake Michigan, despite the fact that the sediments have approximately five times the $^{239,240}\text{Pu}$ activity/g of Lake Michigan sediment (Alberts and Corey, unpublished data).

Examination of the data in Table I reveals striking differences in the distribution of $^{239,240}\text{Pu}$ in the submicron particle fractions of these water samples. With the exception of the September 1974 3-m sample, Lake Michigan water does not have a significant fraction of its filterable $^{239,240}\text{Pu}$ activity in

Table I. Activity Values of $^{239,240}\text{Pu}$ (fCi/L) in Various Physicochemically Defined Components of Natural Waters^a

	pH of water	Filtered water	30 000 MW ultrafiltered water	Ultrafilter backwash	Anion exchangeable	Cation exchangeable	Ultrafilterable noncharged
Lake Michigan							
Sept. 1974 3 m	~8.0	0.40 ± 0.04	0.25 ± 0.03	0.15 ± 0.02	0.42 ± 0.06	<0.01	0.0
Aug. 1975 3 m	~8.0	0.37 ± 0.05	0.31 ^b	0.06 ± 0.02	0.26 ± 0.04	<0.04	<0.03
Aug. 1975 60 m	~8.0	0.65 ± 0.07	0.62 ^b	0.03 ± 0.02	0.35 ± 0.05	<0.03	<0.27
Sept. 1975 3 m	~8.0	0.27 ± 0.05	0.20 ± 0.03	Lost	0.18 ± 0.03	Lost	...
Sept. 1975 60 m	~8.0	0.68 ± 0.12	0.51 ± 0.05	<0.03	0.52 ± 0.08	Lost	...
Banks Lake							
May 1975 Surface	3.9	4.30 ± 0.45	3.60 ± 0.27	0.73 ± 0.07	0.76 ± 0.06	0.33 ± 0.04	2.51
Dec. 1975 Surface	4.0	1.00 ± 0.13	0.87 ± 0.13	0.19 ± 0.03	0.34 ± 0.04	0.07 ± 0.02	0.46
Okefenokee							
Dec. 1975 Surface	~5.0	3.34 ± 0.25	2.87 ± 0.21	0.25 ± 0.03	0.24 ± 0.03	0.09 ± 0.02	2.54
Precipitation							
Nov. 1974 Snow	5.3	1.35 ± 0.26	0.92 ± 0.08	0.02 ± 0.01	0.40 ± 0.05	0.47 ± 0.05	<0.03
Feb. 1975 Rain	4.8	4.8 ± 0.6	3.7 ± 0.4	1.1 ± 0.13	0.84 ± 0.06	0.18 ± 0.03	2.68

^a Due to the long counting times involved in these analyses (4000–5000 min to obtain ~50 counts), values below 0.1 fCi/L have large associated counting errors. Hence, the mass balance calculations involving these numbers may vary from 100%. ^b Ultrafiltered water not analyzed; values obtained by difference of column 3 minus column 5.

the nonultrafilterable size range (i.e., smaller than 0.45 μm but larger than approximately 30 \AA). The other samples, with the possible exception of the snow melt water, have between 7 and 23% of the plutonium activity associated with this size range. The reason for the presence of material in the colloidal size range in the latter samples and not in Lake Michigan waters is not known at this time. However, since all of the $^{239,240}\text{Pu}$ activity in these samples is due to atmospheric fallout, the observed difference must reflect a difference in water chemistry or equilibration time rather than differences in the source term.

The $^{239,240}\text{Pu}$ in these Lake Michigan water samples demonstrates a considerable amount of anionic character, regardless of the total activity in the water or the depth from which the sample was taken as shown in Table II. While some anionic character is observed in all samples, the amount of cationic behavior is small in all samples and almost nonexistent in the samples from Lake Michigan. An exception is the snow sample. The differences in the observed charge characteristics help to support the hypothesis of the importance of carbonate in Lake Michigan waters, as shown by the predominance of anionic behavior in these waters and the relatively low amount of anionic behavior in waters of lower pH, where sulfate and chloride are the dominant anions.

The value for anionic exchangeable material at 60 m in August is felt to represent an analytical difficulty rather than a true decrease in anionic behavior since the design of the resin beds used in that experiment caused some channeling to occur. To ensure that the retention by the anion resin was truly an exchange process and not physical removal by the bed, the order of the resins was changed for several samples, and the cation resin was placed before the anion resin. In all cases, where the reversed resin procedure was carried out, the activity values for the resins were the same as for the resins placed in the normal order. Therefore, it appears that the charge characteristics are real and most likely represent a negative complex of plutonium, most likely carbonate in the case of Lake Michigan.

Perhaps the most significant difference between the plutonium distribution in Lake Michigan waters and that of the other samples, with the exception of the snow, is the percentage of plutonium activity that is in a form smaller than approximately 30 \AA and neutrally charged (greater than 50% in all cases except Lake Michigan and the snow sample where virtually no activity is present in this fraction) (Table II). This fraction can represent a significant quantity of plutonium with as much as four times the total found in Lake Michigan waters present in some cases. The significance of this fraction is enhanced by the realization that water treatment involving filtration or ion exchange may not remove this material. The effect of coprecipitation on this fraction is as yet unknown.

In conclusion, it appears that $^{239,240}\text{Pu}$ derived from atmospheric fallout exists in different forms in natural waters and precipitation samples depending on the pH of the system and the composition of the counterions available. Hence, to form a predictive capability for the geochemistry of $^{239,240}\text{Pu}$ in the environment, care must be exercised to take into consideration other physicochemical factors which will exist in a given body of water. Further studies are under way to quantitatively determine the nature of the anionic complex and that of the large fraction of material which is neutrally charged in the case of low pH waters. Thought should be given to the fact that the snow sample is intermediate in its $^{239,240}\text{Pu}$ distribution patterns between the predominantly anionic species of Lake Michigan waters and the higher total activity and greater fraction of larger than 30 \AA material of the low pH southeastern waters and rain. This may be especially significant when it is remembered that the snow was allowed to melt exposed to atmospheric gas exchange for two days and hence exposed to increasing concentrations of dissolved carbonate and bicarbonate ions. Although the pH of the snow melt water was still relatively low compared to Lake Michigan, this water may represent an intermediate stage of a slow equilibrium which changes the $^{239,240}\text{Pu}$ activity distribution pattern from that observed in the rain sample to that observed in the lake itself.

Table II. Percentage of $^{239,240}\text{Pu}$ from Natural Waters in Various Submicron Particle Size and Total Charge Categories

	Filterable $^{239,240}\text{Pu}$, ultrafilterable	Ultrafilterable $^{239,240}\text{Pu}$, negatively charged	Ultrafilterable $^{239,240}\text{Pu}$, positively charged	Ultrafilterable $^{239,240}\text{Pu}$, uncharged
Lake Michigan				
Sept. 1974 3 m	63	100	<4.0	0
Aug. 1975 3 m	83	90	<14	<10
Aug. 1975 60 m	95	57	<5	<44
Sept. 1975 3 m	75	90	Lost	...
Sept. 1975 60 m	75	100	Lost	...
Banks Lake				
May 1975 Surface	84	21	9	70
Dec. 1975 Surface	87	39	8	53
Okeefeenokee				
Dec. 1975 Surface	86	8	3	89
Precipitation				
Nov. 1974 Snow	68	44	51	<3
Feb. 1975 Rain	77	23	5	72

Finally, it must be stressed that the results of this study are only for the distribution patterns of atmospherically derived plutonium and may not necessarily apply on a one-to-one basis with the distribution of plutonium derived from industry-related sources.

Acknowledgment

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Polychlorinated Biphenyls in Coastal Marine Zooplankton: Bioaccumulation by Equilibrium Partitioning

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■ Chlorobiphenyl concentrations in marine zooplankton from estuarine zones of the North Eastern Pacific Ocean were measured from 1973 through 1975. Concentrations in the lipid fraction of the organisms ranged between 1 and 16 ppm. For the low levels detected in seawater (0.7–3.4 ppt), the data suggest that bioaccumulation is predominantly controlled by equilibrium partitioning of the chemical between the internal lipid pools of the biota and ambient water. Amplification factors of 10^6 are determined in terms of lipid-water concentration ratios, K_l^w . These quantities are uniform over a wide range of spatial and temporal regimes, species composition, and lipid content of the organisms. The results from this study provide good evidence that at least for pelagic biota at the lower trophic levels, food chain biomagnification is not a controlling factor in attaining the observed residue levels.

Polychlorinated biphenyls ($C_{12}Cl_nH_{10-n}$ with $n = 1, 2, \dots, 10$) are well recognized as ubiquitous components in aquatic ecosystems (1–3). Their worldwide occurrence has become an issue of increasing concern due to their continued global production and persistence, their slow rates of chemical and biological degradation, their capacity for bioaccumulation, and their toxicity to living systems.

Coastal ecosystems in particular receive substantial input loads of chlorobiphenyls (CB) with the main sources being industrial and municipal sewage outfalls, river runoff, aerial fallout, and dredge spoil disposal (2, 4–6). Since these regions are capable of providing large quantities of harvestable food resources, as a result of high productivity in the lower trophic levels (7), any biological effects induced by CB are of critical importance to man and the stability of the ecosystem. Furthermore, these compounds have been shown to alter the species composition of mixed phytoplankton cultures (8, 9) and inhibit the reproduction of certain zooplankton (10).

Consequently, adequate information on current residue quantities and distributions in lower pelagic trophic levels is essential for predicting potential effects at the ecosystem level.

Rationale. Although CB residues in marine zooplankton have previously been reported (11–16), interpretation and comparison of these data are difficult for the following reasons: The residues are frequently normalized to different parameters (i.e., zooplankton fresh weight or lipid weight, or volume of water), sample contamination by surface films and floatables during field collection may produce erroneously high results (12, 17, 18), and predictions of biological consequences to zooplankton populations may be meaningless without prior knowledge of the factors that control the biological availability of the chemical.

This paper presents a detailed analysis of CB residues measured in zooplankton in an effort to elucidate factors that control bioaccumulation of these stable organic molecules in lower trophic levels of nearshore ecosystems.

Material and Methods

Sampling. Zooplankton samples were obtained from Puget Sound, Wash., from 1973 through 1975. The regions studied are shown in Figure 1. A detailed description of the station parameters is given elsewhere (19, 20). All collections were made with a modified Juday net (21) designed to minimize contact of both net and sample with surface films and floatables (22). The mesh size and mouth diameter of the net were 333 μ m and 0.75 m, respectively. The volume of water filtered per tow was measured by positioning a TSK flow meter (23) in the mouth of the net. All tows were oblique and traversed a depth range appropriate for representative sampling of the water column. Care was taken to avoid contamination from the vessel's wake by towing amidships. Samples were stored in screw-cap glass jars (pre-rinsed with nanograde hexane) and frozen until the time of analysis. Whole seawater samples were collected using a 60-L stainless-steel sampler (24) and stored with approximately 100-mL nanograde hexane in pre-cleaned 1-gal glass bottles until the time of analysis. The water sampling depths were selected on the basis of the density profiles of the water column and the estimated vertical distributions of zooplankton populations.

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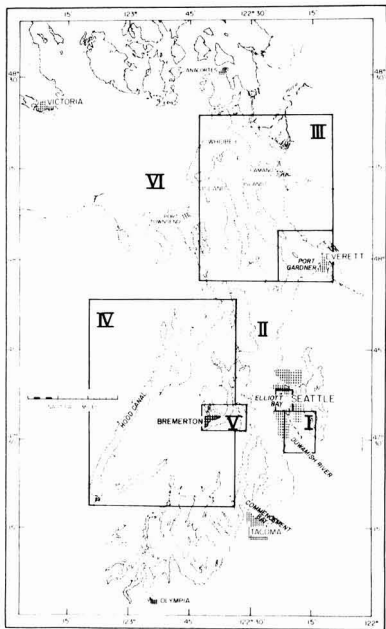


Figure 1. Location of sampling regions in Puget Sound Elliott Bay, adjacent to I; Main Basin, II; Whidbey Basin, III; Hood Canal, IV; Sinclair Inlet, V; Straights of Juan de Fuca and Admiralty Inlet, VI

Analyses. The procedure used for all zooplankton samples was similar to that of Porter et al. (25). Chlorinated hydrocarbons and lipids were extracted by means of four successive homogenations with 30-mL aliquots of a 2:1 (v/v) hexane-acetone solution in a glass and Teflon tissue grinder. Sample cleanup was achieved by means of hexane-acetonitrile partitioning, florisil-column chromatography, and ethanolic-KOH saponification. All solvents were nanograde quality. Chlorobiphenyls were measured on a Tracor gas chromatograph, Model MT-220, equipped with dual ^{63}Ni EC detectors. The stationary phase was 1.5% SP-2240/1.95% SP-2401 on 100/120 Supelcon AW-DMCS (Supelco, Inc.) packed in 2-mm-i.d., 180-cm salinized glass columns. The presence of chlorobiphenyls and pesticides was confirmed in all samples by observing appropriate spectral responses following ethanolic-KOH saponification.

Representative gas chromatographic spectra are shown in Figure 2. Further confirmation was obtained for selected samples by comparing the GC spectral distributions to chlorinated hydrocarbon standards by use of a Silar 10 C on 100/120 Gas-Chromosorb Q column (Applied Science Laboratories, Inc.) and by identifying mass fragmentation patterns on a Finnigan Model 1015C gas chromatograph/mass spectrometer system located at the EPA Region-X Laboratories, Seattle, Wash. Quantitation was accomplished by the procedure of Dexter and Pavlou (26). Recovery experiments were performed with spiked zooplankton samples to test the efficiency of the CB extraction and cleanup procedures. In general, recoveries were better than 80%. The 3- and 7-CB had a high degree of uncertainty due to their relatively small amounts and the presence of impurities with similar GC spectral retention times. Although the largest interference was caused by components of the DDT family, the concentration of total DDT (total DDT = p,p' -DDT + p,p' -DDD + p,p' -DDE + o,p' -DDT + o,p' -DDD + o,p' -DDE + DDMU) in zooplankton was always less than the total CB by at least a factor of seven.

Chlorinated hydrocarbons in seawater were determined by extraction with nanograde hexane and subsequent sample cleanup with 1:1 (V:V) sulfuric acid-fuming sulfuric acid (27).

Determination of Zooplankton Biomass Parameters.

The CB residues were normalized to four biomass parameters: fresh, lipid, dry, and carbon weights. Fresh weight was determined by using a weighed aliquot of thawed sample in the initial hexane-acetone extraction. Lipid weight was obtained by transferring a known volume fraction of the resulting extract to a dry, tared beaker and desiccating until a constant weight was achieved. A supplementary total lipid analysis technique, utilizing chloroform-methanol solvent extraction (28), was performed on selected samples. Comparison of results from the two procedures gave values which were not significantly different at the 95% probability level. Dry weight was determined by placing a weighed, frozen aliquot of zooplankton in a tared beaker and freeze drying to constant weight. Carbon weight was measured by grinding the resulting dried material to a fine powder, transferring a weighed aliquot to an aluminum foil boat, and analyzing for total carbon content with a Coleman Model 33 CH analyzer; percent carbon recoveries for mannitol standards gave a mean of $98(\pm 1)\%$. Triplicate analyses of selected zooplankton samples gave analytical uncertainties for the lipid, dry, and carbon fractions of 10, 1, and 4%, respectively.

Supporting Field Data. Temperature, salinity, and chlorophyll-a were measured at all stations to examine possible correlations with the CB residues in zooplankton (20). For these quantities, the mean values for the upper 30 m of the water column were used.

Results

To discern realistic spatial or temporal trends of trace chemicals in biota, the residue quantities should be normalized to some parameter reflecting the mechanism of accumulation. Since the choice of a normalization parameter for chlorinated hydrocarbons in marine zooplankton has been a controversial issue in the recent literature (29), a systematic

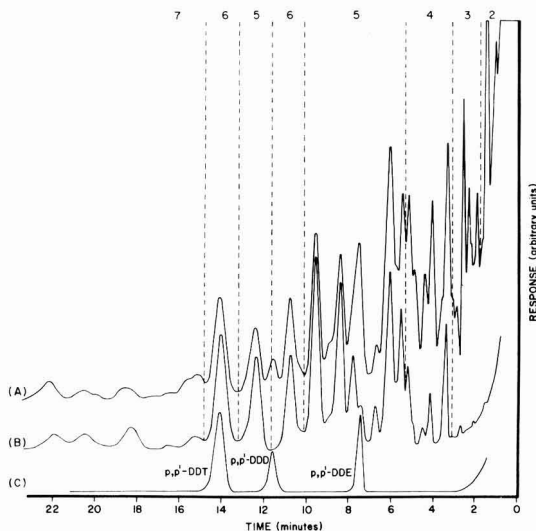


Figure 2. Typical gas chromatographic spectra of chlorinated hydrocarbons obtained in these studies (A) zooplankton extract, (B) mixed chlorobiphenyl standard (Aroclor 1254), (C) selected pesticide standards. Dashed lines: elution regions for chlorobiphenyls of specific chlorine substitution, N , varying from 2 to 7

analysis of the data in this work was undertaken to investigate the dependence of the observed CB distributions on a variety of potentially controlling parameters.

The selection of these parameters was based on the following considerations: Since chlorobiphenyls are hydrophobic compounds, their residue levels should be a function of the organic content of the organisms; if equilibrium partitioning with the dispersive medium is a major contributing factor to bioaccumulation (30-32), residue quantities in the organisms should depend on the ambient water concentrations; earlier investigations suggest that for environmentally stable chemicals, such as chlorinated hydrocarbons, bioaccumulation in plankton depends on the standing stock of biomass (33); grazing studies with herbivorous copepods have shown ingestion rates to be a function of the phytoplankton concentrations (34-36). If input of CB's via grazing were a major contributing factor to zooplankton residue levels, a positive relationship with chlorophyll concentrations might be expected, provided that biological patchiness, i.e., spatial and/or temporal inhomogeneity of the populations, did not tend to randomize the data; and the general accumulation characteristics of CB's in biotic and abiotic phases of aquatic ecosystems may be influenced by salinity and temperature since changes in these parameters would affect the solubility and therefore the biological availability of these compounds.

The zooplankton CB data were first normalized to fresh weight, i.e., the quantity $[N\text{-CB}]^f$, since it most adequately describes the total body burden of the residues. Factors which were considered to have possible effects on $[N\text{-CB}]^f$ were: the lipid, dry, and carbon fractions of the biota ($W_{l/f}$, $W_{d/f}$, and $W_{c/f}$, respectively); the concentrations of CB in water ($[N\text{-CB}]_w$); the standing stock of each biomass parameter per cubic meter of water; chlorophyll-*a*; salinity; and temperature.

In a correlation analysis of these quantities with $[N\text{-CB}]^f$ for $N=4, 5$, and 6 , only $W_{l/f}$, $W_{d/f}$, and $W_{c/f}$ showed consistently high correlations. To test the effects of combinations of parameters on $[N\text{-CB}]^f$, stepwise multiple linear regressions were also performed on the data. The results showed that $W_{l/f}$ was always selected as the first regression variable and accounted for 74-79% of the variance. No other parameter contributed more than 8%. The results are presented in Table I; only the most important effector variables are listed. Plots of $[N\text{-CB}]^f$ vs. $W_{l/f}$ are depicted in Figure 3. Although the scatter of the data is large, a distinct linear behavior is apparent; the regression functions are included in Table I. The high correlations observed for $W_{d/f}$ and $W_{c/f}$ result from semilogarithmic relationships to $W_{l/f}$; the regression functions are shown in Table II.

Since the lipid content is highly correlated with residue levels of CB in the organisms, it was felt appropriate to use lipid as the most meaningful normalization parameter for residue quantities. Values of $[N\text{-CB}]^f$ were therefore computed from the $[N\text{-CB}]^f/W_{l/f}$ ratio. The regional mean distributions of $[N\text{-CB}]^f$ are presented in Table III.

Discussion

A limited discussion regarding the use of environmentally determined partition coefficients to predict the bioconcentration potential of organic stressors in ecosystems was presented previously (37). Although equilibrium partitioning between internal lipid pools of biota and their aqueous environment has been suggested as a bioaccumulation mechanism for hydrophobic compounds (14, 30, 31), no comprehensive investigations have been conducted to test the validity of this hypothesis in marine ecosystems. Preliminary applications of this concept in coastal zones have been reported only recently (38). Since the concept of equilibrium partitioning is

central to our work and to the discussion that follows, a brief review of the fundamental relations is presented below.

The amount of a chemical stressor in any component within an ecosystem depends on the interfacial exchange processes and the endogenous transformation reactions. However, the

Table I. Correlation Coefficient Data for $[N\text{-CB}]^f$ and Highly Correlated Effector Variables^a

Parameter	n	R		
		N = 4	N = 5	N = 6
$W_{l/f}$	42	0.86 [0.74]	0.89 [0.79]	0.88 [0.78]
$W_{d/f}$	38	0.74 [0.63]	0.76 [0.58]	0.74 [0.54]
$W_{c/f}$	38	0.84 [0.70]	0.82 [0.68]	0.80 [0.64]

Regression functions^b with $W_{l/f}$

$$[4\text{-CB}]^f = [13.97 (\pm 1.30) W_{l/f} + 0.55 (\pm 4.55)] \times 10^{-9}$$

$$[5\text{-CB}]^f = [19.77 (\pm 1.60) W_{l/f} - 1.12 (\pm 5.60)] \times 10^{-9}$$

$$[6\text{-CB}]^f = [5.96 (\pm 0.50) W_{l/f} - 0.39 (\pm 1.74)] \times 10^{-9}$$

^a R is the correlation coefficient; N refers to the chlorine substitution on the biphenyl; n denotes the number of data points; numbers in brackets are the R² values. ^b The values in parentheses are the standard errors.

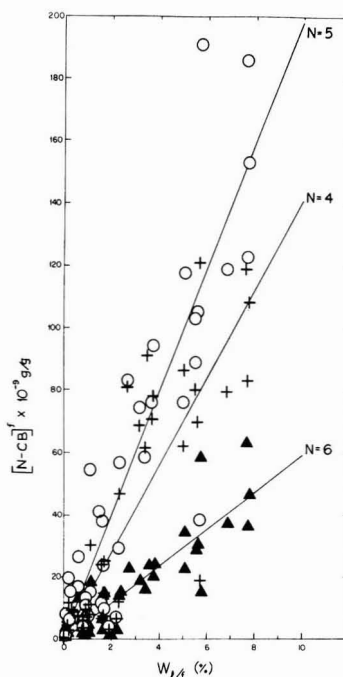


Figure 3. Plots of $[N\text{-CB}]^f$ vs. $W_{l/f}$. +, for $N=4$; O, for $N=5$; \blacktriangle , for $N=6$. Solid lines: linear regression functions

Table II. Regression Functions of $W_{l/f}$ on $W_{d/f}$ and $W_{c/f}$ ^a

Regression function ^b	R ²	n
$\log W_{l/f} = 0.099 (\pm 0.008) W_{d/f} - 1.139 (\pm 0.119)$	0.82	38
$\log W_{l/f} = 0.171 (\pm 0.013) W_{c/f} - 0.750 (\pm 0.083)$	0.83	38

^a n is the number of data points, and R² is the square of the correlation coefficient. ^b Values in parentheses are the standard errors.

Table III. Regional Mean Distributions of Chlorobiphenyls in Marine Zooplankton Collected in Puget Sound from 1973 Through 1975^a

Region	No. of stations	[N-CB] ^l × 10 ⁻⁶ g/g					Total
		N = 3	N = 4	N = 5	N = 6	N = 7	
Elliott Bay	6	0.73 (±0.18)	2.28 (±0.18)	2.43 (±0.18)	0.64 (±0.49)	0.56 (±0.03)	6.63 (±0.45)
Main Basin	4	0.50 (±0.12)	1.73 (±0.43)	2.61 (±0.93)	0.81 (±0.33)	0.58 (±0.25)	6.24 (±2.00)
Whidbey Basin	12	0.25 (±0.01)	1.13 (±0.08)	1.55 (±0.14)	0.45 (±0.05)	0.33 (±0.04)	3.72 (±0.32)
Hood Canal	4	0.13 (±0.01)	0.52 (±0.16)	0.79 (±0.25)	0.21 (±0.05)	0.16 (±0.06)	1.78 (±0.50)
Sinclair Inlet	3	1.57 (±0.36)	3.98 (±1.03)	6.64 (±1.64)	2.21 (±0.47)	1.78 (±0.23)	16.17 (±3.83)
Admiralty Inlet and Straits of Juan de Fuca	3	0.08 (±0.02)	0.29 (±0.08)	0.37 (±0.11)	0.11 (±0.02)	0.07 (±0.02)	0.92 (±0.26)

^a Cruises: OA 552, November 5–8, 1973; OA 608, September 24–27, 1974; and OA 665, July 14–17, 1975. For detailed information on station parameters, see ref. 20. Values in parentheses are the standard deviations of the means; they include spatial variability and analytical uncertainty.

Table IV. Summary of the Regional Mean K₁^N Values for Zooplankton in Puget Sound^a

Region	n	K ₁ ^N × 10 ⁶			Dominant fauna
		N = 4	N = 5	N = 6	
Elliott Bay ^b	6	1.06 (±0.81)	1.42 (±1.06)	2.17 (±1.64)	Euphasiids
Main Basin ^b	4	1.07 (±0.61)	1.90 (±1.25)	3.18 (±2.32)	Copepods
Whidbey Basin ^{c,d,e} (Port Gardner)	12	0.80 (±0.38)	1.09 (±0.51)	1.47 (±0.75)	Copepods/ Euphasiids
Hood Canal ^d	3	0.98 (±0.56)	0.74 (±0.52)	0.43 (±0.32)	Ctenophores
Sinclair Inlet ^c	3	1.12 (±0.68)	3.61 (±2.02)	6.90 (±3.45)	Ctenophores
Admiralty Inlet ^{d,e} and Straits of Juan de Fuca	3	0.34 (±0.21)	0.28 (±0.18)	0.29 (±0.18)	Copepods

^a Computations were based on Method II, as described in the text. Values in parentheses are the standard deviations. ^b Cruise OA 608, September 24–27, 1974. ^c Cruise OA 552, November 5–8, 1973. ^d Cruise OA 665, July 14–17, 1975. ^e These values are based on the chlorobiphenyl concentrations measured at depths greater than 20 m.

net accumulation can be expressed as the product of the concentration of the stresser in the dispersive medium, or any other interacting component, multiplied by a proportionality constant, *K*. This empirical constant, *K*, is defined as the component concentration ratio

$$K = \frac{C_{x(j)}}{C_{x(i)}} \quad (1)$$

where *C_{x(j)}* and *C_{x(i)}* are the concentrations of chemical *X* in components *j* and *i*, respectively. This definition of *K* has been modified to a more specific expression for these studies. Hence, the lipid-water concentration ratio for chlorobiphenyls can be defined as

$$K_1^N = \frac{[N-CB]^l}{[N-CB]_w} \quad (2)$$

The regional mean values of *K₁^N* determined from Equation 2 are presented in Table IV, together with the dominant zooplankton encountered. The in situ [N-CB]^l and [N-CB]_w quantities measured at each sampling station were used to compute *K₁^N*. For certain stations where no water was collected, the [N-CB]_w values were back calculated from the residue concentrations in suspended particulate matter (SPM), obtained at the appropriate density surfaces, and the corresponding SPM-water concentration ratios (39). Mean *K₁^N* were then determined for each region as well as for the total Puget Sound. These data are summarized in Table V and were computed as follows: from the slope of [N-CB]^l vs. [N-CB]_w plots as shown in Figure 4 (I), from the instantaneous values of [N-CB]^l and [N-CB]_w obtained at each sampling station, and subsequent averaging of the individual *K₁^N*

quantities (II), from the intercept of *K₁^N* vs. *W_{l/f}* plots as shown in Figure 5 (III); since the slopes of these plots are essentially zero, the calculated intercepts are close to the average values determined by Method II, and from the instantaneous [N-CB]^l values and the regional mean water values of [N-CB]_w below 20 m depth (IV). The water data used for these calculations are given in Table VI.

By inspection of Table V, a good agreement is shown for *K₁^N* among all computation methods. For *N* = 5 and 6 the results from Method IV do not appear to be statistically different from those of II and III. However, the *K₁⁵* and *K₁⁶* values computed by I are inconsistent in comparison with the other three methods. This reflects the disadvantage in using the

Table V. Summary of Integrated K₁^N Values for Zooplankton in Puget Sound^a

N	K ₁ ^N × 10 ⁶			
	I (n = 31)	II (n = 31)	III (n = 31)	IV (n = 40)
4	1.19 (±0.11); <i>0.81</i>	0.91 [±0.33]	0.99 (±0.09); <i>0.05</i>	1.22 [±0.99]
5	3.44 (±0.87); <i>0.35</i>	1.45 [±0.98]	1.53 (±0.28); <i>0.005</i>	1.02 [±0.68]
6	...	2.26 [±2.16]	2.37 (±0.62); <i>0.002</i>	1.03 [±0.85]

^a The values are computed by Methods I-IV as described in the text; *n* is the number of data points. Values in parentheses are the standard errors; values in italics are the square of the correlation coefficients (*R*²); the numbers in brackets are the standard deviations.

regression technique when confronted with the highly scattered measurements obtained over the narrow range of the $[5\text{-CB}]_w$ and $[6\text{-CB}]_w$ values. In view of the above considerations for the 5- and 6-CB, any of the values computed by Methods II, III, and IV can adequately represent the magnitude of their amplification factor in the zooplankton population.

In general, the K_1^N values appear to be independent of faunal differences within the uncertainty of the data (Table IV). The increasing scatter in the values of K_1^N observed when

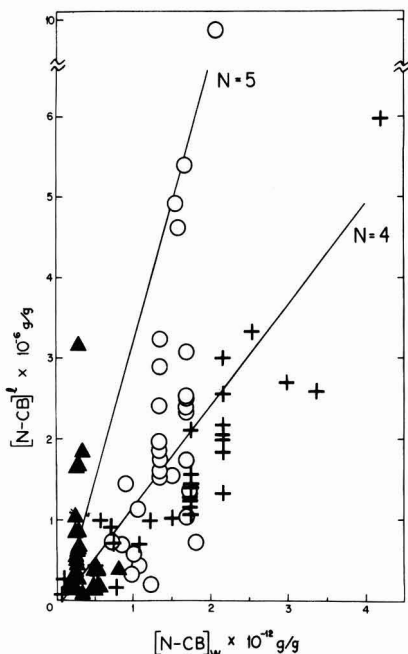


Figure 4. Plots of $[N\text{-CB}]^t$ vs. $[N\text{-CB}]_w$. Symbol designations same as in Figure 3. Solid lines: linear regression functions for corresponding values of N

lipid constituted less than 2% of fresh weight (Figure 5) may define a region in which other parameters influence the degree of accumulation. It should be pointed out here that on a per volume basis the ratio of the absolute quantities of CB in both zooplankton and suspended particulate matter (39) to the quantities measured in seawater was always less than 0.21. Therefore, it is reasonable to consider the dispersive medium as a virtually infinite reservoir of CB for uptake by zooplankton. This conclusion is substantiated by the spatial and temporal uniformity of the K_1^N values observed in these studies.

Interregional Comparisons. Due to the uniformity of K_1^N observed in this work, zooplankton might serve as useful indicators of CB residues in water. This seems very appealing in view of the sampling and analytical difficulties involved in measuring the low concentrations normally encountered in seawater. By using the K_1^N values calculated in this work, CB water concentrations were determined for a number of regions where CB data in zooplankton were available. The results are shown in Table VII. Although in most cases there was good agreement between measured and calculated water values, it appears that some of the North Atlantic data are abnormally high, especially when compared with regions known to receive significant inputs of chlorobiphenyls (e.g., Southern California Bight).

Applicability of Partitioning Concept to Higher Aquatic Trophic Levels. At the present time, the absence of simultaneous measurements of chlorobiphenyls in water and the lipids of higher trophic level organisms, e.g., fish and marine mammals, does not permit direct calculation of their concentration ratios. However, if a lipid-water partitioning mechanism is operable in these species, comparable to that observed in zooplankton, all biota within an ecosystem should have similar residue levels normalized to lipids, especially if collected from a region of uniform CB water values. To test this assertion, the $[N\text{-CB}]^t$ values measured in plankton, several species of pelagic fish, and seals from the Baltic Sea were examined. The data are summarized in Table VIII. It may be noted that, in spite of the wide range of values, residue levels in plankton and fish were reasonably close but lower than those in seals. Earlier studies (31) have implied that biota-water exchange equilibria for environmentally stable compounds are established in fish by a rapid exchange across gill surfaces and subsequent transport to and from internal lipid pools via the circulatory system. Marine mammals, however, possess no equivalent external surface for exchange. Therefore, it is possible that accumulation via equilibrium partitioning may be applicable to a wide variety of, but not all, pelagic organisms.

Conclusions

In summary, the data and computations presented in this paper suggest that the K_1^N quantities are reasonably constant over a range of spatial and temporal regimes; the residue levels in ambient water and in zooplankton normalized to lipid play an important role in controlling the degree of accumulation, particularly when lipid constitutes more than 2% of zooplankton fresh weight; the K_1^N quantities appear to be independent of changes in faunal composition; and the total reservoir of CB in the water was higher than that in the biota. In view of the above considerations and the stability of the ecosystem in which the studies were performed, it appears that the zooplankton are exposed to CB water concentrations for a period of time sufficiently long to establish equilibrium and that the biota possess surface properties favoring establishment of rapid exchange between the internal lipid pools and the aqueous medium.

This type of bioaccumulation mechanism observed for chlorobiphenyls has some important connotations to the

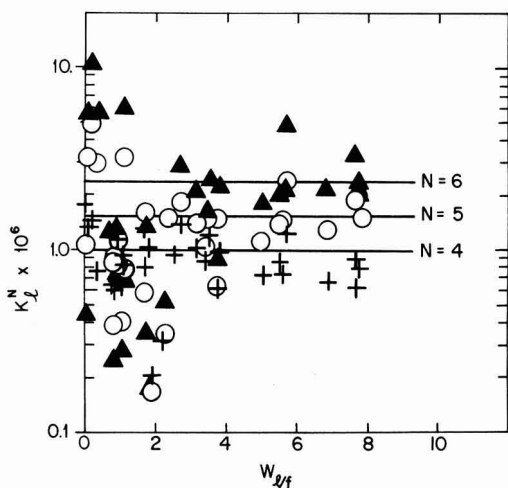


Figure 5. Plots of K_1^N vs. $W_{l/f}$. Symbol designations same as in Figures 3 and 4. Solid lines: linear regression functions for corresponding values of N

Table VI. Regional Mean $[N-CB]_w$ Values for Depths Below 20 m

Region	n ^a	$[N-CB]_w \times 10^{-12}$ g/g		
		N = 4	N = 5	N = 6
Elliott Bay	1	1.40	1.71	0.50
Main Basin	1	1.06	3.37	1.12
Whidbey Basin	3	1.50 (±0.64)	1.99 (±0.96)	0.64 (±0.19)
Hood Canal	4	0.89 (±0.55)	1.29 (±0.67)	0.46 (±0.45)
Sinclair Inlet	1	1.06	3.37	1.12
Admiralty Inlet and Straits of Juan de Fuca	1	0.90	1.40	0.36

^a n is the number of values used; values in parentheses are the standard deviations.

Table VII. Mean Values of Total Chlorobiphenyl Concentrations in Zooplankton and Water for Various Marine Regions

Region	$\Sigma[N-CB]_w \times 10^{-6}$ g/g	$\Sigma[N-CB]_w \times 10^{-12}$ g/g		Ref
		Calcd ^a	Measd	
NE Atlantic	2.3	1.53		(13)
Sargasso Sea			1.1	(6)
NW Atlantic Shelf	82	54.7		(17)
North Atlantic			30	(43)
Baltic Sea	18	12.0		(12)
	25	16.7		(15)
S. Calif. Bight	4.6	3.06	8.8	(16)
			7.4	(40)
Puget Sound	2.20 (±1.8) ^b	1.47 (±2.05)	1.91 [0.70-3.37] ^c	These studies

^a The calculated values were obtained as $\Sigma[N-CB]_w = (K_f^c)^{-1} \Sigma[N-CB]_l$ where $K_f^c = 1.50 \times 10^6$ (based on Methods II or III) and $\Sigma[N-CB]_l$ are the literature values reported as Aroclor 1254 (N ≈ 5). ^b The mean (5-CB); the value in parentheses is the standard deviation. ^c The mean water value for all depths sampled; numbers in brackets are the minimum and maximum values.

Table VIII. Mean Total Chlorobiphenyl Concentrations in Various Marine Species from Baltic Sea^a

Species	$\Sigma[N-CB]_w \times 10^{-6}$ g/g	Ref
Zooplankton	18 (3-35)	(12)
	25 (4-77)	(15)
Herring	14 (0.5-180)	(41)
Salmon	13 (6-25)	(47)
Seal	112 (20-970)	(42)

^a The numbers in parentheses are the minimum and maximum values.

spatial and temporal distributions of other environmentally stable organic chemicals in aquatic ecosystems. Therefore, meaningful environmental impact studies involving trace organic contaminants require an adequate knowledge of the mechanisms responsible for their biological availability and biomagnification within the ecosystem.

Nomenclature

$[N-CB]_w^x$ = mass of Nth chlorobiphenyl (CB) in zooplankton normalized to biomass parameter χ ; N is the number of chlorine atoms on the biphenyl and may vary from 1 to 10, g of CB/g of χ

χ = zooplankton biomass normalization parameter. Designations for χ include f, l, d, and c, which refer to fresh, lipid, dry, and carbon weights, respectively, g

W_{χ/χ^*} = mass ratio of biomass normalization parameter χ to a second biomass normalization parameter χ^* for zooplankton, e.g., $W_{l/f}$ for the lipid fraction of fresh weight, %

$[N-CB]_w$ = mass of Nth chlorobiphenyl homolog in water per unit mass of water, g of CB/g of water, assuming water density of 1

K_f^N = lipid-water concentration ratio for Nth chlorobiphenyl, unitless since it represents an amplification factor in zooplankton from ambient water

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Monitoring of Polynuclear Aromatic Hydrocarbons in Water

I. Extraction and Recovery of Benzo(a)pyrene with Porous Polyurethane Foam

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■ The concentration of trace quantities of benzo(a)pyrene from water with flexible polyurethane foam plug was studied. The recovery from water was independent of flow rates over a wide range but increased to a great extent with increase in temperature of water. Other factors which influenced benzo(a)pyrene retention were: water pH, diameter of the column used for holding plugs, and coating of the foam plugs with chromatographic phases. The foam-sorbed benzo(a)pyrene was stable, and its recovery quantitative after storage of the plug for seven days at 4 °C. Some loss of benzo(a)pyrene occurred when foam plugs were stored at room temperature.

Among the many chemical oncogenic agents, polycyclic aromatic hydrocarbons (PAH) play a unique role because of their demonstrated carcinogenic activity (1, 2) and because of their wide distribution and long persistence in the environment (3). To control the possible intake of PAH compounds by man through drinking water, it is necessary to ascertain their levels. The concentration of PAH compounds in drinking water, however, is so low (4) that concentration of large volumes is required to meet the detection limit of the analytical method.

The effort required for extracting large volumes of samples renders the solvent extraction method unattractive and sometimes infeasible. An instrument employing on-site continuous liquid-liquid extraction (5) has doubtful practical value for routine analysis of PAH because of slow flow rates (~20-35 mL/min) necessary to establish an equilibrium distribution between the aqueous and organic phases. Furthermore, many good PAH solvents (e.g., benzene) cannot be used in the system because of their relatively high water solubility. The limitation of the two most promising sorbents—XAD-resins (6, 7) and Tenax (8)—is their incapability of allowing water flow rates greater than 50 mL/min. Passage of large volumes of water at such flow rates is very time consuming.

The discovery of the ability of polyurethane foams to retain a number of compounds including PCB's and organochlorine pesticides from water (9-11) produced a surge of interest in using this technique to concentrate other compounds as well. Gough and Gesser (12) used polyurethane foams for the recovery of phthalate esters from water. These authors and others (11, 13) used foam plugs coated with gas chromatographic liquid phases with varying degrees of success. Bedford (14), however, reported that polyurethane foam cannot be used reliably to extract PCB's from turbid natural waters. The studies conducted by EPA (15) with paper mill wastewater components, fuel oil, and textile dyes showed that both coated

and uncoated foams are very limited in their extraction ability.

In this paper, the removal of trace quantities of benzo(a)pyrene (BaP), a major representative of carcinogenic PAH, from water with a flexible polyurethane foam plug is reported. The optimum conditions for PAH retention by foam plugs have been determined. The method can be extended to other PAH's, and such studies will be reported separately.

Experimental

Materials and Reagents. The studies were carried out using radiolabeled benzo(a)-pyrene (7-10-¹⁴C) because of the ease and greater sensitivity of ¹⁴C-detection. This also eliminated the necessity for determination of background levels of BaP in water. Radiolabeled BaP in methanol solution was obtained from California Bionuclear Corp. The BaP was of 98% purity and used without further purification.

Polyurethane foam plugs used were diSPo plugs (Scientific Products, Inc.), Identi plugs (VWR Scientific), and plugs cut from UU34 foam sheets (Thomas E. Forrest Co., Inc.).

Tap water used in these studies was obtained from laboratory tap and was derived from Skaneateles Lake. The only treatments the water received prior to distribution were chlorination and fluoridation (16). Raw water was collected from Onondaga Lake (Syracuse, N.Y.) in the month of December. Large floating and suspended particles were removed by filtration through a fine wire screen prior to use.

Chromaflex columns used for holding the foam plugs were purchased from Kontes Glass Co. The oscillating-type pump, Gilmont flow meter, and Haake Model FE thermostated circulator were purchased from Scientific Products, Inc.

All the solvents used were AR grade and purchased from Mallinckrodt Chemical Co. The nematic liquid crystal [*N,N'*-bis(*p*-methoxybenzylidene)- α,α' -bi-*p*-toluidine] was obtained from Eastman Kodak Co., and gas chromatographic phases DC-200 and SE-30 were from Analabs, Inc. Insta-gel and the chemicals for preparing scintillation fluid were purchased from Packard Instrument Co.

Procedure. For sorption studies under static conditions, a preweighed foam plug was left in contact for 4 h with ¹⁴C-BaP solution which had been preequilibrated with the glass container. The difference in the ¹⁴C-activity in initial and final water sample gave the amount of ¹⁴C-BaP sorbed by the foam plug. This was carried out using each foam over a range of BaP concentrations.

In the flow system experiments, one foam plug was wetted with distilled water and placed in a 25-mm Chromaflex column. It was washed successively with acetone, benzene, acetone, and distilled water. Preequilibrated tap water containing

BaP concentration of 0.1 ppb (unless otherwise stated) was drawn through the column with the help of a pump controlled by a variac at a constant flow rate of 250 ± 10 mL/min. The flow rate was continuously monitored with the help of a Gilmont flow meter. Prior to reaching the foam column, the water was brought to a desired temperature by passing it through a custom-made glass coil (10 ft \times 6 mm) which was immersed in a thermostated circulator (Haake Model FE). A water trap with a thermometer was introduced near the column to continuously monitor actual water temperature.

The concentration of radioactive BaP in spiked water and effluent was determined by extracting a known aliquot with benzene and counting ^{14}C -activity in the solvent layer. To account for change in the concentration of BaP in spiked water with time, two effluent samples—one at the beginning and the other at the end of the run—were taken and values were averaged. BaP retained on the foam plugs was eluted with 20 mL acetone followed by 75 mL benzene. Soxhlet extraction of the plugs did not elute more BaP than that recovered by batch column extraction. A 5-mL aliquot of the extracted solution was counted in 10 mL of scintillation fluid (5 g PPO and 0.15 g POPOP/L toluene) with the aid of a Nuclear-Chicago 720 series automatic liquid scintillation system. Water samples were counted when necessary, in Insta-gel.

The plugs containing BaP obtained by passing 2 L of spiked tap water (0.1 ppb) were used in determination of the stability of BaP on foam plugs. They were stored in the Chromaflex columns covered with aluminum foil and analyzed for total ^{14}C -activity at intervals. The concentrated foam eluates were subjected to thin-layer chromatography on cellulose plates with benzene as solvent to ascertain possible BaP degradation. The plates were scanned for radioactive spots on a Nuclear-Chicago Actigraph III.

The calculation of the percent retention of BaP by foam plugs in this paper has been based on the amount of ^{14}C -detected in water by benzene extraction. This eliminated the necessity for quantitation of the BaP adsorbed on the reservoir surface. The total loss of BaP due to adsorption on the glass coil used for heating of the water and on connecting tubes was small and was ignored in the calculation of the percent retention efficiency. Experiments were repeated 2–3 times, and results are expressed as the mean of these values. The deviations from the mean were usually in the range of 3–6%.

Results and Discussion

Sorption data for BaP on three types of foam plugs under static and flow system conditions are shown in Table I. The retention under static conditions was linear over a range of BaP concentrations covering 20–500 $\mu\text{g/L}$. The plugs differed only to a small extent in their sorption characteristics under the two conditions. The chemical nature (ester or ether) and

their density did not appear to be related to the sorption properties. The maximum attainable flow rates with these plugs, however, varied considerably. Cleaning of the foam cells by removing face membranes by treatment with alkaline solution (17) resulted in increased water flow rates but decreased sorption. Columns packed with shredded foams allowed high water flow rates but gave variable retention values. Further studies were undertaken with Identi plugs which offered the best compromise between sorption efficiency and flow rates.

The recovery of BaP from spiked distilled and tap water with Identi plugs at ambient temperature was 65 and 91%, respectively. The decreased retention from tap water was probably not due to competition for sites by contaminants since the retention of BaP from distilled water was not affected by prior exposure to BaP free tap water. The lower efficiency appeared to be linked to the presence of suspended particles since the tap water dosed with BaP following Millipore filtration (0.45 μ) gave retention values equivalent to distilled water.

The diameter of the column holding the plugs had a distinct effect on BaP recovery from tap water. As the column diameter was increased (20–50 mm), the recovery of BaP on the foam plugs steadily decreased; the decrease was as much as 20% with increase in column diameter from 20 to 50 mm. However, as a best compromise between retention efficiency and flow rate, a 25-mm column was found to be most suitable for the plug dimensions used.

The efficiency of the foam plugs to retain BaP at ambient temperature in the examined water flow range (130–520 mL/min) remained unaltered with both tap and distilled water. Furthermore, no measurable removal of BaP from spiked foam occurred by passing water over it regardless of the volume of water and flow rate, suggesting that BaP sorbed on the foam irreversibly. Even though BaP recovery was independent of flow rates, a flow rate of 250 ± 10 mL/min was preferred for further studies. At higher flow rates, foam plugs quite often slid to the bottom of the column which was accompanied by lowering of the retention values. In the studied pH range of 3–10, the retention efficiency of the foam plugs increased steadily with increase in pH. The retention at tap water pH (6.7) was between 62–65%; the retention efficiency at pH 3.0 and 10.0 was 59 and 76%, respectively.

The most dramatic effect on the recovery of benzo(a)pyrene from spiked tap water was observed when the temperature of the water was varied (Figure 1). The relationship between BaP recovery from tap water and temperature was biphasic. The retention steadily increased with increase in temperature up to 40 $^{\circ}\text{C}$, but decreased with further increase in temperature. When the temperature was increased beyond 50 $^{\circ}\text{C}$, the increase in BaP retention was resumed until a plateau was

Table I. Recovery of BaP from Spiked Water

Foam plug	Plug characteristics	Static conditions, ^a μg BaP sorbed from distilled water/g foam	Continuous flow system ^b	
			% Recovery from tap water	% Recovery from distilled water
A, diSPo plugs	Polyester; white; 50 \times 38 mm; density, 24 kg/m^3	150	62	89
B, Identi plugs	Polyether; white; 45 \times 45 mm, density, 25 kg/m^3	135	65	91
C, plugs cut from UU34 sheets	Polyester; green; 45 \times 45 mm; density, 24 kg/m^3	187	66	96

^a BaP concn, 200 $\mu\text{g/L}$. ^b Water temperature, 23 $^{\circ}\text{C}$; volume, 4 L; BaP concn, 0.1 ppb; flow rate, 150 mL/min (± 10 mL); column diameter, 25 mm.

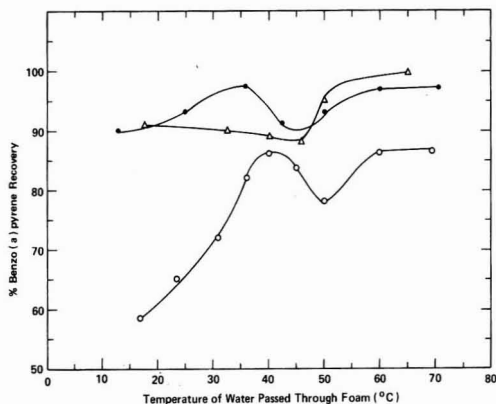


Figure 1. Effect of water temperature, water volume, 4 L; BaP concentration, 0.1 ppb; flow rate, 250 \pm 10 mL/min
 O Tap water (unfiltered), ● filtered tap water, Δ distilled water

reached starting at 60 °C. The recovery of BaP at temperature greater than 60 °C was approximately 87%.

The effect of temperature on BaP recovery from tap water is complex and probably the consequence of many interacting factors. The initial increase appears to be linked to the presence of suspended particles in water. This is due to the fact that such an increase was not seen with distilled water, and that the increase was less pronounced when tap water was Millipore-filtered prior to spiking. The increased retention of BaP beyond 50 °C was observed with tap water and distilled water as well as filtered water and, therefore, appears to be linked to the foam itself. Subjecting polyurethane foam to the action of hot water or steam causes hydrolysis of residual isocyanate and ethyl silicate (18). The increased BaP retention at higher temperature was, however, not linked to these changes because preheated or steam-treated plugs gave recovery of BaP similar to untreated foam.

In view of significant increase in the recovery of BaP on foam plugs with increase in temperature, further studies were carried out at a water temperature of 62 \pm 2 °C.

Table II shows the mass balance of the ¹⁴C-BaP added to 4 L of water. Nearly 25% of the ¹⁴C added to the tap water was adsorbed to the bottle surface compared to a value of 15% with distilled water. The extractability of BaP with benzene from the two types of water also varied to a significant extent. While all the BaP was extractable with benzene from spiked distilled water, the amount recoverable from tap water was only 92%. Whether this is due to transformation of some BaP to a benzene-insoluble form or due to nonextractable particle-adsorbed portion of BaP as suggested by Acheson et al. (19) is not clear. All the ¹⁴C-activity retained by the foam plug from spiked distilled or tap water was in the form of BaP as shown by thin-layer chromatography of the foam eluate.

Coating of the foam plugs with as high as 5–10 wt % of gas chromatographic phases, e.g., SE-30, DC-200, or nematic liquid crystal (11, 20, 21) showed a small increase of 4–9% in recovery over untreated foam at a water temperature of 62 \pm 2 °C (Table III). The eluate from coated foam plugs contained large quantities of the coating material, rendering its concentration to a smaller volume (which would be necessary in the later stages of development) difficult; therefore, coating of foam plugs was not considered further.

The retention of BaP from 4 L of tap water remained between 84–87% in the concentration range of 0.002–25 ppb. A successive increase in the volume of spiked water (0.05 ppb) passed through a single foam plug showed a steady decrease in the efficiency of retention. The efficiency of retention with

Table II. Mass Balance of ¹⁴C-Activity Added to Water^a

Material tested	Tap water, % ¹⁴ C-distribution		Distilled water, % ¹⁴ C-distribution	
	Amount added to water	Amount detected in water ^b	Amount added to water	Amount detected in water ^b
Foam plug + glass column	56.0	86.0	80.0	95.0
Glass bottle	24.4	...	15.0	...
Glass coil and connecting tubes	2.1	2.8	1.8	2.1
Effluent	8.0	11.0	3.2	3.3
¹⁴ C-non extractable	8.0	...	0	...
Total	98.5	99.8	100	100.4

^a Water volume, 4 L taken in a 5-L bottle; flow rate, 250 mL/min \pm 10 mL; temperature, 62 \pm 2 °C; BaP concn, 0.1 ppb. ^b By extraction with benzene.

Table III. Benzo(a)pyrene Retention from Tap Water with Foam Plugs Coated with Chromatographic Phases^a

Chromatographic phase	Concn of coating on plug, % of foam, w/w	Temp of spiked water, °C	% Retention on foam
Uncoated	...	23	62.0
Uncoated	...	62	85.3
DC-200	5	62	87.5
DC-200	10	62	92.6
SE-30	10	62	91.2
Nematic liquid crystal [N,N'-bis(p-methoxybenzylidene)- α,α'-bi-p-toluidine]	3.7	23	66.0

^a Water volume, 4 L; flow rate, 250 mL/min \pm 10 mL; BaP concn, 0.1 ppb.

4 L of tap water was nearly 87%; however, when the sample volume was increased to 10, 20, and 40 L, the efficiency fell respectively to 73, 67, and 49%. The efficiency of retention from distilled water, however, remained unchanged with increasing sample volume. To maintain high retention efficiency with tap water, it was necessary to increase the number of foam plugs. The retention efficiency was increased to approximately 85% with 20 L of spiked tap water when four foam plugs (two each in two different columns) were used. The distribution of BaP retained on individual plugs was as follows: 65% on the first plug, 4% on the second, 13% on the third (first plug of the second column), and 3.5% on the fourth.

Onondaga Lake water was chosen in retention studies with raw water since it would represent a worse possible case of raw drinking water source (total suspended solids in water = 102 mg/L; total dissolved solids = 2.4 g/L). The retention from 4 L of spiked raw water (0.1 ppb) with a single foam plug was 69%. When the number of foam plugs in the column was increased to two, the efficiency of retention increased to 81%. Therefore, with raw water in general, twice as many total foam plugs (not exceeding two plugs per column) should be sufficient to effectively concentrate BaP from the same volume of raw water as with tap water.

The effect of storage of foam plugs sorbed with BaP at room temperature and under refrigeration was examined. All the

activity was recoverable from foam plugs after seven days storage at 4 °C. A small but steady loss of BaP was observed during storage at room temperature; BaP recovered after seven days storage was only 82% of that originally present. Thin-layer chromatography of the eluates from plugs stored at room temperature and at 4 °C revealed that all the ¹⁴C was localized in the BaP spot.

Conclusions

Polyurethane foam plugs are excellent sorbents for benzo(a)pyrene from natural treated-and untreated waters. For sampling 20 L of finished water, four foam plugs (two each in two different columns) should be used. The water should be heated to 60–65 °C prior to passage through the foam column, and flow rate should be maintained at nearly 250 mL/min. Foam plugs following sampling should be shipped in ice to prevent loss of benzo(a)pyrene. For raw water, the four-plug system should be used for concentrating BaP from 10 L only.

The increase in the efficiency of retention of BaP by heating of water appears to be linked to the desorption of benzo(a)pyrene from suspended particles in water as well as to a possible change in the foam itself. It is felt that the retention of other contaminants, e.g., PCB's, on polyurethane foam will also be enhanced if water temperature is increased and should be investigated.

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Total Organic Halogen as Water Quality Parameter: Adsorption/Microcoulometric Method

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■ A method is developed to determine carbon-bound halogen at the $\mu\text{g/L}$ level in water samples with a commercially available instrument and readily obtainable materials. The method, which consists of adsorption from the water onto an XAD-2 or XAD-4 column, followed by elution and injection into the microcoulometer, can be used to recover and quantify 60–100% of the compounds tested (except long-chain aliphatic chlorides), with a lower limit of about 2 $\mu\text{g/L}$. Analysis of drinking water samples from four cities, before and after purging with helium, shows a great variation in nonhaloform organic halogen content, not only in amount but in resistance to purging. The difference between the total organic halogen and the haloform content could prove to be an important water quality parameter.

Since the discovery of haloforms in drinking water (1), there has been intense interest in their source, toxicity, identification, and quantitation. Several methods, including purge techniques (2) and liquid-liquid extraction (3, 4), have been used to quantify these purgable volatile halogen compounds

in drinking water supplies. The growing concern that many, if not most, compounds containing carbon-bound halogen may prove to be toxic has created a need for a method of detection of such compounds in public drinking water supplies.

The methods mentioned above suffer from the disadvantage that the compounds of interest must be chromatographable, which is not the case with, for example, haloform precursors. There are, in addition, other obvious volatility/solubility restrictions on these methods. A liquid-chromatographic method would be a useful complement to gas chromatographic procedures, but there is as yet no halogen-specific liquid chromatographic detection system in common use. The final and perhaps most serious drawback from the standpoint of routine utility is the amount of work required to identify and quantify each peak in the chromatogram. It is desirable, then, to have a method which is halogen specific, not volatility or solubility dependent, and amenable to routine application. Separation by adsorption onto macroreticular resin followed by desorption, pyrolysis in oxygen, and microcoulometric detection comprises a method which satisfies these requirements.

The XAD-2 and XAD-4 polystyrene-divinylbenzene copolymer resins are popular for the adsorption of organic compounds from water (5-8). Although appreciable work has been done on XAD adsorption of organic compounds likely to result from pollution by the chemical industry and agriculture, very little has been published concerning adsorption of the haloforms or substances likely to be their precursors (9-11). In this work, adsorption efficiencies of haloforms were studied, as well as carbon tetrachloride and some less volatile organic compounds. After XAD column parameters were optimized with the model compounds, raw and finished drinking water from various cities was analyzed by liquid-liquid extraction (3) and the XAD/microcoulometric technique described below. In addition, the ether elutions from the XAD columns were analyzed chromatographically to determine the recovery of the individual purgable volatiles.

Experimental

Instruments. The Dohrmann MCTS-20 Microcoulometric Halide System, equipped with an SBI single-boat inlet system was used to determine halogen content of the ether elutions from XAD resins. Gas chromatography of the purgable volatiles was carried out on a Tracor 560 equipped with a ^{63}Ni electron capture detector using a glass 6 ft \times 2 mm i.d. column containing 10% squalane on 100/120 Supelcoport. Nonpurgable volatiles for model compound studies were chromatographed on a Varian 1800 equipped with a flame ionization detector using a glass 6 ft \times 2 mm i.d. column containing 10% OV-11 on 100/120 Supelcoport. In both cases, carrier gas flow rates were 20 mL min^{-1} helium. The electron capture chromatography was isothermal at 68 $^{\circ}\text{C}$, while programming from room temperature at 4 $^{\circ}\text{C} \text{ min}^{-1}$ was adequate to separate the nonpurgable volatiles.

Gases and Reagents. All gases were dried with silica gel traps between the regulators and the instruments. Model compounds were checked chromatographically for purity. Pentane was freed of interfering peaks by distillation from freshly cut sodium. Methanol for XAD processing and storage was Fisher electrograde. Reagent grade diethyl ether directly from the can was found to be sufficiently pure for both chromatography and microcoulometry.

Water free from interfering chromatographic peaks and sufficiently pure to give low system blanks was obtained (Figure 1) by passing tap water through a 75 cm \times 4 cm i.d. glass column filled with 12/40 mesh Calgon Filtrasorb 400 activated carbon, through a deionizing unit, then through a 75 cm \times 1.5 cm i.d. glass column filled with 20/50 mesh XAD-4 which had been cleaned by the same method used from XAD to be used in the columns. It was found advantageous to place a cotton string or fiber filter ahead of the carbon column to prevent premature fouling by gelatinous iron-containing deposits. All tubing was borosilicate glass or copper connected by stainless steel fittings with PTFE ferrules. The resulting "super-D" water was found to consistently contain about 0.1 $\mu\text{g/L}$ of carbon tetrachloride and less than the following amounts of the haloforms: CHCl_3 (0.05 $\mu\text{g/L}$); CHCl_2Br (0.02 $\mu\text{g/L}$); CHClBr_2 (0.02 $\mu\text{g/L}$); CHBr_3 (0.05 $\mu\text{g/L}$).

XAD resins were obtained from Rohm and Haas as 20/50 mesh spherical beads and 100/400 mesh ground powder. Spherical resin, 75/85 mesh, was obtained by the application of a dynamic flotation process to the "20/50" mesh commercial product, and the 75/85 mesh sizing was calculated from particle diameter, measured by a binocular microscope with a stage micrometer. Granules, 100/120 mesh, were obtained by aqueous wet sieving of 100/400 mesh resin.

Glassware was soaked in chromic acid, washed with water, super-D water, and absolute ethanol, then dried at 150 $^{\circ}\text{C}$ for at least 1 h. PTFE-lined septa were used on all sample bottles,

and water samples were taken so as to eliminate any headspace above the water. For the model compound studies, concentrated standard solutions were made up in ethanol, then spiked through the septa, directly into water in the sample bottle. All metal fittings were degreased with distilled acetone and then washed with absolute ethanol on cotton swabs.

XAD Resin Columns. Columns containing the macroreticular resin consisted of a 7-cm piece of $\frac{1}{4}$ -in. o.d. Pyrex standard wall tubing filled with 5 cm of the resin (ca. 200 mg) and plugged at both ends with glass wool. The tubes were tightened into $\frac{1}{4} \times \frac{1}{16}$ in. stainless steel reducing unions with PTFE ferrules. The tubes minus the fittings were stored under methanol when not in use. Consistency and reproducibility of the columns improved with use.

Analytical Procedures. The liquid-liquid (LLE) extraction method (3) has been described elsewhere. The XAD/microcoulometric procedure (XAD/MC) is as follows:

After flushing with 10 mL ether followed by 10 mL of super-D water, the XAD trap is fitted with a syringe needle tapped to accept the 10-32 threads of the $\frac{1}{16}$ -in. end of the Swagelok fitting (Figure 2). This syringe needle is then inserted through the septum of a 120-mL sample bottle. Another syringe needle connected to a helium tank is inserted through the septum, and the helium pressure increased to obtain the desired flow rate through the resin column—25 mL water/min in this work. When the last drop of water goes through, the column is removed and the free end attached to a 10-mL glass syringe fitted with a polypropylene valve and an adapter made by tightening a $\frac{1}{16}$ -in. Swagelok nut and ferrules onto a syringe needle. The syringe is filled with ether, and the needle inserted into a septum-capped cone-shaped sample vial which is then immersed in ice water (Figure 3). Ether is pushed into the trap until about five drops of liquid fall into the sample vial. Elution is continued a few drops at a time until 1 mL of liquid has been eluted over a period of about 10 min. The small water layer which has formed in the bottom of the sample vial is then removed with a syringe (microcoulometric analysis of the residual water showed an insignificant trace of organohalogen), and the elution continued until a total of 1 mL of ether has been collected. The sample vial is then removed and analyzed immediately or stored in the freezer. A system blank is run similarly with super-D water.

Microcoulometric analysis is made by injection of 20 μL of ether eluate into a platinum foil-lined quartz boat on the inlet side of the coulometer. The boat is then positioned at the edge of the furnace to evaporate the more volatile constituents. When the recorder peak reaches its maximum, the boat is inserted the rest of the way into the furnace to pyrolyze any remaining less volatile substances. The pyrolyzed substances pass from the quartz pyrolysis tube to a titration cell where the halides react with silver ion, the concentration of which is maintained electrochemically. When this concentration begins to drop, additional silver ion is generated to replace that which is lost, and the charge required to generate that amount of silver ion is measured by an integration circuit and converted to nanograms of chlorine which is read from a digital meter on the instrument.

The precision of this measurement depends primarily on the baseline noise level of the coulometer, since the coulometer "memorizes" the baseline value at the beginning of the integration. This noise level varies with frequency of use, number of hours in operation, and length of time since the electrodes were plated. Clearly, for a given noise level, measurement of a small quantity of chlorine would be less precise than measurement of a large quantity because of the signal-to-noise ratio and variation in the point that the coulometer picks to reference the beginning of the peak integration. It is, therefore, more meaningful to give the average precision (in percent) as

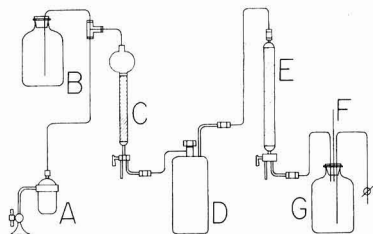


Figure 1. Water purification apparatus

- A: Filter
- B: Five-gal reservoir
- C: Carbon column
- D: Deionizing unit
- E: XAD column
- F: TENAX-filled vent
- G: Super-D water reservoir

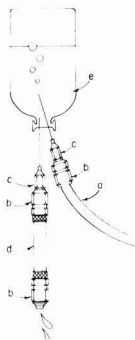


Figure 2. Adsorption of sample onto XAD column

- a: Helium delivery tubing ($\frac{1}{8}$ -in. o.d. Teflon)
- b: Swagelok reducing union ($\frac{1}{16} \times \frac{1}{4}$ in.)
- c: Syringe needle (20 gauge) with Luer fitting tapped to accept 10–32 threads of Swagelok
- d: Glass tubing (8 cm \times 6 mm o.d.) containing XAD resins
- e: Sample bottle, 120 mL with Teflon-lined septum

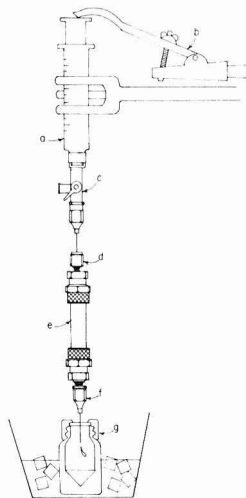


Figure 3. Elution of adsorbed organics from XAD

- a: 10-mL glass syringe containing diethyl ether
- b: Ringstand clamp with one arm removed
- c: Polypropylene three-way valve
- d: $\frac{1}{16}$ -in. Swagelok nut tightened onto a 20-gauge needle
- e: XAD column
- f: Syringe needle (25 gauge) with Luer fitting tapped to accept 10–32 threads of Swagelok
- g: Septum-capped minivial in ice water

a function of the order of magnitude of the value measured. Typical data are shown below:

Magnitude of meas, ng Cl	No. of sets analyzed	No. of points	Mean % SD
10^0 – 10^1	5	14	17.3
10^1 – 10^2	11	25	10.4
10^2 – 10^3	7	22	2.7
10^3 – 10^4	7	21	2.3

At a level of about 100 ng, the precision of the coulometer is comparable to that of the injection volume. Insofar as the practical lower limit of detection for the coulometer is affected, the sample must differ from the system blank by at least twice the standard deviation to get a meaningful result. Since there is a 10^2 -fold concentration step in the method, a water sample originally containing 1 $\mu\text{g}/\mu\text{L}$ (1 ppb) would end up concentrated in the ether eluent at 0.1 $\text{ng}/\mu\text{L}$ (multiplied, of course, by XAD recovery efficiency). A typical blank using a 20- μL injection gives about 5–12 ng response, so that a 20- μL injection of sample giving a response of 4 ng over that of the blank should be easily discernible. This corresponds to 0.2 $\text{ng}/\mu\text{L}$ in the ether eluent, giving 2 $\mu\text{g}/\text{L}$ as a reasonable detection limit for a 120-mL water sample.

Results and Discussion

Column geometry and resin size were optimized by doing recovery efficiency studies on model compound mixtures in super-D water, tap water, and municipal secondary wastewater effluent. The purgable volatiles generally found in drinking water were used, along with a few heavier compounds of varying polarity and structure. The best results were obtained using 100/120 mesh ground resin rather than 75/85 (or larger) mesh spherical resin. Poropak Q, 100/120 mesh, was also tried but gave recoveries 30–50% below those obtained with XAD. [Sized macroreticular resins are marketed by Johns Manville and its various distributors under the trade names Chromasorb 102 and 108, which correspond to XAD-2 and XAD-8. Preliminary results in our laboratory suggest that these materials may be used for the XAD/TOX method if properly cleaned. Current practice is to use a minicolumn containing 1 cm of XAD-8 over 5 cm of XAD-2. The former is included because of its greater affinity for polar compounds; however, we find little difference between XAD-2/8 and XAD-2/2 columns (in series) using Denton, Tex., drinking water. Perhaps, in other cases, the use of XAD-8 will result in greater overall efficiencies.] A column 5 cm long gave better results than the smaller lengths tried, but longer columns were not used because of the increased solvent dead volume. When a sample volume of 900 mL was used, the apparent concentration of chloroform dropped about 50%, dichlorobromomethane dropped 33%, and dibromochloromethane about 25%, as compared to values obtained with 120-mL samples. The final combination of 120-mL sample volume, 5 cm \times 4 mm i.d. column size, and 1-mL ether elution volume was chosen as the best in view of the problems associated with quantitative analysis using ether as a solvent and the desirability of maintaining a 2-ppb lower detection limit.

Since free chlorine is seen by the microcoulometer, it must be quenched in drinking water samples before they are passed through the resin. Model compound recoveries (Table I) were not altered by the addition of sulfite as a quenching agent, with one exception. Standard additions of *o*-dichlorobenzene, dodecyl chloride, and *p*-chlorophenol at the 5–45-ppb level were made to super-D water, Denton, Tex., drinking water, and municipal wastewater (unchlorinated) to determine if there was a matrix effect. No chlorophenol was recovered from the drinking water when unquenched, whereas recoveries from all three matrices were comparable when sulfite was added

to tap water prior to addition of the chlorophenol. The results with chlorophenol point to the desirability of quenching active chlorine when attempting the recovery of reactive organic materials.

The coulometer also will respond to some inorganic chlorides, either because of their volatility or their entrainment in the solvent vapor, but addition of inorganic chloride to samples prior to XAD adsorption did not affect the final results.

Model Compound Studies. Recovery studies were conducted on 11 compounds; carbon tetrachloride, the chlorine-bromine haloform series, cyclohexyl chloride, *o*-chlorophenol, 2,2'-dichloroisopropyl ether, hexadecyl chloride, dodecyl chloride, and *p*-chlorophenol. Table I shows the recoveries obtained for the six "nonpurgeable" compounds in the 5-50 ppb range, and the efficiency of their detection on the microcoulometer/pyrolysis system. Good recovery was obtained for all compounds except hexadecyl and dodecyl chloride. This result is not unexpected, since long-chain aliphatic hydrocarbons have been shown previously (12) to give poor recoveries. The aqueous solution which passed through the columns was analyzed by the LLE method (3) for unadsorbed compound, and no cyclohexyl chloride, *o*-dichlorobenzene, or 2,2'-dichloroisopropyl ether was found. A small amount of chlorophenol was found in the water, but an unfavorable partition coefficient prevented its accurate quantitation. Hexadecyl chloride remained in the water to the extent of 37.6% and dodecyl chloride was not determined.

Results for carbon tetrachloride and the chlorine-bromine haloform series are also shown in Table I, where recovery efficiency is seen to increase in the direction of decreasing volatility/polarity. Table II shows the result of an earlier experiment with 75/85 mesh resin where, at least for the haloform compounds, most of the unrecovered compound is found in the water which passes through the resin. Rinsing the walls of used sample bottles with ether and subjecting that ether to microcoulometric analysis showed that only 0.3% of the total chlorine in the samples remained on the walls of the sample vessel. Incomplete elution of the resin was eliminated

as a source of loss by the observation that in virtually all cases, except dodecyl and hexadecyl chlorides, the quantity of the compound of interest found in successive milliliters of eluate decreased almost exactly two orders of magnitude. The two aliphatic halides decreased by a factor of three from the first milliliter to the second.

Drinking Water Samples. Results of the analysis of drinking water from four cities in different parts of the country are shown in Table III. In each case, the principal raw water source is surface water. XAD/EC values result from electron capture gas chromatography of XAD elutions and are the same samples as have been analyzed by microcoulometry (XAD/MC). LLE values are the result of the liquid-liquid extraction method mentioned above (3). In two-thirds of the cases where the measured value was ≥ 1 ppb (excluding CCl_4 which was in a difficult range and was consistently higher by XAD/EC than by LLE), agreement between LLE and XAD/EC was within experimental error after correcting the XAD/EC values by the recovery factors in Table I.

It is clear from the data in Table III that total organic halogen (as measured by this method) for three of the four cities exceeds the values obtained from the sums of the haloform concentrations. To better understand the nature of this difference, haloform and the total organic halogen content of actual drinking water samples were monitored as a function of purging time. Purging was carried out using a procedure similar to that employed by Kopfler et al. (13). Sample volume and helium flow rate were 120 and 100 mL min^{-1} , respectively. The results are given in Table IV, normalized to the sum of the haloforms present at $t = 0$. The haloforms disappear about four times as quickly as the nonhaloform halogen, the haloform compounds being 92% removed after 1 h, while the nonhaloform compounds required 4 h to drop to 10% of their original value. Although the functional form of the disappearance is not known exactly, a plot of $-\ln(C/C_0)$ vs. $t^{1/2}$ is approximately linear, leading to $C/C_0 = e^{-\alpha t^{1/2}}$ where $\alpha = 2.1 \text{ s}^{-1/2}$ for the haloforms and 0.92 for total chlorine. Different drinking water matrices would not necessarily lead to the same results, but the indication is that there are indeed chlorine compounds present which are considerably less purgable than the haloforms.

The results in Table III indicate the great differences in organohalogen content of drinking water from various locations. City #1 appears to have a large excess of organic halogen above that accounted for by the volatiles, but upon purging, this chlorine is removed from the water. In the water from City #2, a higher portion of the halogen is accounted for by the volatiles, but a larger portion of the excess halogen remains even after purging. The higher ratio of bromine compounds is probably indicative of a higher bromide level in the raw water and/or bromine in the chlorine used to disinfect the water, as it has been shown in this laboratory and others (13, 14) that chlorination of humic acids in the presence of bromide and iodide leads to halogenated methanes containing bromine and iodine. City #3 has a smaller nonhaloform halogen content but demonstrates some resistance to purging, whereas City #4, on the other hand, has essentially no nonhaloform organic halogen in the drinking water.

Finally, note that the XAD method described here has not been compared with the pyrolytic hydrolysis method of Kuhn

Table I. XAD Recoveries and Pyrolysis/Coulometric Efficiencies of Selected Organohalogen Compounds

	% Recovery	ϵ^a
Carbon tetrachloride	63.4 \pm 8.4	0.96
Chloroform	72.7 \pm 7.9	0.97
Bromodichloromethane	78.8 \pm 7.4	1.09
Chlorodibromomethane	86.3 \pm 6.7	0.74
Bromoform	87.5 \pm 7.3	0.52
Cyclohexyl chloride	96.4 \pm 4.3	0.84
<i>o</i> -Dichlorobenzene	103.5 \pm 2.0	1.00
2,2'-Dichloroisopropyl ether	109.7 \pm 2.1	0.68
<i>p</i> -Chlorophenol	97.4 \pm 5.0	0.98
Dodecyl chloride	29.9 \pm 2.6	1.00
Hexadecyl chloride	8.8 \pm 3.1	

^a Pyrolysis-coulometric efficiency = halogen detected (as chlorine) by coulometer/halogen calculated. Efficiencies were determined by injection of standard solutions of the compounds into the pyrolysis/coulometer system. Efficiencies for direct injection of aqueous KCl, KBr, and KI into the titration cell are 1.00, 0.99, and 0.96, respectively.

Table II. Distribution of Volatile Model Compounds Between Ether Elution and Water Having Passed Through 75/85 Mesh XAD Column

	CCl_4	CHCl_3	CHCl_2Br	CHClBr_2	CHBr_3
% in ether	75.8 \pm 0.9	50.7 \pm 5.0	84.4 \pm 1.2	68.3 \pm 6.3	76.0 \pm 6.0
% in water	2.5 \pm 0.3	40.0 \pm 4.0	1.8 \pm 2.0	7.5 \pm 0.8	3.7 \pm 4.0

Table III. Trihalomethane and Total Organic Halogen (XAD/MC) Data from Four Cities^a

Sample ^b	Method	CHCl ₃	CCl ₄	CHCl ₂ Br	CHClBr ₂	CHBr ₃	Σ
City #1							
T	LLE	29.4 ± 2.5	1.03 ± 0.23	12.6 ± 0.7	5.7 ± 0.7	0.43 ± 0.06	49.2 ± 4.2
	XAD/EC	28.1 ± 2.5	1.4 ± 0.1	11.4 ± 1.1	6.5 ± 0.7	0.4 ± 0.1	48.1 ± 8.1
	XAD/MC						73.2 ± 8.9
TP	LLE	4.4 ± 0.4	0.015 ± 0.015	0.40 ± 0.16	5.3 ± 0.6
	XAD/EC	1.0 ± 0.3	1.3 ± 0.1	0.02 ± 0.12	0.001	...	2.4 ± 0.3
	XAD/MC						2.0 ± 3.1
R	LLE	0.98 ± 0.01	1.71 ± 0.01 ^c	0.22 ± 0.01	2.92 ± 0.02
	XAD/EC	1.0 ± 0.4	0.2	0.02	1.3 ± 0.4
	XAD/MC						1.8 ± 2.1
T	LLE	31.9 ± 5.8	0.10 ± 0.02	21.6 ± 2.0	15.0 ± 2.4	2.1 ± 0.6	70.6 ± 8.7
	XAD/EC	14.5	0.1	16.8	10.6	1.6	43.6
	XAD/MC						83.5 ± 2.3
City #2							
TP	LLE	2.6	0.08	0.3	0.9	0.5	4.4
	XAD/EC	1.5	0.17	0.6	0.7	0.4	3.4
	XAD/MC						11.0
R	LLE	0.82 ± 0.01	0.05 ± 0.001	0.88 ± 0.01
	XAD/MC						5.5 ± 0.7
T	LLE	129.7 ± 8.1	0.18 ± 0.01	19.7 ± 1.5	3.10 ± 0.22	0.028	152.7 ± 9.8
	XAD/EC	84.6 ± 1.0	0.25 ± 0.01	16.7 ± 1.1	3.0 ± 0.04	...	104.6 ± 0.5
	XAD/MC						113.4 ± 5.9
City #3							
TP	LLE	6.3 ± 0.9	0.007	1.7 ± 0.4	0.56 ± 0.15	...	8.7 ± 1.0
	XAD/EC	4.3 ± 0.1	0.135 ± 0.005	1.7 ± 0.2	0.28 ± 0.07	...	6.4 ± 0.4
	XAD/MC						8.8 ± 1.6
R	LLE	0.88	0.038 ± 0.008	0.15 ± 0.04	0.002 ± 0.002	...	1.07 ± 0.04
	XAD/EC	0.95 ± 0.24	0.165 ± 0.005	0.12 ± 0.01	1.24 ± 0.25
	XAD/MC						2.8 ± 1.7
City #4							
T	LLE	106.1 ± 1.9	0.19	14.6 ± 0.15	2.27 ± 0.01	...	123.2 ± 2.1
	XAD/EC	87.7 ± 8.7	0.37 ± 0.06	14.4 ± 1.2	2.46 ± 0.25	...	104.9 ± 9.8
	XAD/MC						98.7 ± 3.8
R	LLE	0.64 ± 0.12	0.035 ± 0.007	0.33 ± 0.14	1.0 ± 0.26
	XAD/EC ^c	10.8 ± 2.8	0.245 ± 0.04	0.13 ± 0.02	11.2 ± 2.8
	XAD/MC						4.7 ± 0.04

^a All values in ppb halogen as chlorine. ^b T, treated; R, raw; P, purged 120-mL samples 100-mL helium for 1 h. ^c This value thought to be in error.

et al. (15). That method, which adsorbs organics from aqueous samples on an activated carbon surface and subsequently decomposes the halogenated compounds in a stream of water vapor to halide ions, must be considered as a viable alternative to other total organic halogen methods because of its use of

relatively inexpensive equipment. However, the method may suffer from interferences from inorganic halide ion, and it remains to be seen whether it or the XAD procedure described here, or some other method becomes the acceptable TOX procedure of the future.

Table IV. Comparison of Haloform and Total Organic Chlorine Disappearance with Purging

Purge time, h	Σ Haloform ^a	TOCl ₃ ^b
	Σ Haloform _(t=0)	Σ Haloform _(t=0)
0	1.00	1.81
0.25	0.39	0.85
0.50	0.21	0.67
1.0	0.08	0.25
2.0	0.05	0.36
4.0	0.03	0.19
12.0	<0.001	0.05

^a This quotient is the fraction of the original haloforms remaining at time *t*.

^b Total organic chlorine normalized to sum of haloforms present at *t* = 0.

Conclusions and Summary

A method has been developed to determine carbon-bound halogen at the μg/L level in water samples with a commercially available instrument and readily obtainable materials. The method, which consists of adsorption from the water onto an XAD-2 or XAD-4 column, followed by elution and injection into the microcoulometer, can be used to recover and quantify 60–100% of the compounds tested (except long-chain aliphatic chlorides), with a lower limit of about 2 μg/L. Analysis of drinking water samples from four cities, before and after purging with helium, shows a great variation in nonhaloform organic halogen content, not only in amount but in resistance to purging. The quantity TOX-HALOFORMS could prove to be an important water quality parameter, while comparison of that value with an analogous quantity for the purged water

gives an indication of the "heaviness" of the nonhaloform halogen compounds.

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Photochemistry of the "Sunday Effect"

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■ The "Sunday Effect", in which measured Sunday ozone concentrations in certain urban areas are similar to those occurring on workdays despite markedly decreased emissions, is reproduced by photochemical calculations representing the northern New Jersey troposphere. The near equality of odd oxygen [O_3 , $O(^1P)$, $O(^1D)$] source and sink rates on workdays and Sundays is responsible for the Sunday Effect; this similarity results from the tight balance between ozone production through NO_2 photodissociation and oxygen scavenging by NO, the advection of ozone from less urban areas, and the entrainment of similar quantities of ozone from layers aloft. The higher levels of oxides of nitrogen on workdays increase morning ozone scavenging, produce enhanced NO_2 advection, and result in higher concentrations of organic and inorganic nitrates and an increased rate of reaction of NO_2 with ozone.

Recent statistical investigations of air quality data have clearly disclosed a tendency for similar average ozone levels on summer Sundays and workdays, despite markedly different traffic patterns (1, 2). This circumstance has become known as the "Sunday Effect" and has defied straightforward chemical analyses based on precursor-product concepts.

This paper presents the results of detailed chemical kinetic computations representing workdays and Sundays in Hudson County, N.J. The computational formulation is described, particularly the differences between workday and Sunday parametric inputs. We compare the computational results with air quality data and show that good agreement is obtained for both workday and Sunday calculations. Finally, the concept of "functional oxygen groups" is defined. This concept serves as a unifying analytical technique for smog photochemistry, thus making the Sunday Effect a quantitatively explainable result of the chemistry and meteorology of the urban troposphere.

Computational Formulation

Calculation of the diurnal chemical concentrations in the urban troposphere is based on a chemistry of 143 reactions in 76 species. Extensive descriptions of the chemistry of oxides of nitrogen, hydrocarbons, and sulfur compounds are included in the reaction set, as is a representation of the heterogeneous interactions between gas-phase radicals and the atmospheric aerosol. This chemical formulation is described in detail by Graedel et al. (3). As discussed previously (3), no chemical set can be considered a complete representation of tropospheric photochemistry. The excellent agreement with data that results, however, indicates that our formulation, at the very least, captures the essential processes which control that chemistry.

Sequential computations are performed for adjacent New Jersey counties; we present here the results from Hudson County, the most urban. Details of the emissions inventories and their computational treatment and of the meteorological facets of the computation have been given (3).

Several differences exist between the workday and Sunday computations. The most important is the marked difference in motor vehicle emission and power generation functions for Hudson County (Figure 1). Atmospheric aerosol concentrations are lower on Sundays, and, perhaps as a result, the solar radiation at ground level is somewhat higher (2). In addition to its meteorological effects, the change in aerosol concentration reduces the heterogeneous interactions which have important effects on tropospheric chemistry (4, 5). The increased solar radiation increases the rate of the photosensitive reactions included in the chemical set.

Results

Computations of the kinetic chemistry of the urban troposphere have been performed for Morris, Essex, and Hudson Counties, N.J., for both workdays and Sundays. The workday computations have been described in detail (3), and the

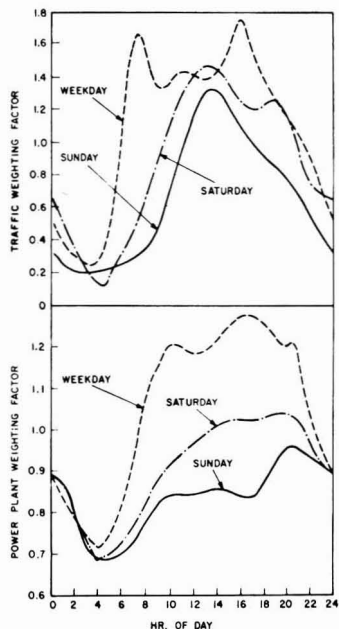


Figure 1. Top: diurnal variation in hourly traffic flow weighting factors for workdays, Saturdays, and Sundays in Hudson County, N.J. Bottom: diurnal variation in variable stationary source weighting factors for workdays, Saturdays, and Sundays in Hudson County, N.J.

agreement with a wide variety of air quality data for Hudson County (across the Hudson River from Manhattan) has been judged to be good. For the Sunday computation, there are insufficient days with appropriate characteristics (i.e., full sun, summer, westerly wind direction, wind speed within the central 50% of all values) to permit a direct comparison between data and computational results. It is possible, however, to make general comparisons with less stringently stratified data. Figure 2a shows the computed diurnal ozone concentrations for workdays and Sundays. The former has been shown to agree well with air quality data (3). The latter reproduces two important characteristics of the Sunday ozone data illustrated by Bruntz et al. (1): the virtual equivalence of the afternoon ozone peak and the higher ozone values on Sunday morning. The calculation demonstrates higher Sunday evening values not reflected in the data; this discrepancy may be a result of inadequate representation of the heavy traffic flow from New Jersey shore points into the metropolitan area that occurs on summer Sunday evenings.

The reduction in the ozone precursors NO and NO₂ on Sundays is shown in Figure 2b and c. Similar reductions occur in air quality data (2) and are representative of concomitant reductions in other species such as CO and nonmethane hydrocarbons.

The results can be succinctly summarized: The computations have succeeded in reproducing the ozone Sunday Effect, while simultaneously demonstrating the reduction in primary emittants known to occur on Sundays.

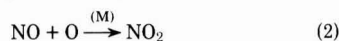
Chemical Analysis

The Sunday Effect is intriguing because of its defiance of the intuitively anticipated precursor-product relationship between ozone-producing species and ozone itself. Having duplicated the Sunday Effect computationally, we then proceeded to deduce a unifying analytical technique that not only demonstrates why the Sunday Effect occurs, but offers po-

tential insight into a wide variety of other atmospheric chemical regimes. The initial step is to divide the oxygen-containing species into groups on the basis of the function of the incorporated oxygen in photochemical reactions. Four groups are distinguished: fixed oxygen (ϕO), accessible oxygen (αO), dissociative oxygen (δO), and odd oxygen (σO).

The chemical species assigned to each group depend on the chemical detail of the analysis. In this study, odd oxygen includes O(³P) (indicated throughout simply as O), O(¹D), and O₃. Dissociative oxygen includes those species that photodissociate to produce odd oxygen: NO₂ and (possibly) N₂O (6). Accessible oxygen species are those that can donate an oxygen atom to permit formation of δO in a single reaction step; in our study this group comprises nine RO₂ radicals, HNO₃, HO₂, N₂O₅, and NO₃. The ϕO group is the largest of the four, and consists of 47 species not included in the other groups. Table I lists the grouping of the oxygen-containing species.

Figure 3 demonstrates schematically how the oxygen species cycle among the groups. The double letter designations (e.g., DO) are termed "group transition rates" and are the sums of all reactions transforming an oxygen atom from one group to another in the direction indicated by the arrow. For example, OD is the sum of the rates of



(Table II gives examples of each of the chemical transformation processes.) The triple letter designations in Figure 3 are group transition rates that are not the result of gas-phase chemistry. Rates SMx represent the sums of all source emission and meteorological rates contributing to changes in the group concentration (note that rates SMx may be either positive or negative), and rates ARx represent group concentration changes because of heterogeneous reactions with atmospheric aerosols (4, 5). No triple letter rates are indicated

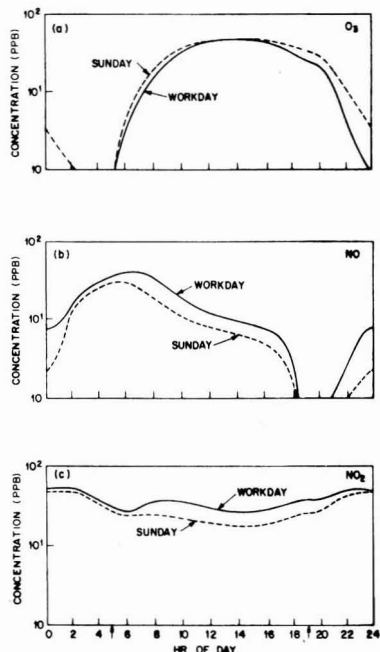


Figure 2. Computed diurnal concentration patterns for workdays and Sundays in Hudson County, N.J.

Table I. Species Comprising Functional Oxygen Groups

ρO	$O(^3P)$, $O(^1D)$, O_3
δO	NO_2 , N_2O
αO	$CH_2CHCH_2\dot{O}_2$, $CH_2(\dot{O})\dot{O}$, $CH_3CH_2\dot{O}_2$, $CH_3CH(\dot{O})\dot{O}$, $CH_3CH(O_2)CH_2OH$, $CH_3C(OH)HCH_2O_2$, $CH_3C(OH)\dot{O}_2$, $CH_3\dot{O}_2$, HNO_3 , HO_2 , N_2O_5 , N_2O_3
ϕO	$\dot{C}_3H_6\dot{O}$, $CH_2CHCH_2SO_2H$, $CH_2CHCH_2\dot{O}$, CH_2CHCHO , $\dot{C}H_2\dot{O}_2$, CH_3CH_2CHO , $CH_3CH_2NO_3$, $CH_3CH_2O_2NO_2$, CH_3CH_2OH , $CH_3CH_2\dot{O}$, $CH_3CH_2SO_2H$, CH_3CHCH_2OH , $CH_3CH(O_2)CH_2\dot{O}$, $CH_3CH(O)CH_2O_2$, CH_3CHO , $CH_3\dot{C}HO_2$, $CH_3CHOHCH_2$, $CH_3\dot{C}HOH$, $CH_3C(OH)HCH_2\dot{O}$, $CH_3C(OH)HO$, $CH_3C(\dot{O})HCH_2OH$, CH_3COOH , CH_3CO , $CH_3(CO)O_2NO_2$, $CH_3(CO)\dot{O}$, CH_3ONO_2 , $CH_3O_2NO_2$, CH_3OH , $CH_3\dot{O}$, CH_3SO_2H , $\dot{C}HO$, CO , CO_2 , H_2O , H_2O_2 , H_2SO_4 , $HCHO$, $HCOOH$, HNO_2 , H_2SO_3 , NO , O_2 , $\dot{H}O$, SO , SO_2 , SO_2^+ , SO_3

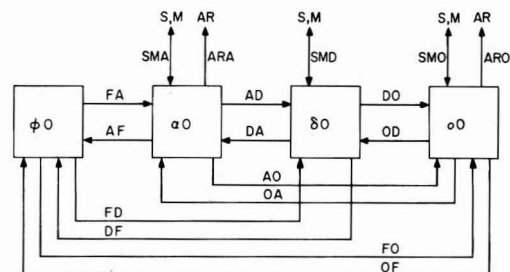


Figure 3. Functional oxygen group diagram
S: emissions sources, M: meteorological sources and sinks, AR: removal by aerosol incorporation. Other symbols explained in text

Table II. Examples of Subgroup Rate Processes

FA	$\dot{H} + O_2 \xrightarrow{(M)} \dot{H}O_2$
AF	$\dot{H}O_2 + \dot{H}O \rightarrow H_2O + O_2$
AD	$CH_3\dot{O}_2 + NO \rightarrow CH_3\dot{O} + NO_2$
DA	$\dot{H}O + NO_2 \xrightarrow{(M)} HNO_3$
DO	$NO_2 \xrightarrow{h\nu} NO + O$
OD	$O_3 + NO \rightarrow NO_2 + O_2$
FO	$\dot{H}O + \dot{H}O \rightarrow H_2O + O$
OF	$CH_4 + O \rightarrow \dot{C}H_3 + \dot{H}O$
FD	$CH_3CH_2ONO_2 \xrightarrow{h\nu} CH_3CH_2\dot{O} + NO_2$
DF	$CH_3\dot{O} + NO_2 \rightarrow CH_3ONO_2$
AO	$N\dot{O}_3 \xrightarrow{h\nu} NO_2 + O$ (also an AD process)
OA	$\dot{H}O + O_3 \rightarrow \dot{H}O_2 + O_2$

on Figure 3 for ϕO , since O_2 dominates the ϕO concentration and is negligibly affected by SMF or ARF processes; since we neglect heterogeneous processes for NO_2 and N_2O , rate ARD does not exist. The total net rates for the oxygen groups are defined by

$$R(\rho O) = DO - OD + AO - OA + FO - OF + SMO - ARO$$

$$R(\delta O) = AD - DA + OD - DO + FD - DF + SMD$$

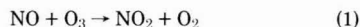
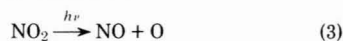
$$R(\alpha O) = FA - AF + DA - AD + OA - AO + SMA - ARA$$

$$R(\phi O) = AF - FA + DF - FD + OF - FO$$

These rates permit ready assessment of the diurnal variations in the oxygen groups; analyses of the individual components responsible for the variations reveal those processes that control the chemical structure of the tropospheric trace species.

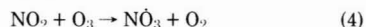
Ozone dominates the concentration of ρO ; hence, the diurnal workday and Sunday variations in ρO are given by Figure 2a. The summed group rates $R(\rho O)$ are the derivatives of Figure 2a and are shown in Figure 4a for the important ozone generating period 6 a.m.–6 p.m. NO_2 dominates the concentration of δO ; the diurnal δO concentrations are thus essentially those of Figure 2c, the derivatives of which comprise Figure 4b. The summed group rates for αO and ϕO on workdays and Sundays complete Figure 4.

From Figure 4a, the integral of $R(\rho O)$ through midafternoon on workdays and Sundays is essentially identical, as it must be if the ozone peak concentrations are to be similar. It can be readily demonstrated that group transition rates DO and OD, although markedly larger on workdays, have a similar net rate (Figure 5a), which represents the close balance between



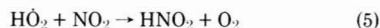
The SMO rate is the largest of those remaining and is virtually identical weekdays and Sundays. This term represents not only the ozone advected into Hudson County from the less urban areas upwind, but also that which enters the "reaction volume" as the rising height incorporates preexisting "fossil" ozone (7) from above. This incorporation was shown to be consistent with air quality data (3) and provides a vital carry-over buffer against the day-to-day perturbations of ozone precursors.

The early morning excess in $R(\rho O)$ on Sundays reflects the ozone reductions that occur when rush hour NO emissions enhance the rate of Reaction 1. These reductions, combined with the slightly higher solar flux levels present on Sundays, produce a somewhat higher value of $(DO - OD)$ on Sunday mornings than on workday mornings. A further factor inhibiting net ozone production on workdays is the increased rate of the ozone scavenging reaction



caused by the higher NO_2 concentrations. The inhibitory factors are eventually overcome by the workday presence of δO (i.e., $NO_2 + N_2O$); the result is virtual equality of resulting peak ozone.

A diurnal analysis can also be made for $R(\delta O)$, for which Figure 4b demonstrates larger workday fluctuations but little difference in the integrated summed group rate. This occurs despite a 28% greater integrated rate for the $\alpha O \rightarrow \delta O$ group transition, as seen in Figure 5b. No significant increase occurs in the $\delta O \rightarrow \rho O$ group transition rate (Figure 5a), which is controlled by the tightly balanced Reactions 1 and 3. Instead, we find increased workday rates of NO_2 advection loss (SMD), an increase in the group transition rate DF, largely through



and an increase in the group transition rate DA, largely through



The product in Equation 7 is, of course, peroxyacetyl nitrate

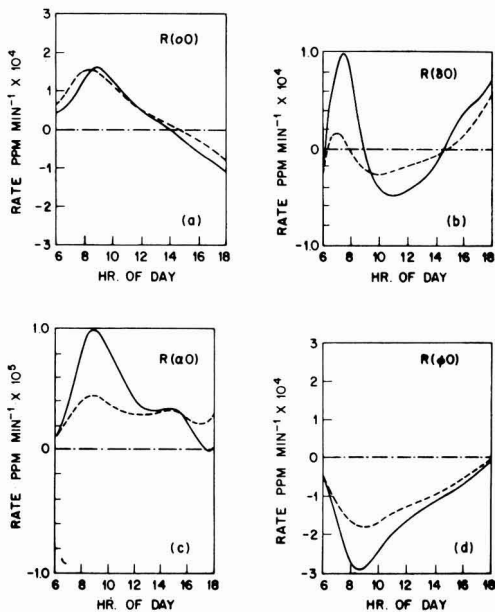


Figure 4. Summed group rates for workdays (—) and Sundays (---), Hudson County, N.J., 6 a.m.–6 p.m. Zero rate line (---) shown for convenience

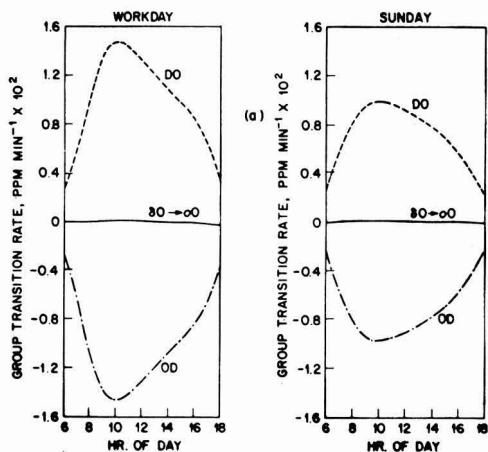


Figure 5a. Group transition rates between dissociative oxygen and odd oxygen

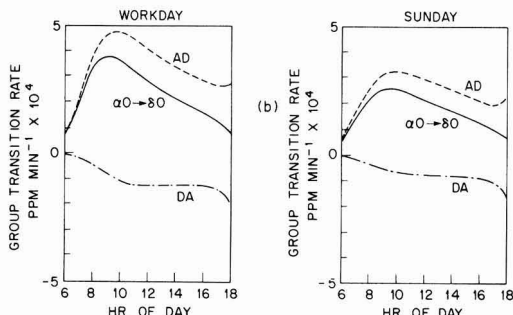


Figure 5b. Group transition rates between accessible oxygen and dissociative oxygen

(PAN), thought to be the principal lachrymator present in photochemical smog (8).

The summed group rates $R(\phi O)$ and $R(\alpha O)$ of Figure 4 demonstrate the increased rates of oxygen incorporation on workdays, largely through oxygen molecule addition to hydrocarbon and aldehyde fragments. Examples of the group transition rates involved in these processes have been presented by Farrow et al. (9).

Discussion

Functional group analysis of oxygen in the troposphere has demonstrated that the Sunday Effect in urban areas results from the near workday-Sunday equivalence of the following factors: tight balance between ozone production through NO_2 photodissociation and ozone scavenging by NO , the advection of ozone from less urban areas, and the incorporation of similar quantities of ozone preexisting above the morning mixed layer. The higher levels of NO_2 on workdays increase the rates of the $NO-NO_2-O_3$ shuttle Reactions 1 and 3, but do not significantly alter the similar behavior of odd oxygen on workdays and Sundays. The increased levels of oxides of nitrogen on workdays have other consequences, however. The advective transport of NO_x is somewhat enhanced relative to Sundays, with a concomitant expansion of the downward impact of the urban area. In addition, the rates of secondary reactions are higher on workdays, resulting in higher concentrations of organic and inorganic nitrates (Table III) and concomitant increases in the potential of the atmosphere to cause lachrymation.

The functional group diagram for tropospheric oxygen allows one to readily see the function of different components of the ozone production system. The existence of oxides of nitrogen is vital, since NO_2 is the only significant tropospheric carrier of dissociative oxygen, and since odd oxygen results almost exclusively from dissociative oxygen precursors. Hydrocarbons provide the chemical fragments utilized for the bulk of the $\phi O \rightarrow \alpha O$ transitions (generally through alkyl radical to alkoxy radical reactions) and for the bulk of the $\alpha O \rightarrow \delta O$ transitions (principally NO oxidation by alkoxy radicals). Meteorological effects are significant perturbers of the oxygen group concentrations, in processes that bypass the transition reactions. Aerosol incorporation effects are of consequence only for accessible oxygen; they differ from the transition reactions by virtue of their irreversibility. The presence of solar photons not only allows the $\delta O \rightarrow \alpha O$ transition, but also creates the free radicals that interact with the atmospheric hydrocarbon compounds.

It is important that the results of this study are not regarded as automatically applicable to all urban areas. The meteorology and the emissions densities, types, and diurnal patterns are specific to each urban region and would thus require separate calculational treatment in each case. The chemical approach and interpretive techniques are of general utility, however, and allow one to order the kinetic system in such a way as to illustrate in true perspective the closely balanced processes with high reaction rates and significant but subtle

Table III. Peak Diurnal Concentrations of Organic and Inorganic Nitrates

Compound	Workday ^a	Sunday ^a
$CH_3(CO)O_2NO_2$	2.9	2.5
$CH_3O_2NO_2$	10.2	9.8
HNO_2	0.34	0.24
HNO_3	3.9	2.3

^a All concentrations are expressed in parts per billion by volume.

secondary processes whose importance is often obscured in a complicated kinetic computation. It is with this perspective that the Sunday Effect is revealed as a quantitatively explainable consequence of the chemistry and meteorology of the urban troposphere.

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Correction of S-Type Pitot-Static Tube Coefficients When Used for Isokinetic Sampling from Stationary Sources

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■ Factors that affect the pitot tube coefficient, including blockage, misalignment, proximity, turbulence, Reynolds number, and calibration system characteristics, are considered. Two different calibration facilities are used to demonstrate these effects with six different sampling probes. Results from the two facilities are in agreement only after application of correction factors for the effects mentioned above. Experimental data are given as well as relations for accomplishing these important corrections. Probe coefficients determined in this study range from 0.74 to 0.78 after the corrections are accomplished. A technique is also presented for determining the uncertainty in the pitot tube coefficient. The resulting uncertainty in probe coefficients of this study is between 2 and 3%. Finally, revised calibration techniques are suggested for determination of coefficients for those S-type pitot-static tubes attached to sampling probes. The results of this study indicate that probe coefficients can be obtained to an accuracy typically within $\pm 2\%$ if the appropriate precautions and corrections are applied.

In pollutant sampling from stationary sources, the Stauscheibe (or S-type) pitot-static tube is the instrument most commonly used to determine stack gas velocity (1-3). Because the S-type pitot-static tube is normally attached to the particulate sampling probe (4, 5) in stationary source sampling, one must calibrate the S-type pitot-static tube to ascertain the correct value of the probe coefficient (C_p).

The probe coefficient (C_p) for the S-type pitot-static tube is considerably different from that of the conventional pitot-static tube. Typical values for the probe coefficient are 0.85 ± 0.05 (3) for the S-type pitot-static tube and 0.99 ± 0.01 (4) for the standard pitot-static tube. The value of C_p is normally determined (1) by measuring the velocity in a flow stream with the S-type pitot-static tube and comparing the result with the same velocity measurement via a standard pitot-static tube. In many instances when the value of C_p is unknown, a value of 0.85 has been recommended (6-8) for the S-type pitot-static tube without calibration. Use of this value

for an uncalibrated S-type pitot-static tube can result in erroneous emission values which are higher than the true values (9).

The stack gas time-average velocity at a point in the flow is calculated according to the relationship

$$(V_{ST})_{AVG} = KC_{pp} \left(\frac{(\Delta P_{ST})_{AVG} (T_{ST})_{AVG}}{P_{ST} M_{ST}} \right)^{1/2} \quad (1)$$

where $(V_{ST})_{AVG}$ is stack gas time-average velocity, C_{pp} is S-type pitot tube coefficient, $(\Delta P)_{AVG}$ is time-average stack gas velocity head, $(T_{ST})_{AVG}$ is time-average absolute stack gas temperature, P_{ST} is absolute stack gas pressure, and M_{ST} is molecular weight of the stack gas. The constant K includes the universal gas constant and appropriate conversion factors depending on the units used in the various measurements. Thus, any error in the calibrated probe coefficient causes an error in the calculated average stack gas velocity and, consequently, whether or not the sampling is performed isokinetically.

Objectives

Our own experiences as well as those of investigators in a number of very recent studies (9-15) have demonstrated the need for a more detailed and systematic calibration procedure than is now available under the current Environmental Protection Agency guidelines (1, 2).

Correspondingly, the first objective of this study was to examine and measure a variety of factors believed to be important in affecting the flow field and pressure distribution around the S-type pitot-static tube. These factors would then govern the value of the probe coefficient (C_p) for a given S-type pitot-static tube and calibration facility. Specifically, the factors to be studied were aerodynamic interference (proximity effect) of the nozzle, misalignment (yaw and pitch angle effects), blockage (area effect), turbulence intensity (turbulence effect), Reynolds number effect, and calibration facility effect (flow tube effect).

The second objective of this study was to develop and perform an uncertainty analysis on the probe coefficient as corrected for by the variety of effects mentioned in the previous paragraph.

The third objective was to recommend improvements in the current guidelines for the calibration of sampling probes used for particulate sampling from stationary sources.

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Probes and Calibration Facilities

Probes. Three different brands of sampling probes were calibrated in this study. They were manufactured by Research Appliance Corp. (RAC), Microchemical Specialties Corp. (MISCO), and Iowa State University (ISU). A typical frontal view of these probes is shown in Figure 1. A 1/2-in. (1.27 cm) i.d. sampling nozzle was used with these probes in all calibration runs of this study where the sampling nozzle was attached to the sampling probe.

Wind Tunnel. A wind tunnel as illustrated in Figure 2 was used to calibrate the various sampling probes. Sampling probes were calibrated at the test site location shown in the wind tunnel schematic. The test site was positioned in the forward portion of the wind tunnel test section. Probes were calibrated in the wind tunnel at flow velocities which varied from 20 to 120 ft/s (6.1–36.6 m/s). Five stages of screens were located upstream in the wind tunnel to reduce the turbulence intensity of the flow. Static temperature and pressure, as well as the pressure across the pitot-static tube, were measured. These measurements and knowledge of the standard pitot-static tube probe coefficient allowed the velocity to be ascertained.

Flow Tube. To ascertain the effect of using a different facility for sampling probe calibration, the various types of sampling probes were also calibrated in a flow tube as illustrated in Figure 3. Probes were calibrated in the 10 3/8-in. (26.35 cm) diameter duct at a centerline flow velocity which varied from 10 to 80 ft/s (3–24 m/s). The test site location in the flow tube is at least a distance of twice the duct diameter upstream of any flow disturbance and at least a distance of eight times the duct diameter downstream of any flow disturbance as suggested by Environmental Protection Agency guidelines (1, 2) for probe calibration. There were no turbulence intensity reducing apparatus used in this flow tube. Thus, the turbulence intensity was measured and compared to that in the wind tunnel to ascertain its effect on the probe coefficient. This correction is discussed in the Results and Discussion section.

Standard Pitot-Static Tube. The standard pitot-static tube was calibrated in an air jet at the exit of a converging nozzle. The application of the Bernoulli equation along a streamline connecting the inlet of the nozzle to the exit of the nozzle results in the following equation for the probe coefficient (C_{ps}):

$$C_{ps} = C(\Delta P_T / \Delta P_s)^{1/2} \quad (2)$$

where C_{ps} is the probe coefficient of the standard pitot-static tube, ΔP_T is the pressure drop across the nozzle as measured by a manometer, ΔP_s is the difference between the total and static pressures as sensed by the standard pitot-static tube and as measured by a manometer, and C is a factor to account for nonideal flow through the nozzle. This factor was determined to be 0.990 ± 0.005 by methods presented in ref. 16. Equation 2 was used to determine the probe coefficient of our standard pitot-static tube over a jet velocity range which varied from 20 to 140 ft/s (6–43 m/s).

Instrumentation. All S-type and standard pitot-static tube pressure measurements were made with Meriam null-balance 20-in. differential pressure measuring micromanometers. These manometers are capable of measuring the pressure differences to the nearest thousandth of an inch of water. Temperature measurements of the air flow in all the ducts were made by suspending a calibrated thermometer or thermocouple in the exit air flow. The pressure of the air stream in the calibration facility was determined by applying the appropriate static pressure reading to the local barometric pressure. The turbulence intensity of the different flow sit-

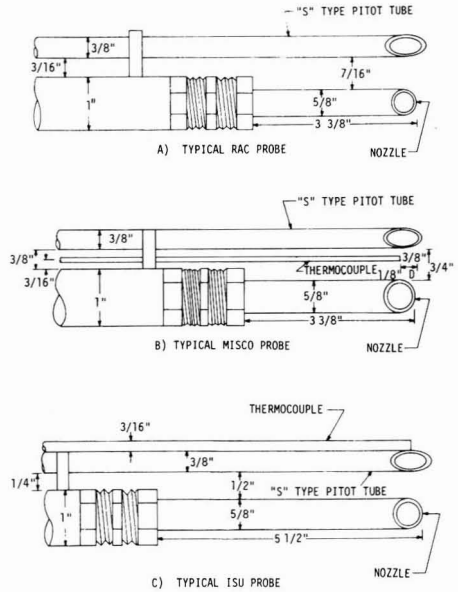


Figure 1. Typical probe configurations

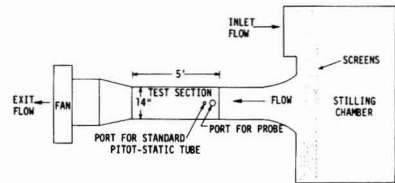


Figure 2. Wind tunnel

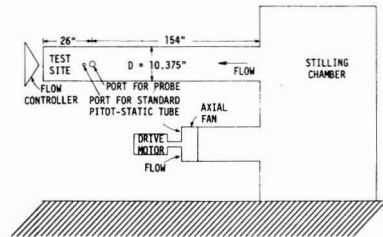


Figure 3. Flow tube

uations in the two calibration facilities was investigated using hot wire anemometry.

Calibration Procedure. The current S-type pitot tube calibration guidelines are contained in the *Federal Register* (1, 2). These guidelines specify that calibrations be accomplished in the laboratory by measuring the velocity head at some point in a flowing gas stream with both an S-type pitot tube and a standard pitot-static tube of known probe coefficient. The calibration is to be performed at a velocity intermediate to the velocity range expected in field operations and after use at each field site. Also, the average coefficients obtained with first one side (the "A" side) of the S-type pitot-static tube and then the other side (the "B" side) pointed upstream are to be compared. Use of the S-type pitot-static tube is to be discontinued if these two coefficients for each side differ by more than 0.01.

The same calibration procedure was used in both the wind tunnel and the flow tube. The flow rate was first adjusted by means of fan rotation speed and/or dampers to a specific setting in the calibration facility. Next, the sampling probe was placed in the duct through a port hole in the side of the duct. A special rubber stopper was designed to fit around the probe while the probe was in the duct to prevent air leaks. Also, the rubber stopper was contoured to the inside of the duct to avoid any unnecessary flow obstructions. Once a ΔP_p reading was recorded for the sampling probe, it was taken out of the facility, and the standard pitot-static tube was placed in the flow, keeping the flow setting constant. The standard pitot-static tube was inserted into the duct through a port hole located to the rear of the sampling probe port hole. The standard pitot-static tube port hole was located on the side of the duct so that the tip of the standard pitot-static tube and the tip of the S-type pitot-static tube on the sampling probe was positioned exactly at the same point in the flow field. A rubber stopper was also made for the standard pitot-static tube. Once the ΔP_s reading was recorded for the standard pitot-static tube, the probe coefficient was calculated for the sampling probe by applying Equation 1 to both the sampling probe and the standard to yield

$$C_{pp} = C_{ps} \left(\frac{\Delta P_s}{\Delta P_p} \right)^{1/2} \quad (3)$$

Finally, the appropriate correction factors were applied to the calculated sampling probe coefficient as found from Equation 3 to obtain the proper value of the sampling probe coefficient.

Results and Discussion

The pitobe assembly consists of the S-type pitot-static tube, a sampling nozzle, and a thermocouple wire or a thermocouple wire protective tubing. Various factors affect the flow field and pressure distributions around the pitobe assembly which, in turn, governs the probe coefficient of the S-type pitot-static tube. Investigation of these factors and the experimental results of this study are presented in the following sections.

Aerodynamic Interference. A series of very recent studies (9, 11-15) has demonstrated that when an S-type pitot tube is used as a component of a pitobe assembly, the proximity of the sampling nozzle, the thermocouple, and the probe sheath can cause a significant lowering of the value of the S-type pitot-static tube probe coefficient.

To ascertain the aerodynamic proximity effect of the sampling nozzle on the probe coefficient, data were taken in the wind tunnel over a range of Reynolds numbers both with and without the sampling nozzle attached to the pitobe assembly. Typical data are presented in Figure 4. From this figure it is apparent that the sampling nozzle has a distinct effect on the probe coefficient which amounts to a lowering of the probe coefficient by about 4% with the sampling nozzle attached. This change in the probe coefficient is in agreement with data presented in ref. 13. Note also from Figure 4 that the probe coefficient decreases slightly with increasing Reynolds number during these experimental runs. The effects of the thermocouple and probe sheath were not investigated in this study but are given elsewhere (12-15).

Misalignment. When the pitot-static tube openings are not perpendicular to the direction of flow, an alignment error occurs (4, 9, 10). This results in erroneous flow velocities when using the pitobe assembly for source sampling. There are two specific misalignment effects to consider for a properly constructed pitot tube when it is placed in a flow situation. These are yaw and pitch angle misalignments.

Pitch Angle. If the pitobe assembly is inserted in the flow so that it is perpendicular to the duct wall but is rolled

(pitched up or pitched down) so that the pitot tube openings are not perpendicular to the flow, the pitobe is said to have a pitch angle.

The effects of pitch angle over a range of Reynolds numbers are demonstrated in Figure 5. In Figure 5A and B the change in probe coefficient is expressed as a fraction equal to C_p at a particular pitch angle divided by C_p at a pitch angle of zero degrees. The same pitobe was used to obtain the data of Figure 5A and B, but Figure 5A represents side A of the pitobe upstream, and B represents side B of the pitobe upstream. Pitch angles of up to ± 10 degrees increase or decrease the probe coefficient within a range of at least 2%. These observations are in basic agreement with the data presented in refs. 9 and 10 where pitch angles of up to ± 10 degrees were found to increase or decrease the probe coefficient within a range of about 4%. It may also be concluded from Figure 5 that drastic changes (larger than about 30 degrees) in pitch angles cause drastic changes in the probe coefficient. The asymmetry is believed to be caused by the slightly different configuration presented to the flow by the probe nozzle because of nozzle asymmetry as the probe is rotated from positive to negative angles of pitch.

Yaw Angle. If the pitobe assembly is inserted in the flow so that it is not perpendicular to the duct wall, the pitobe is said to have a yaw angle. The effects of yaw angle over a range of Reynolds numbers are plotted in Figure 6. Again, the same

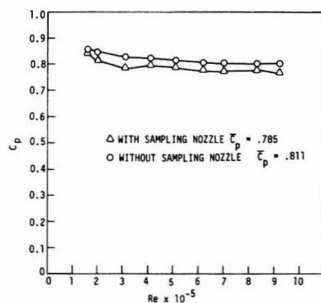


Figure 4. Typical sampling nozzle effect on probe coefficient [$\frac{1}{2}$ -in. (1.27 cm) nozzle]

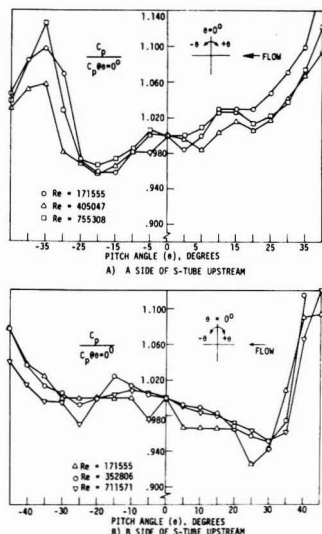


Figure 5. Typical pitch angle effect on probe coefficient

pitobe was used to obtain the data of the plots, but Figure 6A represents side A of the pitobe upstream and B represents side B of the pitobe upstream. Also, C_p is expressed as a fraction equal to C_p at a particular yaw angle divided by C_p at a yaw angle of zero degrees. Yaw angles up to ± 5 degrees yield either a decrease or an increase of up to 4% in the pitobe coefficient. Yaw angles greater than ± 5 degrees will cause significant changes in the probe coefficient. These results are also in basic agreement with results of refs. 9 and 10 where yaw angles up to ± 5 degrees yield either a decrease or an increase (depending on the direction of yaw) in the probe coefficient up to about 4%.

Reynolds Number. The pitot tube coefficient not only depends on the pressure distribution around the pitobe assembly but also on the velocity and fluid properties of the flow stream (1-4, 9, 12, 17). One of the important dimensionless numbers found to be essential in characterizing fluid flow situations is the Reynolds number (16). The Reynolds number of the duct flow is defined by the relation

$$Re = \rho VD/\mu = VD/\nu \quad (4)$$

where V is the velocity, D is the duct diameter (or equivalent diameter), ρ is the fluid density, μ is the dynamic or absolute viscosity, and ν is the kinematic viscosity. With the viscosity, density, and duct diameter constant, the Reynolds number varies directly with velocity. Another Reynolds number of importance is that characterizing the flow over a sampling probe. For the probe the significant dimension could be the nozzle length, the nozzle diameter, or the length of probe insertion into the duct or exhaust stack.

The Reynolds number has been found to characterize the type of boundary layer and, correspondingly, the frictional losses in the flow around any obstruction in a flow stream. In our case, the obstruction is the pitobe assembly. Both increases and decreases in the probe coefficient have been observed (4, 12) with increasing velocity. Thus, it appears to be important to calibrate the S-type pitot tube over the complete range of velocities and corresponding Reynolds numbers anticipated for its use in source sampling.

If the probe coefficient is approximately constant with Reynolds number over the appropriate Reynolds number range, the correction will be small or negligible. Under these conditions, simulation of velocity only is satisfactory. However, if a particular probe coefficient varies significantly with Reynolds number, the probe coefficient used must be that for the Reynolds number of the exhaust stack. This is mainly because of the large differences in densities and viscosities between the fluids in the exhaust stack and the calibration

facility. For example, exhaust stack Reynolds numbers can be as low as 10^2 to 10^3 . If the pitobe assembly has been calibrated at the same velocity but at Reynolds numbers on the order of 10^4 or 10^5 , the question naturally arises as to what probe coefficient should be used in the field application.

Blockage. When sampling or calibrating in a relatively small diameter (or equivalent diameter) duct, the pitobe assembly can reduce the cross-sectional flow area by a significant amount (9, 12, 15). The reduction in flow area causes the flow velocity to increase if all other flow parameters remain fixed. This can be demonstrated by the application of the continuity equation to the flow situation. If the cross-sectional flow areas are different for the standard pitot-static tube as compared to when the pitobe assembly is in the flow, an error in the probe coefficient will occur due to a change in the flow area. A blockage of 2-3% has been demonstrated to decrease the probe coefficient by 1% (15). Thus, for all blockages larger than 2% based on the projected area of the pitobe assembly, one must correct the observed probe coefficient.

A correction factor due to blockage effects was applied to all the C_p data of this study. The blockage correction was developed by the authors in ref. 18 and is given by A_s/A_p in Equation 5. A_s is the cross-sectional flow area with the standard in the stream, and A_p is the cross-sectional flow area with the sampling probe in the stream. In all cases of this study, the blockage correction factor raised the calibrated probe coefficient from 3 to 5%, depending on the size of the facility in which the pitobe was calibrated.

$$C_{pp} = C_{ps}(\Delta P_s/\Delta P_p)^{1/2}(A_s/A_p) \quad (5)$$

Calibration Facility. Different facilities used for calibration can yield different probe coefficients for S-type pitot-static tubes because of factors different from those previously mentioned. Descriptions and examples of some of these items are contained in the following paragraphs.

Velocity Profile in Facility. The velocity profile in the calibration facility should be as uniform or flat as possible. If the velocity profile is nonuniform, the S-type pitot-static tube and the standard pitot-static tube will not be immersed in the flow at points with the same flow velocity. If no correction is made for this effect, significant errors in the probe coefficient can result.

Before any calibration data were obtained, velocity profiles in the calibration facilities were ascertained over a wide range of velocities and corresponding Reynolds numbers. Uniform velocity profiles were observed over a range of Reynolds numbers from 1×10^5 to 6×10^5 in the flow tube and from 1×10^5 to 9×10^5 in the wind tunnel.

Flow Rate Correction. The change in flow rate, due to a change in the system operating point, when the pitobe assembly is in the flow stream as compared to when the standard pitot-static tube is in the flow stream will cause significant errors in the calibrated probe coefficient. The operating point of a system depends on the combination of head-flow characteristics of the blower or fan and the flow-resistance characteristics of the ducting and probes used in the calibration facility.

The flow rate correction Q_p/Q_s as determined by the authors in ref. 18 yields

$$C_{pp} = C_{ps} \left(\frac{\Delta P_s}{\Delta P_p} \right)^{1/2} \frac{Q_p}{Q_s} \frac{A_s}{A_p} \quad (6)$$

where Q_p is the volumetric flow rate with the sampling probe in the duct, and Q_s is the volumetric flow rate with the standard in the duct. If the flow rates do not change (as was determined in the wind tunnel but not the flow tube of this study), $Q_p/Q_s = 1$, and the correction factor to be applied to the measured probe coefficient reduces to the blockage cor-

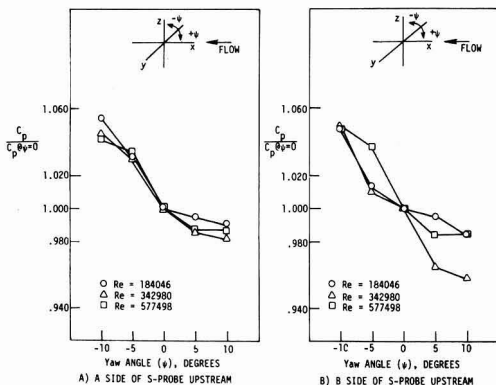


Figure 6. Typical yaw angle effect on probe coefficient

rection A_s/A_p . To ascertain the volume flow rate correction factor Q_p/Q_s , velocity profiles were measured in the flow tube when the pitot assembly and then the standard pitot-static tube were in the flow tube. These velocity profiles were then plotted, and the resulting plots were integrated with the Trapezoid Rule (19) to determine the average flow velocity. The volume flow rate was then calculated by taking the average flow velocity times the flow area, and the ratio Q_p/Q_s was calculated and plotted as a function of the velocity sensed by the standard pitot-static tube. The resulting plot is shown in Figure 7. In Figure 7 the equation of the flow rate correction factor $Q_p/Q_s = 0.933 + 0.000624 V_s$ was determined by a least-squares technique. This volume flow rate correction varied from 0.939 to 0.983 in this study and was applied to all measured probe coefficients determined in the flow tube.

Flow Pulsations. Finally, the possibility of flow pulsations caused by the blower or fan in the calibration facility is another point to consider. A suggested correction technique is presented in ref. 20. However, in this study no pulsations were present, and no correction was ascertained.

Turbulence Level. If there is turbulence in the flow stream, a pitot-static tube will sense an additional pressure difference due to the turbulence intensity present at the pitot-static tube impact and static openings (20-22). Because of the configuration and relative size of the S-type pitot-static tube impact and static openings, the turbulence effect sensed at each opening is identical and is canceled in the measurement process. However, a standard type pitot-static tube will sense different turbulence effects at its impact and static openings because of its configuration. Thus, when performing a calibration to determine the probe coefficient, a correction for turbulence intensity in the flow duct must be accom-

plished. The correction for turbulence intensity has been shown (22) to depend on the particular pitot probe-tip shape and size of openings compared to tube diameter, as well as the level of turbulence intensity. The correction is significant when the turbulence intensity is larger than 1%. The correction increases significantly and nonlinearly for a turbulence intensity above 1%. For square-nosed probes and at a turbulence intensity of 10%, the correction can be anywhere from 1 to 8%, depending on the ratio of pitot-static tube outside diameter to impact hole diameter. It has been suggested (21) that use of pitot-static tubes be avoided in turbulent flows whenever possible because of the unknown effects of turbulence on the static pressure reading. In this study the turbulence intensity ($i = \bar{V}_x/V$) was measured where V is the mean free stream velocity and \bar{V}_x is the rms value of the fluctuating component in the direction of flow. A turbulence correction factor developed by the authors in ref. 18 was applied to Equation 6 as shown by the following relation:

$$C_{pp} = C_{ps} \left(\frac{\Delta P_s}{\Delta P_p} \right)^{1/2} \frac{Q_p A_s}{Q_s A_p} (1 + \alpha i^2)^{-1/2} \quad (7)$$

Ower and Pankhurst (20) suggested the introduction of parameter α to account for the scale of turbulence (i.e., the size of component eddies) where α varies between 1 (for turbulence of small scale) and 5 (for turbulence of large scale).

In both the flow tube and the wind tunnel the turbulence intensity was less than 1%, which yielded a negligible correction factor to the data of this study. This result is in agreement with ref. 22, which suggests that turbulence effects do not become important until the turbulence intensity is greater than 1%.

Presentation of Results. Table I is a tabulation of the calibrated probe coefficients of this study. The probe coefficients listed were calculated according to Equation 7. The average probe coefficients vary from 0.744 to 0.784, depending upon the individual probe. Figures 8-10 are plots of the probe coefficients as a function of velocity and Reynolds number. These plots were made for each type of probe calibrated and contain the data obtained in both the wind tunnel and flow tube. The dashed lines on the plots are an indication of the average of the coefficients obtained in the two different facilities. The same probe coefficient values were obtained in two different facilities only after application of the different correction factors previously discussed. This fact places emphasis on the validity and the necessity of making these corrections.

Probe coefficients in the order of 0.76 as obtained from this study demonstrate the significant effect that the previously

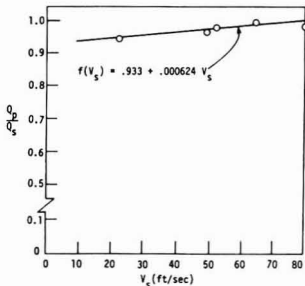


Figure 7. Volume flow rate correction

Table I. Tabulation of Probe Coefficients

Probe	Facility	T, °F (°C)	P, in. Hg	\bar{C}_{PA}	\bar{C}_{PB}	$\bar{C}_p = \frac{\bar{C}_{PA} + \bar{C}_{PB}}{2}$	Probe coeff uncertainty
MISCO 5 ft ^a	WT ^b	80 (27)	29.13 ^a	0.756	0.772	0.764	±0.013
MISCO 5 ft	FT ^c	85 (29)	29.13	0.740	0.750	0.745	±0.019
MISCO 11 ft ^d	WT	76 (24)	29.30	0.764	0.758	0.761	±0.013
MISCO 11 ft	FT	82 (28)	29.13	0.767	0.758	0.762	±0.020
ISU 3 ft	WT	80 (27)	29.25	0.747	0.742	0.744	±0.013
ISU 3 ft	FT	86 (30)	29.21	0.771	0.747	0.759	±0.020
ISU 4 ft ^e	WT	80 (27)	29.23	0.762	0.750	0.756	±0.013
ISU 4 ft	FT	84 (29)	29.21	0.764	0.764	0.764	±0.020
ISU 5 ft	WT	78 (26)	29.40	0.761	0.727	0.744	±0.013
ISU 5 ft	FT	87 (31)	29.20	0.748	0.751	0.749	±0.019
RAC 3 ft ^f	WT	80 (27)	29.32	0.786	0.782	0.784	±0.013
RAC 3 ft	FT	80 (27)	29.20	0.781	0.775	0.778	±0.020

^a Ft (0.3048) = m; in. (2.54) = cm. ^b WT refers to wind tunnel. ^c FT refers to flow tube. ^d Data obtained with this probe are plotted in Figure 10. ^e Data obtained with this probe are plotted in Figure 9. ^f Data obtained with this probe are plotted in Figure 8.

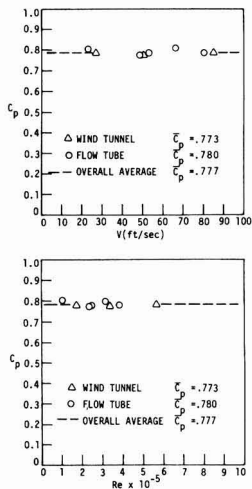


Figure 8. Typical probe coefficients for RAC probes

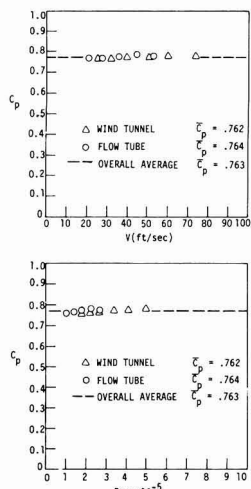


Figure 10. Typical probe coefficients for MISCO probes

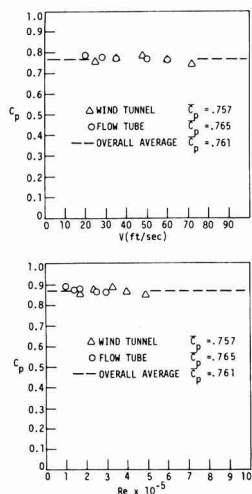


Figure 9. Typical probe coefficients for ISU probes

discussed items have on the S-type pitot tube. Thus, the value of 0.85 as suggested in the *Federal Register* (1) is only valid when all of these effects such as blockage, aerodynamic interference, misalignment, Reynolds number, and turbulence are negligible. Calibration as suggested by the most recent *Federal Register* (2) indicates the probe coefficient can be determined within $\pm 3\%$ over a velocity range from 1000 to 5000 fpm. This reference also suggested a blockage correction and proper alignment of the sampling probe. However, the Reynolds number effect, the flow facility effect, and the turbulence effect should also be considered.

Uncertainty of Results

An uncertainty analysis was performed to determine how uncertainties in the measured quantities would affect the uncertainty in the probe coefficient. For this purpose, a propagation of uncertainty equation suggested by Kline and McClintock (23) was used. If y is calculated from X_1, X_2, \dots, X_n measured variables by the function $y = f(X_1, X_2, \dots, X_n)$,

the uncertainty in the computed result due to uncertainties in the measured entities can be estimated from the relation (23)

$$W_y^2 = \sum_{i=1}^n \left(\frac{\partial f}{\partial X_i} \right)^2 W_{X_i}^2 \quad (8)$$

In this case, the uncertainty interval W is taken to be the maximum error (equivalent to three standard deviations from the mean) or approximately 99% confidence level. The uncertainties W_{X_i} in the measured variables X_i are estimated by the experimenter. In this regard the W_{X_i} terms represent the best estimates of the uncertainty based on use of the measuring instrument and experimenter experience.

All pressures measured in this study were accomplished by means of micromanometers capable of resolving to the nearest 0.001 in. (0.00254 cm) of water column equivalent pressure. The maximum uncertainties in the micromanometer readings were less than 1% during the wind tunnel operation and less than 2% during the flow tube operation.

This analysis yielded maximum uncertainties for the probe coefficient of $\pm 2.6\%$ in the flow tube and $\pm 1.7\%$ in the wind tunnel. These uncertainties resulted in probe coefficients of typically 0.76 ± 0.01 in the wind tunnel and 0.76 ± 0.02 in the flow tube. The probe coefficient C_{ps} for the standard pitot-static tube was determined to be 0.962 ± 0.007 . A summary of the uncertainties determined for this study is presented in Table II.

Conclusions and Recommendations

Conclusions. Probe coefficients can typically be obtained in the laboratory with approximately 2–3% uncertainty in their values. Such effects as turbulence, blockage, aerodynamic interference, misalignment, Reynolds number, and calibration facility idiosyncrasies can each contribute to the error in the calibration of the probe coefficient. Corrections for these effects must be incorporated into a consistent calibration procedure. The guidelines (1, 2) given by the Environmental Protection Agency for the calibration of the S-type pitot-static tube when used as part of a sampling probe assembly need revision to include more of these effects.

The probes used in this study did not have significant variation of the probe coefficient with Reynolds number or velocity as shown in Figures 8–10. Thus, a Reynolds number correction was not applied to the data of this study. However,

Table II. Uncertainties of Measured and Calculated Quantities

Meas'd* or calcd variable	Max uncertainty, %
* Pitot-static tube pressure	1.0 (Wind tunnel operation)
* Pitot-static tube pressure	2.0 (Flow tube operation)
* Barometric pressure	1.0
* Temperature	1.0
* Length	0.5
Area	1.0
Standard pitot-static tube coefficient	0.7
Velocity	1.4
Flow rate	1.6
Probe pitot-static tube coefficient	2.6 (Flow tube operation)
Probe pitot-static tube coefficient	1.7 (Wind tunnel operation)
Standard pitot-static tube	0.7 (Calibration facility)

this effect does warrant further study. For this reason, it appears that the best calibration technique is to use the exhaust stack, or the facility in which the sampling is to take place, to accomplish the calibration. In this way, all of the flow parameters are exactly simulated. However, the number and type of corrections necessary, as demonstrated by this work, preclude the use of the exhaust stack on the basis of practicality. Instead the simplicity of using the laboratory remains the more attractive choice.

Recommended Calibration Procedures. In the event one must calibrate a pitobe assembly in the laboratory, the following recommended calibration technique is suggested. To calibrate an S-type pitot-static tube attached to a sampling probe (pitobe assembly), the velocity head at some point in a flow field must be measured both with a pitobe assembly having the same configuration as that in which it will be used and a standard pitot-static tube. If the probe coefficient of the standard pitot-static tube is not known, it must also be calibrated to ascertain the correct value of its probe coefficient. When inserting the pitobe assemblies into the calibration facility, particular attention should be made to ascertain the zero pitch and yaw angles of the pitobe and standard pitot-static tube. This is to alleviate possible errors in the calculated probe coefficients. Calculate the S-type pitot-static tube probe coefficient, attached to the sampling probe, using the following relationship

$$C_{pp} = C_{ps} \left(\frac{\Delta P_s}{\Delta P_p} \right)^{1/2} \frac{A_s}{A_p} \frac{Q_p}{Q_s} (1 + \alpha_i^2)^{-1/2} \quad (9)$$

In Equation 9 A_s/A_p is the blockage correction, Q_p/Q_s is the flow rate correction, and $(1 + \alpha_i^2)^{-1/2}$ is the turbulence correction. These corrections are applied to the basic equation recommended for calibration by the *Federal Register* (1, 2). The resulting C_p , as demonstrated by this study, can be ob-

tained to within 2–3%, depending mainly on the amount of uncertainty in the ΔP measurements.

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Sorption and Diffusion Interactions with Fly Ash of SO₂ in Air, SO₃ in Air, H₂O in Air, SO₂+H₂O in Air, SO₃+H₂O in Air

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■ Sorption isotherms with fly ash as sorbent are determined with a quartz spring microbalance and a gas-flow apparatus for the following flowing gaseous sorbates: SO₂ in dry air, SO₃ in dry air, H₂O in air, SO₂+H₂O in air, SO₃+H₂O in air. Diffusion coefficients for mass transfer of sorbate molecules into a sample of fly ash particles are deduced from the time behavior of the sorption measurements, and equilibrium sorption isotherms are determined from the steady-state data. These measurements are conducted at 20, 90 and 150 °C. Static sorption measurements with Ar at 22 °C are also performed to measure the BET surface area and the porous structure of the ash. The data obtained offer an elucidation of the mechanism of electrical conductivity in layers of fly ash—especially from the standpoint of the influence of the gaseous environment on the electrical resistivity of the ash. This type of behavior is of vital importance in the practice of electrostatic precipitation, during which SO₃, H₂SO₄, and H₂O are frequently added to flue gas to improve the efficiency of removal of fly ash. In particular, the results are discussed from the standpoint of a model (published elsewhere) which accounts for the effect on the electrical resistivity of fly ash of capillary condensation at the contact points of the particles.

The efficiency of electrostatic precipitation is strongly influenced by the electrical conductivity of the fly ash which in turn depends upon ash composition and particle size as well as upon the composition of the flue gas, especially the content of H₂O and SO₃ (1, 2). In fact, it has become customary (3) to add SO₃ to the flue gas to "condition" the fly ash (thereby lowering its electrical resistivity). Experiments and correlation of data suggest (1, 2, 4) that the transport of alkali metal ions contributes significantly to the electrical conductivity of fly ash, but that Fe also influences conductivity in a more complex way. In the presence of moisture and a conditioning agent such as SO₃, the electrical resistivity of fly ash can be lowered by several orders of magnitude as compared to the dry ash. The effect of SO₃ appears to be very small without the simultaneous presence of water. Since it appears that the influence of flue gas composition on the electrical properties of the ash may be ascribed to sorption phenomena, the present work was undertaken with the aim of providing more information and better understanding regarding such phenomena.

In the investigation reported here, transient gravimetric sorption measurements were carried out in steadily flowing gas streams of known and adjustable composition. Such measurements have permitted estimation of the diffusion coefficient for transport of sorbate into a layer of ash particles, provided steady-state data from which equilibrium isotherms could be constructed, and yielded indirect evidence of the absence of chemical reaction between SO₃ and ash. Moreover, static volumetric measurements of sorption have also provided information as to BET surface area of the fly ash as well as evidence of capillary condensation within a sample of ash.

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Theory

The equilibrium relationship at a constant temperature T between amount of sorbate q sorbed per unit mass of sorbent and the sorbate concentration c_g of the fluid surrounding the solid sorbent can frequently be represented by one of the following expressions:

$$\text{Linear isotherm: } q = a \cdot c_g \quad (1)$$

$$\text{Freundlich isotherm: } q = a_F \cdot c_g^m \quad (2)$$

$$\text{Langmuir isotherm: } q = \frac{a_L \cdot c_g}{1 + b_L c_g} \quad (3)$$

where the constants a , a_F , m , a_L , and b_L are determined experimentally.

Evaluation of Diffusion Coefficients from Experiments. Neglecting the small effects of the cylindrical sample holder mass transfer into the fly ash sample can be viewed as transport by diffusion into an infinite slab of effective diffusivity D . According to this model, as theoretically formulated and solved by Crank (5), the rate of mass transfer in a plane sheet having a pore structure independent of position x is governed by the differential equation

$$DP \frac{\partial^2 c}{\partial x^2} = P \frac{\partial c}{\partial t} + \rho_p \frac{\partial q}{\partial t} \quad (4)$$

with the boundary conditions:

$$c = c_o \text{ at } t = 0 \quad 0 < x < l \quad (5a)$$

$$\frac{\partial c}{\partial x} = 0 \text{ for } x = l \quad t \geq 0 \quad (5b)$$

$$\partial c = \partial c_g \text{ for } x = 0 \quad \text{at } t \geq 0 \quad (5c)$$

The third boundary condition implies that mass transfer resistance (or concentration gradient) within the gaseous phase is negligible.

If we assume a linear adsorption isotherm $q = a \cdot c_g$ (Equation 1) as expressing the dependence of adsorbed amount on the adsorbate concentration in the gas, we can obtain the well-known solution in the final form:

$$\Gamma = \frac{\bar{q} - \bar{q}_o}{\bar{q}_\infty - \bar{q}_o} = 1 - 2 \sum_{n=0}^{\infty} \frac{e^{-b_n^2 \tau}}{b_n^2} \quad (6)$$

where

$$b_n = \frac{2n+1}{2} \pi \quad (7)$$

and

$$\tau = \frac{DP}{l^2(\rho + \rho_p)} t \quad (8)$$

Numerical values of $\Gamma = f(\tau)$ (obtained with a digital computer) are plotted in Figures 4 and 5. For a given value of Γ , and reading the corresponding values of τ from Figures 4 and 5, the value of the diffusion coefficient was calculated from Equation 8. An average value of D over experimental time was taken as representative.

Regarding the assumptions of uniform diffusivity and pore structure implicit in Equation 4, it should be noticed that although the pore structure of an individual ash particle may

be nonuniform, nevertheless, a fly ash layer from the macrostructural point of view satisfies the assumption of structure independence required by Equation 4. This has been generally confirmed by examination of ash samples under the electron microscope. Consequently, the values of D obtained according to the present analysis refer to the fly ash layer and not to the diffusion into a single particle.

Experimental Apparatus and Procedure

The flow apparatus for gravimetric sorption measurement incorporated a quartz spring balance supplied by Worden Quartz Products and is shown schematically in Figure 1. It consists of a Pyrex chamber with HUS-type joints and two stopcocks for control of gas flow or for evacuation. The chamber has a double-wall, thermally insulated section with thermometer well and connections for temperature control by circulation of oil from a constant temperature bath. Additional heat could be supplied to the lower part of the chamber by heating tapes connected to a transformer. This configuration provided accurate adjustment of gas temperature along the entire chamber. The temperature inside the chamber could be controlled within $\pm 0.2^\circ\text{C}$ accuracy. The fly ash sample was held in a cylindrical fused quartz pan 15 mm in diameter hung on the lower hook of the spring in the center of the chamber. An upward flow of gas containing the adsorbate was established in the chamber and at a rate sufficiently large to eliminate the influence of external mass transfer resistance. The flow was also sufficiently large that the effect of adsorption on gas concentration was negligible. Extension of the spring due to adsorption was measured with a microscope equipped with $10\times$ ocular with an 8-turn (100 dial divisions per turn) micrometer screw and a 50-mm objective. Sensitivity of all measurements was about $\pm 10^{-5}$ g/g fly ash. The ash depth within the sample pan was varied, and this dimension was accounted for in fitting the data to the trans-

port model of Equations 4–8. The sorption apparatus was calibrated with weights and pretested with H_2O and dry CuSO_4 , a known system.

The sorption gases were SO_3 , SO_2 , and H_2O in air prepared by mixing as shown in the diagram. Volumetric flow rates of SO_2 and dry air were controlled by sensitive flow meters and adjusted to the required values by precision, capillary valves. Concentration of H_2O and SO_3 was regulated by saturating the flowing air with the respective liquid held at a controlled temperature. Dried air flowed through a Gilmont rotameter and then passed through a frit inserted in a flask containing distilled water or oleum in the case of SO_3 addition. H_2O or oleum was maintained at a regulated constant temperature. The concentration of H_2O in the gas entering the apparatus was calculated from mass balance assuming that saturation concentration was reached in the thermostated moisturizing beaker 11 of Figure 1. Concentration of SO_3 was measured by chemical analysis of liquid in an impinger bubbler placed on the outlet of the apparatus. The amount of SO_3 was taken as that titrated according to the EPA method and discussed in ref. 6. Concentration of SO_2 was calculated from the mass balance and in some cases checked by the EPA analytical method, whereby SO_2 from gas is absorbed in an impinging bubbler containing distilled water and hydrogen peroxide. Good agreement was found between calculated and measured concentrations.

The gas mixtures were also passed through a heated tube to adjust the temperature of the gas fed into the sorption apparatus. The total flow rate of gas was in the range 500–3000 mL/min. With these flow rates aerodynamic forces influencing the sample pan are not negligible, but by maintaining a constant value of flow rate using precision valves, the effect of flow on spring vibration could be minimized and held within the error in readability. Another important fact was that the apparatus had to be thermally equilibrated to eliminate changes in volumetric flow rates due to temperature changes.

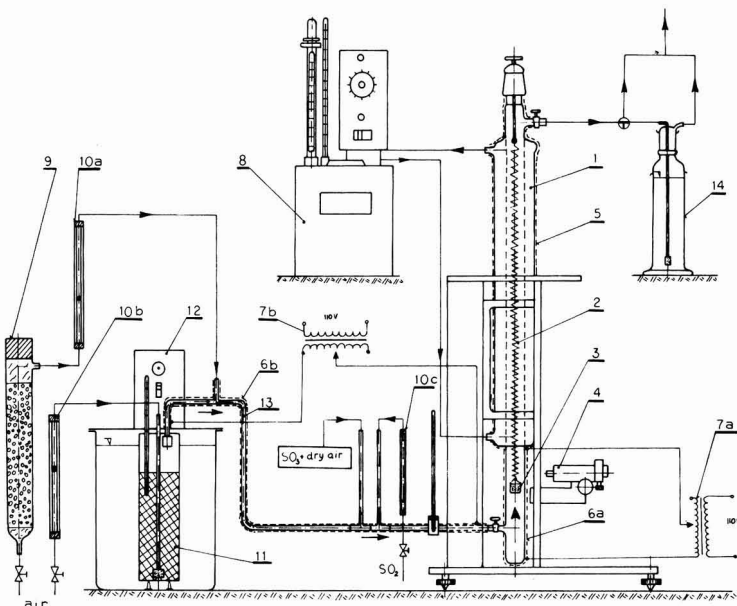


Figure 1. Schematic diagram of apparatus

1: Mass sorption spring balance, 2: fused quartz spring (extension 450 nm/4.5 g), 3: cylindrical fused quartz sample pan, 4: microscope, 5: thermoinsulator, 6a,b: electric heating tapes, 7: transformers, 8: circulator, 9: air-dryer, 10a,b,c: flow meters, 11: moisturizing beaker, 12: thermostatic bath, 13: heated tubing, 14: absorber

All fly ash used was pretreated by heating 12 h in air at 800 °C to burn off any carbonaceous contaminants whereupon it was stored in a closed flask. Immediately before the sorption experiments the ash specimens were again heated in dry air for 12 h at 400° and then brought to a steady state in the apparatus at the desired temperature with a constant flow of dry air. (The weight loss resulting from heating from room temperature to 400 °C was consistent with the sorbed amounts of H₂O indicated by the H₂O adsorption isotherms experimentally determined as described below.) The extension of the spring was measured vs. time beginning before the time of injection of an adsorbate into a flowing carrier gas. Adsorbed amounts as a function of time were calculated from the spring extension. After sorption equilibrium was reached, the sorbate concentration was changed, and a new experiment started from an initial nonzero adsorbate concentration. Only equilibrium measurements were made in this way. Diffusion coefficients for transport of adsorbate into the fly ash layer were evaluated using Equation 6, but only from the data in the low concentration range of experiments which were started from zero initial sorbed amount; for such low concentrations the adsorption isotherms are essentially linear, as required by Equation 6. Plotting adsorbed equilibrium amount vs. adsorbate concentration also gave adsorption equilibrium isotherms.

Physical Properties of Fly Ash

Fly ash obtained from the Portland Pennsylvania plant of the Pennsylvania Electric Co. was used in all sorption experiments. Results of chemical analysis of the ash and its characteristic physical properties are given in Table I. That the components analyzed add to only 92% suggests the ash contained other materials—perhaps several percent of carbon which was removed by heating to 800 °C in air as mentioned above. Fly ash was not screened so that polydisperse samples were measured. Mean particle diameter was in the range 15–25 μm as determined by sieving analysis. By use of argon as the adsorbate, the adsorption-desorption curves and the BET surface area of the ash were also measured. These experiments were carried out separately at $T = 21.9$ and 150 °C with a nonflow sorption apparatus for measurements of pressure difference changes during the adsorption. For these measurements the fly ash was preactivated by heating 18 h in high vacuum at 150 °C. BET surface areas and pore size distributions were evaluated with the data obtained. In industrial practice, temperature is usually above 110 °C, and concentrations of SO₂ can range up to about 3000 ppm (about 0.006 kg/m³ at 150 °C).

Results

The adsorption-desorption hysteresis curve measured with argon as the adsorbate is depicted in Figure 2 where the hysteresis loop itself is evidence of capillary condensation, and the shape of the loop suggests that the size distribution of the capillary pores is rather wide but the number of pores is rather small. In any case, the data clearly indicate the existence of capillary condensation and, therefore, significant capillary phenomena in the ash samples even in the range of low relative vapor pressures.

Sorption properties of the system SO₂-dry air were studied in the range of adsorbate concentrations 0–0.08 kg SO₂/m³, and the measurements were conducted at temperatures of 22, 90, and 150 °C. The constants of the Langmuir (Equation 3) and Freundlich (Equation 2) isotherms were statistically evaluated from the experimental data, and these values are given in Table II. Equilibrium data can be represented by the linear isotherm (Equation 1) in the low range of adsorbate concentrations, and the values of the corresponding parameter a are also given in Table II.

Graphical representation according to Equations 2 and 3 and experimentally obtained data are shown in Figure 3. From this figure, a better fit of the Langmuir adsorption isotherm is obtained at the temperature of 90 °C, whereas a better fit of the Freundlich isotherm is obtained at 22 °C. The adsorbed amount at 150 °C is so small that the relative error of these measurements is about ±50%. An important observation is

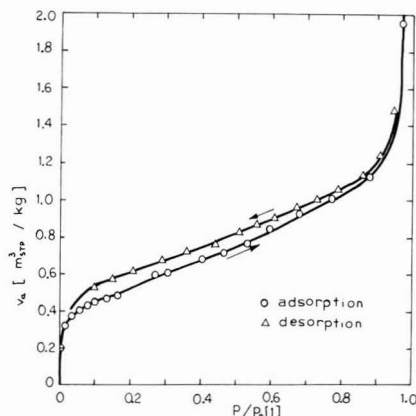


Figure 2. Adsorption-desorption hysteresis curve obtained for Portland ash, with argon as adsorbate

Table I. Physical Properties of Fly Ash Obtained from Portland Pennsylvania Power Station of Pennsylvania Electric Co.

Chemical	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	SO ₃	P ₂ O ₅	Na ₂ O	K ₂ O
Compn, wt % ^a	38.76	26.13	22.54	1.01	0.63	0.77	0.09	0.50	1.57
Pycnometer helium density, ^a kg/m ³ of solid phase									2350
Particle density, ^a kg/m ³ of particles									1099
Bulk density, ^b kg/m ³ of bulk sample									810–990
Total porosity, $P,^{b,c}$ %									66–58
Particle porosity, $a,^d$ %									53
Surface area, ^b m ² /g, based on 13.8 Å ² for argon molecule									1.62
Surface area, ^b m ² /g, based on 16.0 Å ² for argon molecule (measured by BET method)									1.88

^a Determined before ignition. ^b Determined after ignition. ^c Total porosity: fraction of total sample volume—internal pores plus interparticle space. ^d Particle porosity: fraction of particle volume—internal pores.

the common fact that the adsorbed amount decreases with temperature (under the same adsorbate concentration). This trend suggests that chemical reaction of SO₂ with fly ash does not play a dominant role for this range of temperatures, although SO₂ can react with many solids (e.g., limestone) at higher temperatures (7).

Diffusion coefficients for transport of adsorbate into the fly ash layer were evaluated as described above. The results of the experiments at 20 °C are plotted in Figure 4 as dimensionless adsorbed amount Γ vs. dimensionless time. The solid curve of Figure 4 was computed by Equation 6 with a mean value of D . Mean values of D obtained from experiments at 20, 90, and 150 °C are listed in Table II. These values of D are lower than comparable values of molecular diffusivity for SO₂ in air (for example, the Gilliland equation predicts $D_{\text{SO}_2\text{-air}} = 10.9 \times 10^{-6} \text{ m}^2/\text{s}$ at 22 °C). Similar enhanced values of $D_{\text{H}_2\text{O-air}}$ within the pores of alumina (e.g., $3.6 \times 10^{-6} \text{ m}^2/\text{s}$ at 20 °C) were observed by Marcassen (8). An increase of diffusivity with decreasing temperature is apparent in the present work as well as in the experiments cited above (8) for transport in porous alumina.

Simultaneous sorption of H₂O and SO₂ was investigated in experiments carried out at 150 °C and at volumetric concentrations of water $c^v = 3$ and 9%. The presence of SO₂ had no material effect on the sorbed amount observed—that is, the total amount of measured sorption corresponded approximately to that measured for the sorption of H₂O alone.

Adsorption isotherms for the system *water vapor-air-fly ash* were measured at temperatures 20, 90, and 150 °C. Adsorption equilibrium curves are depicted in Figure 5. Adsorbed amount decreases with increasing temperature as expected and in the adsorbate concentration range investigated, the adsorbed amount at $T = 150$ °C is very small. Because the occurrence of capillary condensation plays a major role in this system at $T = 20$ °C, the data cannot be satisfactorily represented by Freundlich or Langmuir isotherms for the entire range of relative pressure $0 \leq p/p_0 \leq 1$. The data at 20 °C indicate by hysteresis the capillary condensation of water and, of course, ordinary condensation as the saturation concentration are approached; they are included for this purpose. There is no reason, however, not to expect such capillary condensation of H₂O at the higher temperatures of 90 and 150 °C, although the data presented for such temperatures do not represent sufficiently high relative pressures to show such phenomena. The tremendously large water vapor content required at 90 °C and above to even approach saturation precluded such experiments. The practical ranges of temperature and water vapor contents lie above about 90 °C and 0.05 kg/m³, but it has already been shown (9) that a capillary condensation model can explain the combined effects of water vapor content and temperature on fly ash resistivity under these conditions, i.e., such a model explains the significant decrease in ash resistivity caused by the introduction to dry air of a few percent of water vapor at 150 °C.

Note that the 90 and 150 °C data points on Figure 5 do

represent the range of practical importance, as do many of the SO₂ data in Figure 3. The relative vapor pressures p/p_0 of practical importance for SO₂ are much lower than the corresponding relative pressures for H₂O; it is clear, therefore, that capillary condensation is much more likely in a system that contains the water vapor content of practical importance than a system that contains only SO₂ contents of practical importance but in air that is dry.

The diffusion coefficients for transport of water vapor into the fly ash layer were calculated from kinetic data obtained in the range of adsorbate concentrations where the adsorption isotherm can be supposed linear. These values of the diffusion coefficients are given in Table III, and Figure 6 shows a comparison of the experimental data at $T = 20$ °C with the theo-

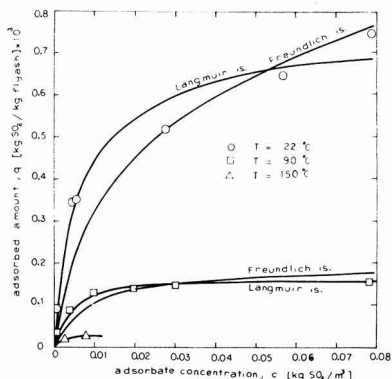


Figure 3. Adsorption isotherms for system SO₂-dry air-Portland fly ash

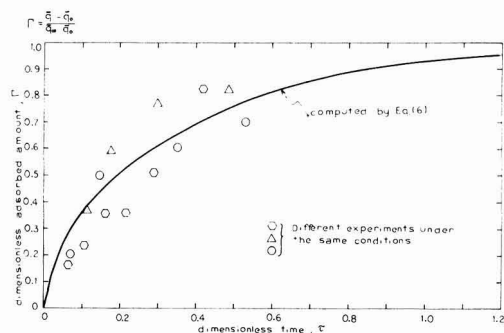


Figure 4. Results of kinetic experiments for system SO₂-dry air-Portland fly ash at $T = 20$ °C

Solid line represents Equation 6 with a mean value of D

Table II. Constants of Adsorption Isotherms and Values of Effective Diffusion Coefficients for Transport into Fly Ash Layer for System SO₂-Dry Air-Fly Ash

T , °C	Freundlich is., Eq. 2 a_F , kg SO ₂ /kg fly ash(m ³ /kgSO ₂) ^m m, L	Langmuir is., Eq. 3 a_L , m ³ /kg fly ash b_L , m ³ /kg SO ₂	Linear is., Eq. 1 a, m ³ /kg fly ash	$D \times 10^6$, m ² /s
22	$2.0 \cdot 10^{-3}$ 0.38	0.122 164	0.069 for $c_g < 0.05 \text{ kg SO}_2/\text{m}^3$	1.35
90	$0.44 \cdot 10^{-3}$ 0.30	0.058 326	0.024 for $c_g < 0.04 \text{ kg SO}_2/\text{m}^3$	1.3
150	$0.077 \cdot 10^{-3}$ 0.22	0.03 994	0.011 for $c_g < 0.002 \text{ kg SO}_2/\text{m}^3$	1.15

retical prediction of Equation 6. From Table III, the diffusion coefficient decreases with increase in temperature. Two different experiments (designated as O and Δ in Figure 6) were carried out at 20 °C in the usual way: desorption was measured by progressively lowering the gas-phase concentration. Several points of the hysteresis curve obtained in this way are depicted in Figure 5—when desorption occurs in a gas of zero moisture content (a dried gas fed to the flow sorption system), a residual moisture content remains irreversibly bound to the fly ash. This amount, however, can be removed by heating to about 250 °C. Such behavior may be due at least in part to hydrolysis of the water on the oxide surface with the formation of surface hydroxyl groups as discussed by Zettlemoyer and McCafferty (10). These types of phenomena could be of further impor-

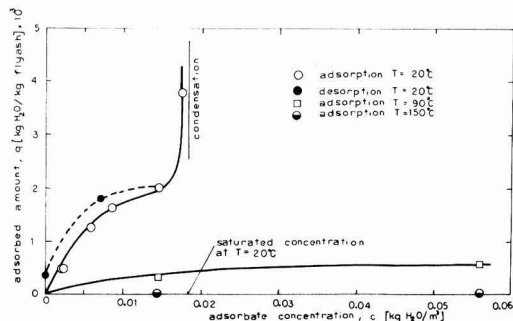


Figure 5. Equilibrium curves of system H₂O-air-Portland fly ash at T = 20, 90, and 150 °C

Table III. Values of Effective Diffusion Coefficients for Transport of Water Vapor into Fly Ash Layer

T, °C	a, m ³ /kg adsorbate	Concn range ^a × c _g , kg H ₂ O/m ³	Exp. diffusivity D × 10 ⁶ , m ² /s	Free gas diffusivity ^b D × 10 ⁶ , m ² /s
20	0.21	<0.007	2.15	24.4
90	0.22	<0.015	1.5	33.7

^a These concentrations were in the linear isotherm range as can be seen from Figure 5. ^b Diffusivity taken from ref. 15.

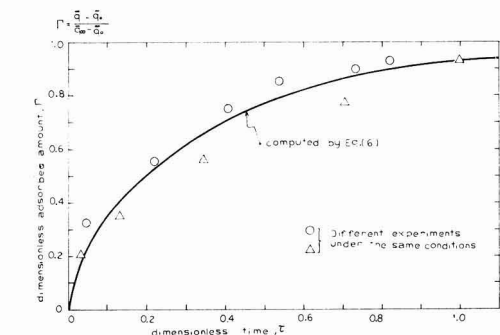


Figure 6. Results of kinetic experiment for system H₂O-air-Portland fly ash at T = 20 °C

tance for fly ash conductivity especially in view of the possibility that polarization could strongly influence conduction by ionic transport through the fly ash layer. Interaction of water with fly ash is discussed in ref. 1, and treatises on glass (11, 12) review the surface chemistry of that material which is similar to fly ashes (primarily glassy).

Adsorption of SO₃ from concentrations of about 100 ppm in dry air onto the fly ash was measured at 150 °C. Under such dry conditions the adsorbed amount of SO₃ on the fly ash surface was very small ($q < 3 \times 10^{-5}$ kg SO₃/kg fly ash) within limitations of the sensitivity of apparatus. These measurements suggest that there is no chemical reaction at 150 °C between fly ash and the SO₃ in the dry air.

Sorption in the system SO₃-H₂O-air-fly ash was measured at two different water concentrations *c*^v and 5 and 9% and for selected values of relative SO₃ vapor pressure in the range $0 \leq (p/p_0) \leq 1$. Values of the dew point partial pressure of SO₃, *p*₀ were also determined experimentally and compared with the theoretical prediction by Müller (13). The dew point partial pressure of SO₃, *p*₀ depends strongly on the H₂O concentration because it represents the concentration of SO₃ at which condensation (of H₂SO₄ when H₂O is present because SO₃ reacts very rapidly with H₂O to form the acid in very high equilibrium yield) occurs. Experimental determination of *p*₀ was achieved by observing the onset of condensation on a small mirror in the apparatus; since SO₃ was introduced into dry air flowing to the apparatus from liquid SO₃ held at a constant temperature, the value of *p*₀ could be computed from vapor pressure of the liquid SO₃ (with which the dry air stream was equilibrated), the H₂O content of the moist air mixed therewith in the apparatus, and the relative amounts of such moist air and SO₃-saturated dry air fed to the apparatus, as shown in Figure 1. At SO₃ partial pressure higher than *p*₀, significant increase in sorption of the fly ash was also observed by measurement of spring extension.

Agreement between the measured values and theoretical (Müller) predictions was within about 10%. Experimental results are graphically depicted in Figure 7, and they are correlated by the same equilibrium curve $q = f(p/p_0)$. A very large increase of adsorbed amount was observed as relative vapor pressure was increased within the range $0 < (p/p_0) < 0.2$ and in the range $0.7 < (p/p_0) < 0.8$. The shape of the equilibrium curve for relative pressure $p/p_0 > 0.35$ appears to be determined by the occurrence of capillary condensation as deduced from adsorption-desorption measurements with argon as adsorbate, in which hysteresis loops were found even for relative vapor pressure less than 0.3. An additional important observation is that, based on BET surface area, a monolayer of water on the fly ash (assuming that the H₂O molecule occupies 7.1 square Å) corresponds to about 0.7×10^{-3} kg H₂O/kg ash. According to Figure 7 the adsorbed mass of H₂SO₄+H₂O at which capillary condensation begins is significantly less than the mass of a monolayer of H₂O.

Based on findings as to particle structure obtained with an electron microscope (14), we concluded that sorption (followed probably by capillary condensation in the few intraparticle pores and surface pits) starts within the minute crevices formed between particles at their points of contact. A physical model has recently been published (9) which provides a quantitative prediction of the effect of water vapor on the electrical conductivity of fly ash based on capillary condensation of water at the points of particle contact as predicted by the Kelvin equation. Moreover, surface roughness would also appear to favor enhanced sorption at points of contact between particles as compared to locations on the open particle surface.

A significant increase of sorption at very low values of *p/p*₀ can be explained in terms of condensation within tiny intraparticle pores as well as in terms of formation of hydroxyl

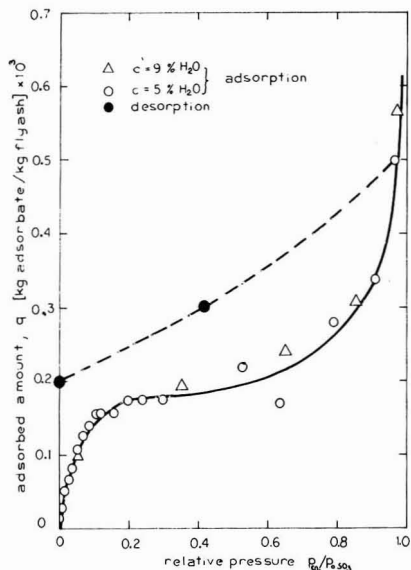


Figure 7. Adsorption and desorption curve for system $\text{SO}_3\text{-H}_2\text{O-air-Portland fly ash}$ at $T = 150^\circ\text{C}$ ($c = 5$ and 9% H_2O)

groups on the surfaces of the ash as discussed in ref. 10 for metal oxides. Glassy ash particles formed at high temperatures might be expected to have unsatisfied oxygen valences at their surfaces which can react with H_2O to form surface hydroxyls as the temperature is lowered. Beyond this, H_2O and H_2SO_4 would be expected to abstract cations from the glassy ash. The surface hydroxyls might be expected to act as nucleation sites for the sorption of H_2O and H_2SO_4 , whereas the abstracted cations could be expected to contribute the electrical conductivity of the sorbed aqueous phase. Electron microprobe studies (14) of sectioned particles of H_2SO_4 -conditioned fly ash reveal that the sulfur does not migrate to the interior of the particles in any significant quantities, even over the course of days. In any event, the liquid mixture of $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ which condenses on the particles may be expected to be enriched in H_2SO_4 , the higher boiling component, as compared to the composition in the gas phase; this is well-known behavior during condensation of mixtures. Because such condensed liquid may have a higher fugacity of H_2SO_4 as compared to the gas phase, desorption or evaporation of this liquid may proceed by a pathway entirely different from that of the condensation, thereby introducing obvious irreversibility which may partially account for the significant hysteresis evident in Figure 7 for the sorption-desorption cycle.

The expected influence of the condensed sulfuric acid on electrical conductivity of the fly ash is obvious in that the electrical conductivity of aqueous solutions is significantly enhanced by the presence of mobile charge carriers such as would be formed by addition of H_2SO_4 to H_2O . In another report (9) we present a simple model for such "conditioning" of fly ash based on an idealized structure of the packed ash particles and the contribution to electrical conductivity from the liquid condensed within the crevices formed at the points of contact between the particles. In particular, such a model can explain the complex behavior of electrical resistivity of packed fly ash as a function of temperature in the system fly ash-air- $\text{SO}_3\text{-H}_2\text{O}$.

Nomenclature

- a = constant in linear adsorption isotherm, m^3 gas/kg adsorbent
 a_F = constant in Freundlich isotherm, $\text{kg adsorbate/kg adsorbent} \cdot (\text{kg adsorbate/m}^3 \text{ gas})^{-m}$
 a_L = constant in Langmuir isotherm, m^3 gas/kg adsorbent
 b_L = constant in Langmuir isotherm, m^3 gas/ m^3 adsorbent
 b_n = parameter defined by Equation 7
 c = adsorbate concentration of gas phase within interstices of a layer of fly ash particles, kg adsorbate/m^3 gas
 c_g = average adsorbate concentration in flowing gas, kg adsorbate/m^3 gas
 c^v = volumetric concentration, %
 D = effective diffusion coefficient for transport of adsorbate within a layer of fly ash, m^2/s
 l = thickness of fly ash layer, m
 m = exponent of Freundlich isotherm, L
 P = porosity of fly ash layer m^3 pore volume/ m^3 fly ash layer
 p = partial vapor pressure, N/m^2 , mm Hg
 p° = saturated vapor pressure at temperature, T , N/m^2 , mm Hg
 p_o = dew point partial pressure of SO_3
 q = adsorbate concentration on solid at position x within layer of ash, $\text{kg adsorbate/kg adsorbent}$
 \bar{q} = average of q over layer volume, $\text{kg adsorbate/kg adsorbent}$
 \bar{q}_o = value of \bar{q} at time $t = 0$, $\text{kg adsorbate/kg adsorbent}$
 \bar{q}_∞ = value of \bar{q} at equilibrium, $\text{kg adsorbate/kg adsorbent}$
 t = time, s
 T = temperature, $^\circ\text{C}$
 v_a = adsorbed amount of argon under standard conditions ($\text{m}^3_{\text{STP}}/\text{kg fly ash}$)
 x = length parameter, m

Greek Letters

- Γ = dimensionless adsorbed amount defined in Equation 6
 ρ_p = bulk density of fly ash layer kg/m^3 fly ash layer
 τ = dimensionless time defined in Equation 8

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Size Distributions of Flocculated Particles: Application of Electronic Particle Counters

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■ A review of currently used particle size analyzers for liquid suspensions reveals that only the electronic resistance devices measure the particle volume directly. Although the electronic analyzer's ability to measure singlet particles is well documented, two major difficulties occur in measuring aggregate size distributions in flocculating systems. Since electronic counters measure only the particulate matter within a floc, the equivalent spherical diameters so recorded do not coincide with the microscopically observed diameters. Also, evidence exists that electronic counters only partially measure the total particulate matter within an aggregate because of the physical separation which exists between the component singlets. In this research the recorded electronic response is correlated with the aggregate porosity, and equations are derived to enable the investigator to correct for porosity effects. The new relationships between aggregate size and counter response are based on a modification to the existing equations for the passage of a singlet particle through the measuring aperture. The validity of the new equations is established in a flocculating *E. coli*-polyethyleneimine suspension in which the complete particle size distribution is recorded. Since a conservation of volume condition must exist between the unflocculated and flocculated state, this condition is used to determine the limiting porosity value in well-flocculated suspensions.

Within the past 10 years, several new experimental methods have been developed to measure the extent of aggregation produced in coagulation/flocculation treatment processes. These methods enable the researcher to quantitatively record the effectiveness of varying the flocculent type and dose, the velocity gradient and time of mixing, the number of mixing chambers and type of stators, and other factors known to influence the coagulation/flocculation treatment process. In the past, many experimental methods were either qualitative in degree or measured only the phase separation aspect of the flocculation process, which often led to errors when laboratory bench tests were scaled up to full-size facilities. To some extent, the emphasis on measurement of phase separation alone biased the investigator toward improvement of the physical parameters of the system, at the expense of possible chemical alterations which would enhance the destabilization phase of coagulation. The new aggregate measurement techniques enable the researcher to investigate thoroughly and accurately the destabilization of suspended colloidal matter as it occurs, in lieu of measuring just the end result: phase separation.

Table I summarizes the experimental techniques which are currently available to record the extent of aggregation of particulate matter in liquid suspensions. Each technique is characterized by some disadvantages, which are often more pronounced in the measurement of aggregate size distributions than in the measurement of singlet size distributions. Some techniques offer significant advantages in particular applications, such as the ability of the light interruption technique to operate in the continuous flow, real-time mode (1) or of the membrane refiltration technique to rapidly

evaluate changes in the specific surface area of aggregates utilizing simple, inexpensive equipment (2-4). With the exception of the electrical resistance method which measures aggregate volume, all the techniques measure either the aggregate cross-sectional area, or a parameter such as sedimentation velocity, which depends directly on the aggregate cross-sectional area. Because of its unique ability to measure aggregate volume, the electronic counting and sizing technique was selected for further study.

The electronic particle counting and sizing technique appears ideally suited to evaluating changes in the number distribution of suspended particulate matter brought about by the addition of coagulants in a water or wastewater system. Since the aggregate volume is measured directly, a differential volume distribution can be readily determined, thereby providing an indication of the equilibrium aggregate volume attainable under selected flocculation conditions. The detectable size range for the method (0.5-900 μm) enables the investigator to evaluate the extent of orthokinetic flocculation, which primarily affects particles greater than 1 μm in diameter (5). Because of the difficult experimental procedures involved in recording a complete size distribution by this method, and because of the cost of the data acquisition and data reduction equipment, electronic particle sizing is limited to laboratory experiments. However, particle size distributions evaluated by this technique have been correlated with turbidity and refiltration rate measurements, both of which are currently used in treatment practice (4).

The electronic particle counting and sizing technique has been successfully employed with suspensions of singlet particles for 20 years. Results have been verified with respect to count via hemacytometers and with respect to size via calibrated oculars, grids, or known particles (6-9). However, no effort has been made to verify whether the electronic sizing technique can be successfully used to count and size unflocculated flocs of primary particles. Consequently, research was undertaken to determine if the principles of operation of the electronic particle counter could be extended to flocculated particles similar to those found in water and wastewater treatment operations.

Prior Applications of Electronic Particle Counting

In 1956 W. H. Coulter announced the development of a precise counter for discrete microscopic particles (10). This counter found immediate application in many medical and industrial situations. Mattern et al. (6) used a 100- μm aperture to measure the number and size of red blood cells; they found the instrument counts to be more accurate than those obtained via the hemacytometer and deduced a linear relationship between pulse height and particle volume. Kubitschek (7, 8) extended the instrumental technique to bacteria with the use of a 10- μm aperture, and also found a strictly linear performance of the counter in response to particle volume, as long as the particle diameter was greater than 10% and less than 40% of the aperture diameter. Further experimental improvements, coincidence counts, background reduction, and size distributions for discrete particles, are discussed in the work of Wachtel and LaMer (9).

Higuchi et al. (11) were among the first to study the aggregation of particles (in this case, an oil-in-water emulsion) with a Coulter counter. They prepared a relatively monodis-

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persed emulsion, with droplets of about 1 μm diameter, by an electrical dispersion technique and then measured the aggregation/deaggregation of this emulsion with varying concentrations of dioctyl sodium sulfosuccinate (AOT). Fortunately, their emulsion particles coalesced upon contact; therefore, detection of aggregated particles was no different from detection of singlets.

Further improvements in measuring the particle size distribution of aggregating systems included the introduction of the multiaperture analysis procedure (12, 13) and the application of a pulse height analyzer (PHA) with multichannel storage (MCA) (14, 15).

The accuracy of the electronic counter in enumerating and sizing singlets within the size range 10–40% of aperture diameter has been verified with both the optical and electron microscope. In the case of particle aggregates, only qualitative checks have been made on aggregate sizes recorded by the counter. The first indication that the electronic counter may

not accurately record the aggregate size was noted by Camp (16) in his analysis of a series of experiments by Hannah et al. (17) who evaluated the floc strength of a kaolin-alum floc in a modified Couette mixing apparatus which contained a 70- μm aperture capable of recording six size ranges from 1.3 to greater than 9.0 μm . Using their data, Camp estimated the volume fractions for mixing times of 1, 5, and 10 min to be 4.7, 3.0, and 2.2 ppm, respectively. The initial volume of clay and Al_2O_3 was estimated at 4.3 ppm, and the velocity gradient was set at 50 s^{-1} to promote rapid floc formation without settling. Camp attributed the recorded loss of volume during flocculation to the dissolution of kaolin within the system.

Camp (18) attempted a similar volumetric analysis of the data of Ham and Christman (14), in which the formation of silica floc with alum was studied with a 240- μm aperture. Camp determined that the volume concentration increased from 1.6 to 3.6 ppm as the flocculation proceeded from 10 to 36 min. This result is expected since the 240- μm orifice re-

Table I. Experimental Techniques to Determine Extent of Aggregation

Technique	Property measured	Size range, μm	Description of process	Disadvantages
Optical				
Microscope	Length/width	0.2–400	Visual observation and comparison of aggregates with calibrated slide or lens	Time consuming and laborious; judgment errors in estimating size
Microscope automated	Length/width	0.5 and up	Microscope slide or photograph electronically scanned to record aggregate images	Time consuming; expensive peripheral equipment
Light scattering (also laser scattering)	Light intensity	2–500	Intensity of light energy scattered from particle in direction of sensor	Varying refractive indices of heterogeneous particles; multiple scattering effects in aggregates; criticality of sensing angle
Light interruption	Light blockage	2–9000	Reduction of light intensity on sensor as aggregate passes by detector	Opacity of fluid medium; identical refractive indices of particle and fluid
Spectrophotometric	Light intensity	0.002 and up	Observation of reduction in light intensity upon passing through suspension of aggregates (turbidity)	Complicated relationship between turbidity and size, i.e., $T = \sum_i n_i \pi r_i^2 K_i$, where n_i = number of particles of radius r_i , K_i = extinction coefficient which is function of relative refractive index, wavelength, and radius
Visual	Length/width	20 and up	Observation of appearance and size of aggregates	Time consuming and laborious; judgment errors in estimating size
Sedimentation/filtration				
Gravity sedimentation	Velocity	0.1–100	Observation of steady-state aggregate velocity through suspending media	Density and shape factors of aggregate unknown; time-consuming and laborious
Centrifugal sedimentation	Velocity	0.02–10	Observation of steady-state aggregate velocity as centrifugal force drives aggregate through suspending media	Density and shape factors of aggregate unknown; shearing and distortion of aggregates
Membrane refiltration	Filterability	0.45 and up	Formation of filter cake on 0.45- μm filter by filtering suspension, followed by refiltration of filtrate through filter cake	Filtration time a function of both filter cake porosity and specific surface area of aggregates
Electronic				
Electrophoretic mobility	Velocity	0.1–100	Observation of steady-state aggregate velocity as potential difference draws aggregate through suspending media	Density and shape factor of aggregate unknown; velocity a function of both unbalanced charge density and aggregate diameter
Electrical resistance	Resistivity	0.5–900	Aggregate passes through aperture causing resistance change in electrolyte between two electrodes. Resulting voltage pulse is proportional to aggregate volume	Blocking of aperture; expensive peripheral equipment

solves only the upper end of the total particle size distribution, i.e., due to background noise, small agglomerates and individual silica particles are not detected in the initial size distribution measurement. With the 240- μm aperture, large aggregates are detected, but the loss of small particles within the total size distribution goes unnoticed. Using the data of Ham and Christman, Camp calculated the water content of the silica-alum floc to range from 74 to 99.9%.

Ham (19) recognized that the aggregate sizes recorded by the electronic counter for a coagulated silica suspension did not correspond to the sizes measured optically. The discrepancy between the two methods was attributed to either aggregate distortion upon passing through the orifice of the counter or to the large porosity of the aggregate, which resulted in a larger visual size than justified by the particulate content. Ham alleviated the first problem by using a large (240 μm) aperture, and recognized that the aggregate porosity prevents a direct comparison between sizes determined by the counter (which measures only the particulate content) and microscopic observation (which measures total floc size including entrapped electrolyte).

Recently, Neis et al. (20) recorded a decrease in the specific resistance of polystyrene latex agglomerates during electronic counting experiments. This decrease was attributed to the higher electrolyte content of the aggregates and resulted in counter responses to the aggregate size which were smaller than the actual aggregate size. Neis et al. (20) presented similar results for the particle size distribution of a suspension of *Bacillus Cereus* in 0.25 M NaCl.

Measuring aggregate size distribution with an electronic particle counter appears to have two distinct liabilities, both of which are related to the aggregate porosity. First, the electronic counter measures only the particulate matter (treated as a coalesced solid sphere) within a floc, whereas microscopic observation measures floc size including the enclosed electrolyte. The size of the coalesced particulate matter is obviously not comparable with the total visual floc size. Second, the calibration of the counter with monodisperse, impermeable singlets does not permit the direct measurement of aggregate volume distributions, since the aggregate porosity causes a counter response to the aggregate particulate matter which is smaller than justified by the actual particulate content. Thus, while the traditional view has been that the particulate matter can be treated as equal in size to a coalesced singlet of the same volume, the distribution of particulate matter throughout the aggregate causes a reduced counter response.

In spite of these difficulties, the electronic counter-multi-channel analyzer technique offers the potential for precise quantitative measurement of the flocculation of colloidal particles, provided that compensations for aggregate porosity are made. The following paragraphs present suggested improvements to the normal operation of the electronic counter-PHA-MCA in the measurement of aggregate size distributions.

Theory of Electronic Particle Counting

The operation of the Coulter counter-PHA-MCA in counting and sizing singlets has been thoroughly developed (6, 9, 12-15). The resistance change caused by the passage of a cylindrical particle through the measuring aperture is expressed:

$$\Delta R = (4 \rho_o / \pi D^4) \frac{d^3}{[1.5 / (1 - \rho_o / \rho)] - (d^2 / a D^2)} \quad (1)$$

where ρ_o = resistivity of electrolyte, ρ = resistivity of particle, D = aperture diameter, d = diameter of equivalent spherical particle, and a = shape coefficient.

The response to a singlet is directly proportional to the particle volume, except as modified by the second term in the denominator. Both Kubitschek (7, 8) and Wachtel and LaMer (9) found that d/D should not exceed 0.4 to minimize aperture blockage and preserve linearity of response.

For singlets, the relationship between the particle diameters (d_i and d_j) and the corresponding storage channels in the MCA (C_i and C_j) is

$$d_j = d_i y^{(C_j - C_i) / 3} \quad (2)$$

where y = logbase used in the storage of voltage pulses produced by particle passage.

If d_i , C_i , C_j are known from zeroing experiments, then d_j is readily computed, provided that the particle is not an aggregate.

In the case of aggregates, however, these equations cannot be utilized because of the porosity of the aggregate itself. When a large aggregate of tightly bound singlets (1 μm in diameter) passes through a small (11 μm) or medium (30 μm) aperture, the aggregate tends to feather itself along the streamlines of the rapidly flowing sample volume. This elongation of the aggregate as it passes through the aperture results in a pulse having both height and width. Although the pulse height can be calibrated with monodisperse polystyrene latex particles, the pulse width goes uncalibrated. A similar result was noted by Mattern et al. (6) in their analysis of coincidence passage by singlet particles. Figure 1A depicts the critical volume in which the particle size is measured. Figures 1B and C show that the separation distance of two particles during coincident transit of the critical volume determines the relative pulse height and width. For small tightly bound aggregates, the pulse height should be directly proportional to the number of singlets in the aggregate. However, as the porosity increases and the aggregates elongate within the critical volume, the pulse width increases at the expense of pulse height.

A second problem occurs when a large aggregate passes through a medium (30 μm) or large (70 μm) aperture. If the porosity of the aggregate is large, then the aggregate sizing system (aperture, current, and amplification) is required to size and sum the many smaller pulses created by the primary particles which comprise the total aggregate. However, only the small 11- μm aperture is able to precisely detect and size singlets (1 μm in diameter); the larger 30- and 70- μm apertures only detect tightly aggregated singlet cells, and thus the system response is only a partial response to the total particulate volume within the aggregate. Neis et al. (20) recorded these effects as increases in the calibration factor during the course of coagulation, the calibration factor being the ratio of actual particulate volume to Coulter counter measured volume.

Proposed Modification to Theory for Aggregate Passage

To compensate for the effect of aggregate porosity upon the measured volume following flocculation, determinations of

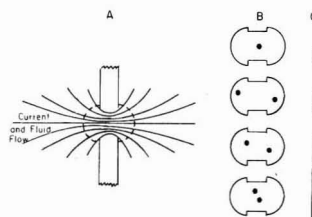


Figure 1. A: schematic representation of aperture, current density lines, and critical volume. B: particle separation distances within critical volume. C: resulting voltage pulses. Adapted from Mattern et al. (6)

aggregate porosity, as a function of the number of primary particles within an aggregate, were made either from calculations or from literature survey. These porosity values are summarized in Table II.

Some authors have attributed high porosity values to electrostatic repulsion between primary particles, a condition ameliorated by the adsorption of cationic coagulant to the negative colloidal surface and by the continuous agitation of the suspension during flocculation. Nevertheless, colloid-coagulant systems do produce open porous flocs, as observed via electron microscopy.

Figure 2 depicts a smooth curve of porosity vs. number of singlets per aggregate, drawn from the data of Table II so that two conditions are satisfied: For aggregates with less than eight singlets, the curve passes through the calculated porosity values; for larger aggregates, the curve is asymptotic to the porosity value between 0.50 and 0.95 which enables a conservation of volume condition to be met between unflocculated and flocculated state.

The shape of the curve relating the calculated porosity f to the number of cells per aggregate n suggests an exponential relationship of the form

$$n = ab^f \quad (3)$$

Table II. Typical Value of Aggregate Porosity as Function of Number of Singlets per Aggregate and Singlet Diameter

Singlets/aggregate	Configuration	Porosity	Ref
2	Linear	0.20	
3	Linear-triangular	0.25–0.26	
4	Linear-tetrahedral	0.27–0.29	
8	Cubic-rhombohedral	0.26–0.48	(21)
	Coarse sand	0.39–0.41	(22)
	Medium sand	0.41–0.48	(22)
	Fine sand	0.44–0.49	(22)
	Fine sandy loam	0.50–0.54	(22)
	$d \leq 20 \mu\text{m}$	0.50	(23)
	$d \leq 2 \mu\text{m}$	0.95	(23)
Silica powder	$d \leq 21 \mu\text{m}$	0.38	(24)
Silica powder	$4 \leq 16 \mu\text{m}$	0.43	(24)
Silica powder	$d \leq 6 \mu\text{m}$	0.38	(24)
Silica powder	$d \leq 16 \mu\text{m}$	0.43	(24)
Silica powder	$d \leq 6 \mu\text{m}$	0.75	(24)
Silica powder	$d \leq 2.3 \mu\text{m}$	0.89	(24)
Silica powder	$d \leq 5 \mu\text{m}$	0.71	(25)
Clay and alum	$d \leq 15 \mu\text{m}$	0.74–0.99	(18)

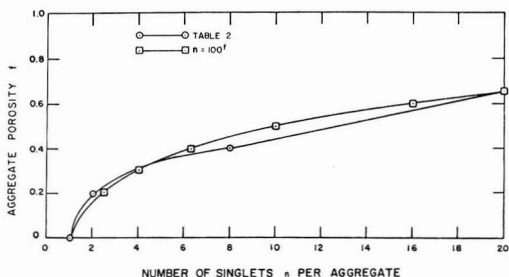


Figure 2. Aggregate porosity as function of number of singlets per aggregate

Since $n = 1$ at $f = 0$, $a = 1$. Further calculation provides a best fit when $b = 100$, yielding

$$n = 100^f \\ f = 0.5 \log n \quad (4)$$

During subsequent experiments an asymptotic porosity value of 0.69 was found to provide conservation of volume of the total suspended particulate matter between the unflocculated and flocculated state.

The formation factor F is defined as the ratio of the resistivity of the porous material, ρ_f , saturated with an electrolyte to the bulk resistivity of the same electrolyte, ρ_o :

$$F = \rho_f / \rho_o$$

Archie (26) has determined an empirical relationship between porosity and formation factor which applies to most porous materials:

$$F = \rho_f / \rho_o = f^{-m} \quad (5)$$

where $m = 2.0$ for clean sands, and slightly less than 2.0 for all other materials, i.e., $m \cong 1.9$.

Letting $m = 1.9$ for the aggregates and substituting Equation 4 into Equation 5 yields

$$\rho_f = \rho_o (0.5 \log n)^{-1.9} \quad (6)$$

As the aggregate size increases, larger apertures must be used to maintain d/D less than 0.4, and d^2/aD^2 insignificant. Substituting Equation 6 into Equation 1 yields:

$$\Delta R = 4 \rho_o d^3 [1 - (0.5 \log n)^{1.9}] / 1.5 \pi D^4 \quad (7)$$

In Equation 7 the response ΔR of the Coulter counter to the aggregate passage is a function of two unknowns: d , the equivalent spherical diameter of the aggregate, and n , the number of singlets per aggregate. However,

$$n = (\pi d^3/6) / (\pi d_o^3/6) \quad (8)$$

where d_o = singlet diameter.

Therefore

$$\Delta R = 4 \rho_o d^3 [1 - 1.5 \log (d/d_o)]^{1.9} / 1.5 \pi D^4 \quad (9)$$

Theoretically, for $d \leq d_o$

$$f = 1.5 \log (d/d_o) = 0$$

and

$$\Delta R = 4 \rho_o d^3 / 1.5 \pi D^4 \quad (10)$$

In this case the electronic counter response is directly proportional to the particle diameter d .

For $d_o < d < 2.9 d_o$ ($1 < n < 24$)

$$f = 1.5 \log (d/d_o) \cong 0.69$$

$$\{1 - [1.5 \log (d/d_o)]^{1.9}\} \cong 0.50$$

and

$$\Delta R \cong 2 \rho_o d^3 / 1.5 \pi D^4 \quad (11)$$

Finally, for $d > 2.9 d_o$ ($n > 24$)

$$f = 1.5 \log (d/d_o) = 0.69$$

$$\{1 - [1.5 \log (d/d_o)]^{1.9}\} \cong 0.50$$

and

$$\Delta R = 2 \rho_o d^3 / 1.5 \pi D^4 \quad (12)$$

Consequently, in the intermediate size range the response of the electronic counter to aggregate particulate matter does not increase linearly with the increase in aggregate particulate

matter. After the limiting porosity value ($f = 0.69$) is reached, the response again increases linearly with the aggregate size.

When an aggregate of diameter d_j passes through the aperture, the normal counter response, given by Equation 10, must be modified to compensate for the aggregate porosity so that:

$$\Delta R_j = 4 \rho_a d_j^3 [1 - [1.5 \log (d_j/d_o)]^{1.9}] / 1.5 \pi D^4 \quad (13)$$

$$\Delta R_j = \Delta R_{d_o} y^{(C_j - C_{d_o})} = 4 \rho_a (d_o)^3 y^{(C_j - C_{d_o})} / 1.5 \pi D^4 \quad (14)$$

Therefore:

$$d_j^3 [1 - [1.5 \log (d_j/d_o)]^{1.9}] = (d_o^3) y^{(C_j - C_{d_o})} \quad (15)$$

In Equation 15, d_o , y , C_j , and C_{d_o} are known; therefore, d_j can be calculated via an iterative technique using an initial estimate that:

$$d_j \geq d_o y^{(C_j - C_{d_o})/3} \quad (16)$$

The porosity factor $[1 - [1.5 \log (d_j/d_o)]^{1.9}]$ decreases until it reaches 0.5, which corresponds to the asymptotic value of the porosity for large aggregates, $f = 0.69$. The overall effect at a porosity of 0.69 is to increase the aggregate diameter 25% above that recorded by the Coulter counter.

Experimental Materials and Methods

A series of polyethyleneimine (PEI) polymers was selected as coagulants because of the range of molecular weights available from 600 to 60 000, corresponding to 14–1400 monomer (C_2NH_5) units. PEI in solution functions as a cationic polyelectrolyte strongly attracted to negatively charged colloids (27). The colloid was *E. coli* strain CR 63, grown in batch culture to a cell concentration of $2.5 (+0.5) \times 10^7$ cells/mL in the following medium:

Ingredient	g/L
Casamino acid (acid hydrolyzed casein)	1.20
Glucose	1.00
NH ₄ Cl	1.00
KH ₂ PO ₄	0.10
Collidine-HCl buffer, pH 7.0	50 ml/L
MgSO ₄ , 1 M	2 ml/L
FeCl ₃ , 10 ⁻³ M	1 ml/L

At the end of log phase growth, the relatively monodisperse coliform has a cylindrical shape: 0.8 μ m in diameter, 2–3 μ m in length, with a mean equivalent spherical diameter of 1.3 μ m.

Two serial dilutions of 10:1 of the initial cell concentration resulted in 2.5×10^5 cells/mL or 1.25×10^4 cells/50 μ L. At this concentration the 11- μ m aperture will give a true count of cell concentration without requiring coincidence corrections (6). The ionic strength of the growth medium and the dilutant was 0.06 M NaCl, the temperature 25 °C, and the pH 7.0 (± 0.1).

Following removal from the chemostat, the *E. coli* suspension (900 mL of 2.5×10^7 cells/mL) was rapidly mixed in a stirrer-reactor assembly (4) at a mean temporal velocity gradient $G = 190 \text{ s}^{-1}$ for 2 min while simultaneously adding 100 mL of PEI solution. Following rapid mix the flocculating suspension was stirred at a velocity gradient of 20 s^{-1} for 4 h. Particle size distributions were recorded every 60 min during the 4-h flocculation period, primarily to determine if the aggregate would reach an equilibrium size determined by the imposed velocity gradient and the PEI molecular weight, but also to verify the proposed modifications to normal electronic counter operation over a wide range of aggregate sizes.

The current and amplification settings of the Model B Coulter counter were determined for three different aperture

diameters (11, 30, and 70 μ m) by passing suspensions of monodisperse polystyrene latex in 0.06 M NaCl through the aperture. The settings, summarized in Table III, provide strong signal-to-noise ratios and maintain the ratio of particle diameter d to aperture diameter D greater than 0.07 and less than 0.20.

A voltage pulse generator was used with the Nuclear Data Model 555 pulse height analyzer (PHA) and multichannel analyzer (MCA) to determine the coarse and fine gain settings so that the logbase of input signals remained constant over the full range of channels, i.e., from channel 1 to 128. Varying the frequency of the voltage pulse within the recovery time of the electronic circuitry did not shift the channel of record.

A detailed particle size distribution could be obtained by using 80 channels of data from the 11- μ m aperture, 80 channels of data from the 30- μ m aperture, and 100 channels of data from the 70- μ m aperture. All 128 channels could not be utilized because of overlap between the 11- and 30- μ m apertures, and between the 30- and 70- μ m apertures. Bacteria of equivalent spherical diameter less than 1.13 μ m could not be detected by the 11- μ m aperture because of background electronic noise at this low signal level.

Prior to seeding the culture, the growth medium was filtered through 0.45- μ m Millipore filters to remove any large particulate matter. After culture growth, plate counts and hemacytometer counts were made to verify the accuracy of the Coulter counter measurements. As was previously noted by Mattern et al. (6), the counts from the Coulter counter had better reproducibility than either of the other techniques.

Samples of the flocculating *E. coli* suspension were withdrawn from the stirrer-reactor with a 2-mm bore pipet to prevent aggregate breakup, and then diluted with 0.06 M filtered NaCl. The dilution ratio depended upon the number of aggregates per unit volume, i.e., the reactor suspension was diluted only to the degree necessary to ensure significance of count and adequate relaxation time of the electronic circuitry. Since little difference exists in densities between the *E. coli* cells and the suspending electrolyte, sedimentation of the particle aggregates during the time required to make a count and size distribution was negligible. The aggregates did not appear to fragment as they passed through the aperture, in spite of the high shear forces encountered there (17).

The smaller apertures (11 and 30 μ m) were prone to blocking by the aggregated bacterial cells. Generally, blockages could be cleared with a small paint brush; the more difficult cases were cleared by briefly immersing (1 s) the entire aperture tube into the bath of an ultrasonic vibrator. Occasionally, single cells would adhere to the sides of the aperture, resulting in an effective reduction in the aperture size, and therefore increased pulse heights. By using a stopwatch to record the sampling time, such minor blockages were immediately detected, and the aperture could be cleared with the ultrasonic vibrator.

Using the calibration techniques discussed earlier, aggregate size distributions were prepared from the Coulter counter data

Table III. Summary of Calibration Data for Coulter Counter

Aperture diam, μ m	Particle diam, μ m	Counter settings		Peak channel	Logbase
		Amp	Current		
11	1.3	0.5	8	38	1.024
	2.0	0.5	8	94	
30	2.0	2.0	4	24	1.045
	5.7	2.0	4	95	
70	5.7	8.0	4	20	1.032
	9.5	8.0	4	70	

taken each hour after addition of the PEI. The aggregate count in each channel C_i was converted to aggregate count at diameter d_i via a computer program utilizing Equations 15 and 16. This aggregate count, divided by the diameter change corresponding to the size range stored in each channel, yielded the differential number distribution. Similarly, a differential volume distribution was prepared by dividing the aggregate volume by the log of the diameter change corresponding to the size range stored in each channel.

Experimental Results

Figure 3A reflects the change in the differential number distribution over a 4-h period of stirring at $G = 20 \text{ s}^{-1}$ when no polymer has been added. The peak in the particle number distribution occurs at the mean cell diameter $1.3 \mu\text{m}$. Cell aggregates are present, though in small concentrations. These aggregates are caused by bioflocculation, which increases with time because of the continuous release of extracellular biopolymers, and to coagulation by the 0.06 M NaCl dilutant. Figure 3B is the corresponding differential volume distribution when no polymer has been added.

Figure 4A is the differential number distribution for *E. coli* cells flocculated with the optimum dose (5.0 mg/L) of the low-molecular-weight PEI 6 (MW = 600). The extent of flocculation increases continually with agitation at $G = 20 \text{ s}^{-1}$. At this molecular weight and velocity gradient, most aggregates are concentrated in the range $1\text{--}4 \mu\text{m}$, with the number

of the latter increasing with time as the number of the former decreases. Figure 4B indicates the shift in the volume distribution caused by the addition of cationic polymer PEI 6.

Figure 5A is the differential number distribution for *E. coli* cells flocculated with the optimum dose (5.0 mg/L) of PEI 18 (MW = 1800). Continuous growth of larger aggregates in the $8\text{--}12\text{-}\mu\text{m}$ range occurs at the expense of the smaller $1\text{--}4\text{-}\mu\text{m}$ aggregates. The presence of these larger aggregates indicates an increasing shear resistance with the higher-molecular-weight polymer species, since no aggregates in this size range occurred with PEI 6 or PEI 12. Figure 5B, the corresponding differential volume distribution, illustrates the shift in volume distribution from the initial distribution (singlet particles with diameters in the range $1\text{--}2 \mu\text{m}$) to the distribution after 60 min of flocculation (aggregates with diameters in the range $8\text{--}12 \mu\text{m}$, or 230–790 singlets/aggregate).

Finally, the effect of the cationic polymer PEI 600 (MW = 60 000) upon the dispersed *E. coli* cells is shown in Figure 6A at the optimum polymer dose (0.5 mg/L). A dramatic decrease in the number of singlet cells (from 10^8 to $10^6 \text{ cells cm}^{-3}/\mu\text{m}$) and a dramatic increase in the size of the largest aggregate (greater than $12 \mu\text{m}$) are observed. The growth of very large aggregates occurs at the expense of small ($1\text{--}4 \mu\text{m}$) and medium ($4\text{--}8 \mu\text{m}$) sized aggregates, both of which are an order of magnitude less in number than when flocculated with PEI 12 or PEI 18. The shift in the differential volume distribution to aggregates in the $10\text{--}20\text{-}\mu\text{m}$ range ($1540\text{--}3640$ singlets/aggregate) is given in Figure 6B.

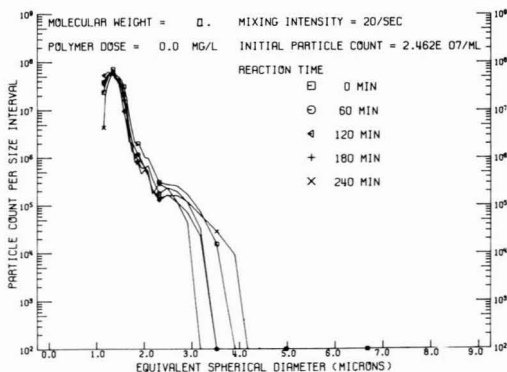


Figure 3A. Differential number distribution of *E. coli* aggregates with added flocculent

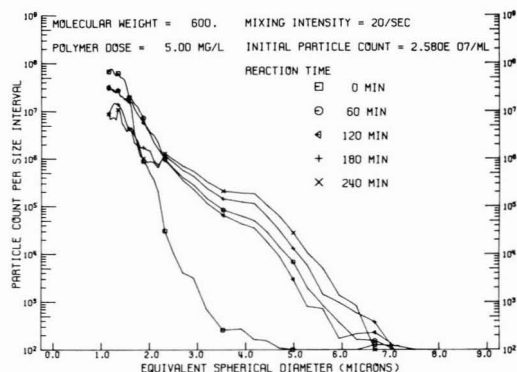


Figure 4A. Differential number distribution of *E. coli* aggregates at optimum dose of PEI 6 flocculent

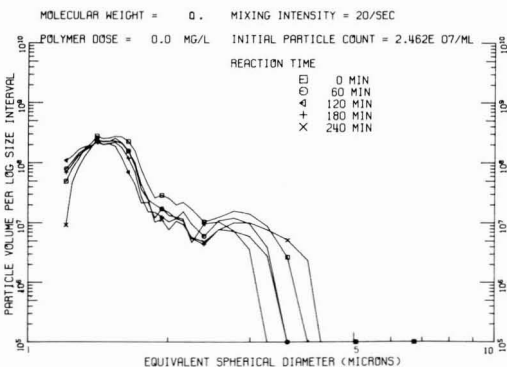


Figure 3B. Differential volume distribution of *E. coli* aggregates with no added flocculent

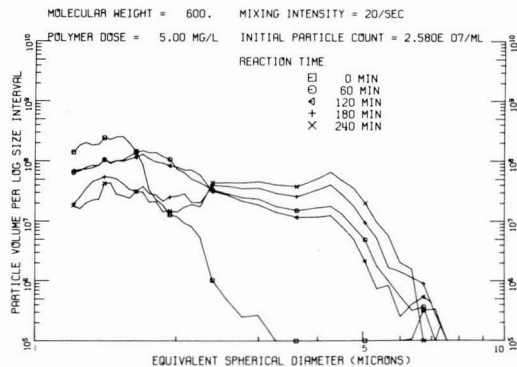


Figure 4B. Differential volume distribution of *E. coli* aggregates at optimum dose of PEI 6 flocculent

Discussion

When the *E. coli* suspension was continuously stirred without polymer addition, the total particulate volume as measured by the Coulter counter-PHA-MCA remained constant within the experimental limitations ($\pm 5\%$) of the sampling and measuring technique. However, as aggregates were formed because of the addition of cationic polymer, the measured total particulate volume decreased in spite of the agitation ($G = 20 \text{ s}^{-1}$) which prevented aggregate sedimentation. Losses to the sides of the stirrer-reactor did not occur because of the very smooth polyethylene and Teflon surfaces and the continuous stirring. The recorded decrease in the volume of suspended matter is attributed to the inability of the electronic circuitry to record the width of the pulse produced as the aggregate passes through the aperture, and to the inability of the larger aperture combinations to precisely size and sum the many singlet particles which comprise the total aggregate volume. Both of these phenomena can be related to the amount of electrolyte contained within the floc particle, and thus to the porosity of the aggregate. The application of the theoretically derived porosity correction to the basic Coulter counter-PHA-MCA data resulted in conservation of volume between the unflocculated and flocculated state of the suspended matter. This porosity correction does not measure the actual porosity of large aggregates, but rather enables the researcher to evaluate the effect of this aggregate porosity upon the response of the electronic counter. The porosity correction, as expressed in Equations 13, 15, and 16, was experimentally verified in flocculation conditions extending

from monodisperse size distributions ($n = 1$) to large aggregates ($n \leq 4000$).

Summary

To measure a constant volume of suspended particulate matter in a coagulating suspension, modification of the normal operating procedure for electronic particle sizing is required. This modification results in considering the effects of aggregate porosity upon the electronic response to aggregate passage through the aperture. The equation for the electronic response to singlet passage was modified to account for aggregate porosity with the porosity increasing with aggregate size up to an asymptotic value. This theoretical correction was then verified experimentally using *E. coli* cells as the suspended colloid and the cationic polymer, polyethyleneimine, as the coagulant.

The electronic counter responds only to the particulate matter within a floc; consequently, the equivalent spherical diameter so determined represents that of a coalesced sphere. For this reason the floc size recorded via electronic particle counting cannot be directly correlated with the floc size recorded microscopically.

By recording the complete size distribution from singlet particle to the largest aggregate, the conservation of volume condition can be utilized to determine the effect of aggregate porosity on counter response. Once this correction is made, the Coulter counter-PHA-MCA can be effectively utilized to evaluate the flocculation process as it occurs in the reactor basin.

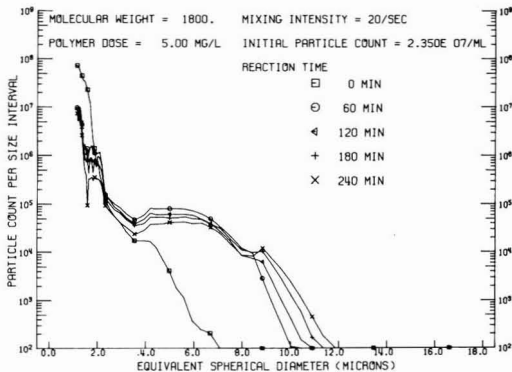


Figure 5A. Differential number distribution of *E. coli* aggregates at optimum dose of PEI 18 flocculent

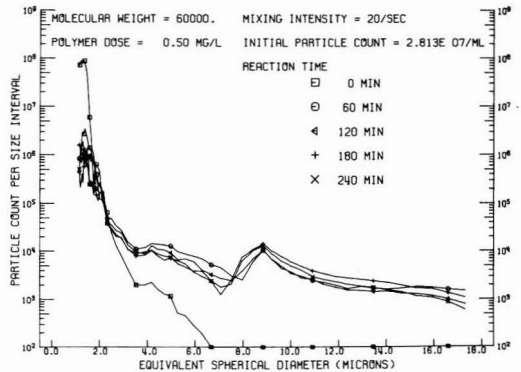


Figure 6A. Differential number distribution of *E. coli* aggregates at optimum dose of PEI 600 flocculent

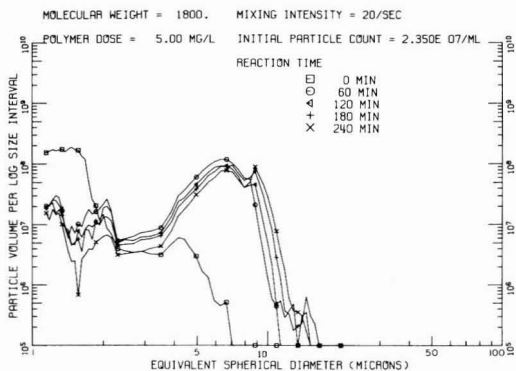


Figure 5B. Differential volume distribution of *E. coli* aggregates at optimum dose of PEI 18 flocculent

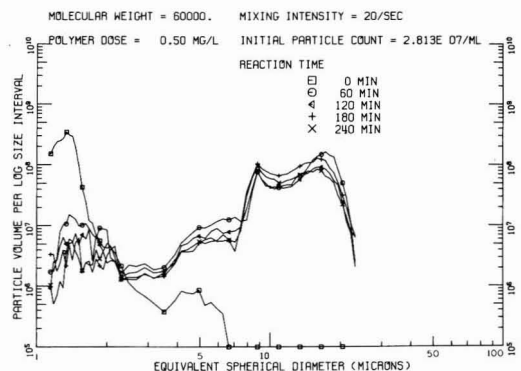


Figure 6B. Differential volume distribution of *E. coli* aggregates at optimum dose of PEI 600 flocculent

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Trimmed Spearman-Kärber Method for Estimating Median Lethal Concentrations in Toxicity Bioassays

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■ Several methods for treatment of data from toxicity tests to determine the median lethal concentration (LC50) are discussed. The probit and logit models widely used for these calculations have deficiencies; therefore, a calculational method, named the "trimmed Spearman-Kärber method", is developed. Examples of actual and hypothetical bioassay test data are given, and comparisons are made of the abilities of these three methods to treat these data. The trimmed Spearman-Kärber method is not subject to the problems of the probit and logit models, has good statistical properties, is easy to use, and is recommended for accurate and precise calculation of LC50 values and their 95% confidence interval end points.

The most widely used methods for estimating the median lethal concentration (LC50) for a toxicant are based on either the integrated normal (probit) or logistic (logit) models. These models often describe the relationship between mean mortality and concentration of toxicant. Estimates of LC50 based on the probit or logit models have some deficiencies which have not previously been described to biologists. These deficiencies are sufficiently important that methods based on the probit and logit models should probably not be used for routine analyses of an extended series of bioassay experiments.

Where many sets of bioassay data are analyzed on a routine basis, it is important that all analyses be based on a single statistical method. The appropriate statistical method must have three characteristics: be reasonably accurate and precise; be programmable so that all calculations can be done on a digital computer; and be robust enough that it will not fail when the data are somewhat unusual. When a large number of bioassays are run, some anomalies are bound to occur, and

the statistical method must be able to produce reasonable LC50 estimates from such anomalous data.

The following is a critical discussion of methods based on the probit and logit models and a description of a recommended alternative, named the "trimmed Spearman-Kärber method".

Discussion of Probit and Logit Models and Methods for Estimating LC50

Preliminaries. Let an acute toxicity bioassay yield the following information: x_1, x_2, \dots, x_k , which are the natural logarithms of the k concentrations of toxicant used and which are arranged in order of increasing concentration so that $x_1 < x_2 < \dots < x_k$; n_1, n_2, \dots, n_k , which are the numbers of fish exposed to the k concentrations, respectively; r_1, r_2, \dots, r_k , which are the numbers of fish that die within a fixed time of exposure to the k concentrations, respectively.

It is not unusual in a toxicity bioassay experiment to have more than one of the low concentration tanks yield no mortalities and/or to have more than one of the high concentration tanks yield 100% mortalities. For such an experiment, let x_1 be the highest \log_e -concentration producing no mortality where all tanks of lower concentration also produce no mortality. Let x_k be the lowest \log_e -concentration producing 100% mortality where all tanks of higher concentration also produce 100% mortality. In essence, all tanks below \log_e -concentration x_1 and above \log_e -concentration x_k are not used in the analyses.

Because the fish used in the experiment were drawn at random from some large population of fish, one can talk about the population proportion of mortality at each of the k concentrations. Let $P(x)$ be the true, unknown proportion of the underlying population which would die within the fixed duration time if exposed to a \log_e -concentration of x . Then the observed proportion mortality $p_i = r_i/n_i$ is an estimate of

¹ Statistical Laboratory.

$P(x_i)$. Call $P(x)$ the true response curve; it is typically S-shaped.

One can also assume that each fish in the underlying population has a unique upper limit of tolerance to some concentration of the toxicant, which is that concentration just sufficient to kill the fish within a fixed exposure time; at any concentration less than this, a fish would live longer than the fixed exposure time. The frequency distribution of log tolerance concentrations for all fish in the population is called the tolerance distribution. Denote the mean of this population tolerance distribution by μ . All of the statistical methods discussed in this paper require that the population tolerance distribution is symmetric around μ . This means that μ is also the median of the tolerance distribution. Because the true response curve, $P(x)$, is the cumulative relative frequency curve for the tolerance distribution, $P(\mu) = 1/2$. The symmetry of the distribution forces $P(x)$ to be symmetric in the sense that $P(\mu - \delta) = 1 - P(\mu + \delta)$, for every $\delta > 0$. Experience shows the true response curve to be nearly symmetric for acute toxicity data when x is log concentration of toxicant. The parameter of interest, LC50, is the antilog of μ . All methods described here estimate the LC50 by taking the antilog of an estimate of μ .

Probit and Logit Models. The probit model for $P(x)$ is

$$P(x) = \int_{-\infty}^{(x-\mu)/\sigma} \frac{1}{\sqrt{2\pi}} e^{-u^2/2} du \quad (1)$$

where σ is the standard deviation of the tolerance distribution (1).

The logit model for $P(x)$ is

$$P(x) = [1 + e^{-(x-\mu)/\beta}]^{-1} \quad (2)$$

where β is a constant [0.55133] times the standard deviation of the tolerance distribution (1).

Equations 1 and 2 are presented to show how specific the probit and logit models are. The probit model is appropriate only if $P(x)$ is closely approximated by Equation 1; similarly, the logit model is appropriate only if $P(x)$ is closely approximated by Equation 2.

It is difficult to choose between the logit and probit models. If the true response curve is closely approximated by one model, it probably is closely approximated by the other (2, 3).

After one has decided that either the probit or logit model is appropriate, there are a number of statistical methods available for estimating μ . The most often-used method is the maximum likelihood procedure. An iterative technique is required (1). Computer programs are available to perform the calculations (4, 5).

The Litchfield and Wilcoxon (6) method, which is popular in the field of acute toxicity bioassays, is a rapid graphical method for finding the maximum likelihood estimate of μ for the probit model. The Litchfield and Wilcoxon method usually will not produce the exact maximum likelihood estimate and is not totally programmable because it requires drawing lines after visual inspection of plotted data.

The next most popular procedure for estimating μ under either the probit or logit models is the minimum transform chi-square method. The simplest version of this method amounts to fitting a single weighted least-squares linear regression line, where transformed- p is the dependent variable and x is the independent variable (1, 3).

Two response curve models and two methods of estimation for each model have been discussed. One should not speak of "the probit method" but should specify the method more precisely by saying, e.g., "the maximum likelihood estimate based on the probit model".

Criticism of Methods Based on Probit and Logit Models. The maximum likelihood iterative procedure can be very

unstable if the data do not conform to the assumed model. Two common types of instability are that the iterations may not converge, and that the iterations may converge to different values depending on the initial guesses used to start the program. This means that if all LC50's are to be estimated by the maximum likelihood method, then some sets of potentially useful data cannot be analyzed.

Another criticism pertains to comparisons of results from duplicate experiments. Suppose that an acute toxicity bioassay is performed twice using the same toxicant concentrations and numbers of fish in each bioassay. Let the k proportional mortalities for bioassay A be $p_1^A, p_2^A, \dots, p_k^A$ and let those for bioassay B be $p_1^B, p_2^B, \dots, p_k^B$. Suppose that $p_i^A \leq p_i^B$, for every $i = 1, \dots, k$, with $p_i^A < p_i^B$ for at least one concentration. Then because the mortality in bioassay B is greater than the mortality in bioassay A, one would want the LC50 estimate for B to be no larger than the LC50 estimate for A. Using either maximum likelihood or minimum transform chi-square methods, for either the probit or logit models, it can happen that the bioassay with the greater mortality yields the higher LC50 estimate.

Tables I and II show examples of these deficiencies. Table I gives five sets of actually observed experimental percentage mortality data for a control tank and five test tanks of increasing toxicant concentration. Table II gives some estimates of LC50 for the experimental data. Maximum likelihood estimates do not exist for data sets 1A and 1B. The Daum (5) program did not converge for data sets 1A and 1B. Surprisingly, the BMD (4) program did converge for these same two data sets when a good initial guess of μ was entered. The Litchfield and Wilcoxon (6) method failed on data sets 1D and 1E. The proportions of mortality for data sets 1B and 1C are greater than for data set 1A, but the estimated LC50's for 1B and 1C, calculated by the BMD program and the logit program, are larger than that for 1A; they are identical to that for 1A when calculated by the Litchfield and Wilcoxon method.

These examples of deficiencies are very disconcerting. It is true that the data of 1B-1E did not fit the probit and logit models. This is principally because of the unusual death of a single fish in tank 2. Even if the population tolerance distribution does correspond to the probit or logit models, it is certainly possible that an especially sensitive fish could be randomly assigned to a low concentration tank; that fish would die although no fish die in the tank of next highest concentration. The statistical methodology should not be so delicate that it is seriously affected by such a mortality.

Trimmed Spearman-Kärber Method for Estimating LC50

Description of Calculations. Both the conventional and trimmed Spearman-Kärber methods are model-free, requiring only the symmetry of $P(x)$. The conventional Spearman-Kärber method is described in Finney (2). The trimming is employed in much the same way as in calculating the trimmed

Table I. Sets of Experimental Bioassay Data—Percentage Mortality

Tank	1	2	3	4	5	C
Concn, mg/L	15.54	20.47	27.92	35.98	55.52	Control
No. of test fish	20	20	20	19	20	20
Data set						
1A	0	0	0	5.26	100	0
1B	0	5	0	5.26	100	0
1C	0	5	0	15.79	100	0
1D	0	5	5	94.74	100	0
1E	0	5	5	100.00	100	0

Table II. Some Estimates of LC50, with Lower and Upper 95% Confidence Interval Endpoints, for Data of Table I

Data set		Probit			Logit ^d	Spearman-Kärber, ^e %			
		Daum ^a	BMD ^b	L-W ^c		0	5	10	20
1A	LC50	MF ^f	39.67	40.0	42.47	43.89	44.16	44.16	44.16
	Lower	NC ^g	NC	37.4	37.37	41.73	41.75	35.98	35.98
	Upper	NC	NC	42.7	48.26	46.17	46.71	55.52	55.52
1B	LC50	MF	41.98	40.0	46.91	43.27	44.16	44.16	44.16
	Lower	NC	NC	37.4	31.22	41.35	42.09	35.98	35.98
	Upper	NC	NC	42.7	70.48	45.27	46.32	55.52	55.52
1C	LC50	40.48	40.48	40.0	44.94	41.73	42.53	42.79	42.91
	Lower	NC	NC	37.5	33.04	39.14	39.30	39.20	35.98
	Upper	NC	NC	42.7	61.14	44.49	46.02	46.70	55.52
1D	LC50	30.98	30.98	MF	30.77	31.36	31.71	31.71	31.71
	Lower	NC	NC	NC	27.00	29.74	30.65	30.70	30.70
	Upper	NC	NC	NC	35.07	33.07	32.80	32.75	32.75
1E	LC50	30.44	30.44	MF	32.37	30.80	31.48	31.48	31.48
	Lower	NC	NC	NC	25.08	29.37	27.92	27.92	27.92
	Upper	NC	NC	NC	41.77	32.30	35.98	35.98	35.98

^a Maximum likelihood estimate based on the probit model (5); confidence interval using the Fieller procedure (7). ^b Maximum likelihood estimate based on the probit model (4); confidence interval end points from $\log_e(\text{LC50}) \pm 2 \times \text{SE}[\log_e(\text{LC50})]$ (7). ^c Litchfield and Wilcoxon (6) method. The method was said to fail if 10 attempted graphs drawn did not give an acceptable line. ^d The minimum transform chi-square estimate based on the logit model. The logit transform suggested by Anscombe (17) was used. ^e α %-Trimmed Spearman-Kärber estimates; $\alpha = 0, 5, 10, 20$. ^f MF indicates that the method failed. ^g NC indicates 95% confidence interval end points are not calculable.

Table III. Example of Trimmed Spearman-Kärber Calculations. Data Set 1C from Table I

Tank	(i)	1	2	3	4	5
Concn	mg/L	15.54	20.47	27.92	35.98	55.52
Log _e concn	x_i	2.7434	3.0190	3.3293	3.5830	4.0167
No. of fish	n_i	20	20	20	19	20
No. of mortalities	r_i	0	1	0	3	20
Mortality proportion	p_i	0.0	0.05	0.0	0.158	1.00
Adjusted mortality proportion	\bar{p}_i	0.0	0.025	0.025	0.158	1.00

Table IV. Examples of Calculation of 0- and 10%-Trimmed Spearman-Kärber Estimates of μ for Data of Table III

10%					
(1) Log _e of concn interval: (x_{j-1}, x_j)		(3.4724, 3.5830)	(3.5830, 3.9652)	Total	
(2) Relative frequency: ${}_{10}\bar{p}_j - {}_{10}\bar{p}_{j-1}$		0.0725	0.9275	1.000	
(3) Midpoint of interval: $(x_{j-1} + x_j)/2$		3.5277	3.7741		
(2) × (3)		0.25576	3.50048	3.7562	
The estimate of μ is 3.7562, and the estimate of LC50 is thus $e^{3.7562} = 42.79$ mg/L.					
0%					
(1) Log _e of concn interval: (x_{j-1}, x_j)	(2.7434, 3.0190)	(3.0190, 3.3293)	3.3293, 3.5830	(3.5830, 4.0167)	Total
(2) Relative frequency: $\bar{p}_j - \bar{p}_{j-1}$	0.025	0.0	0.133	0.842	1.000
(3) Midpoint of interval: $(x_{j-1} + x_j)/2$	2.8812	3.1742	3.4562	3.7999	
(2) × (3)	0.07203	0.0	0.45967	3.19952	3.7312
The estimate of μ is 3.7312, and the estimate of LC50 is thus $e^{3.7312} = 41.73$ mg/L.					

mean (7). The experimenter must choose a constant α , where $0 \leq \alpha \leq 50$, which is the percent of extreme values to be trimmed from each tail of the tolerance distribution before calculating the estimate of μ . The choice of $\alpha = 0$ produces the conventional Spearman-Kärber estimate. The estimation procedure will now be described in detail using data set 1C of Table I.

The first step is to adjust p_1, \dots, p_k if these mortality proportions do not satisfy $p_1 \leq p_2 \leq \dots \leq p_k$. This adjustment is necessary because it is known that $P(x_1) \leq P(x_2) \leq \dots \leq P(x_k)$, and we require the p_i 's to have this same monotone nondecreasing order. Thus, we will define new mortality proportions $\bar{p}_1, \bar{p}_2, \dots, \bar{p}_k$ by combining the mortalities (r_i 's) and the numbers of fish (n_i 's) of any adjacent p_i 's which are not in the proper monotone order to give a new averaged estimate of mortality proportion, \bar{p} , at the two adjacent doses. Consider Table III. Because $p_3 = 0.0$ is less than $p_2 = 0.05$,

adjustment is necessary. Both \bar{p}_2 and \bar{p}_3 are set equal to $(r_2 + r_3)/(n_2 + n_3) = 1/40 = 0.025$. This process is continued until the \bar{p}_i 's are in a monotone nondecreasing sequence. If monotonicity is violated for more than pairs, the order in which averaging is performed is unimportant since the final \bar{p}_i 's will always be the same (8).

The second step is to plot the (x_i, \bar{p}_i) points and connect them with straight lines as shown in Figure 1a. The polygonal figure formed is an estimate of $P(x)$, the cumulative relative frequency curve for the tolerance distribution.

The third step is to trim off the upper α percent and lower α percent of the polygon. Change the ordinate scale by replacing \bar{p} with ${}_\alpha\bar{p} = (\bar{p} - \alpha/100)/(1 - 2\alpha/100)$. Ignore those ${}_\alpha\bar{p}$ values which are less than zero or greater than one. The resulting polygon is an estimate of the cumulative relative frequency curve for the central $(100 - 2\alpha)$ percent of the tolerance distribution. If the experimenter does not want to

trim, then $\alpha = 0$, and this third step does not alter the polygon formed in step 2.

The trimming procedure for the example is shown in Figures 1a and 1b for $\alpha = 10$. By linear interpolation one finds that in Figure 1a, $\bar{p} = 0.10$ (or equivalently, $10\bar{p} = 0.0$) corresponds to $x = 3.4724$ and $\bar{p} = 0.90$ (or equivalently, $10\bar{p} = 1.0$) corresponds to $x = 3.9652$. Figure 1b is an estimate of the cumulative relative frequency curve for the central 80% of the population tolerance distribution; it is the end product of the trimming procedure.

The fourth and final step is to calculate the mean associated with the cumulative relative frequency polygon formed in step 3. This mean is the $\alpha\%$ -trimmed Spearman-Kärber estimate of μ . The procedure for calculating this mean for $\alpha = 10$ is illustrated in Table IV for the polynomial of Figure 1b. The \log_e -concentrations x_1, \dots, x_k form $k - 1$ adjacent intervals $(x_1, x_2), (x_2, x_3), \dots, (x_{k-1}, x_k)$. The estimated proportion of population tolerance \log_e -concentrations which are in the interval (x_{j-1}, x_j) is $10\bar{p}_j - 10\bar{p}_{j-1}$, where $j = 2, 3, \dots, k$, and where $10\bar{p}_j$ is the proportion on the polygon corresponding to x_j . Each product of the proportion $10\bar{p}_j - 10\bar{p}_{j-1}$ times the interval midpoint $(x_{j-1} + x_j)/2$ is found, and the sum of these products is the mean associated with the polygon. This mean is the 10%-trimmed Spearman-Kärber estimate of μ for the data of Table III; the LC50 estimate is then the antilog of the estimate of μ .

Consider the data of Table III and Figure 1a; let $\alpha = 0$. Then the frequency distribution and sample mean which one would associate with the polygon are calculated as shown in Table IV. Notice that neither the 0%-trimmed (the conventional Spearman-Kärber estimate) nor the 10%-trimmed Spearman-Kärber estimates are greatly affected by the anomalous response in tank 2.

The above description is appropriate if no mortalities occurred in the control tank. If mortalities did occur in the control tank, one should adjust the p_i 's by Abbott's formula (7) before starting the calculations.

Properties of Trimmed Spearman-Kärber Estimator.

The trimmed Spearman-Kärber estimator does have the necessary three characteristics previously stated. The calculations described can be programmed for a computer and/or can be done on a desk calculator. If $\alpha \geq 100\bar{p}_1$ and $\alpha \geq 100(1 - \bar{p}_k)$, the method *never fails*, no matter which unusual mortality pattern is observed. (One can revise the method to calculate the $\alpha\%$ -trimmed Spearman-Kärber estimate, where α^* is the maximum of the three values: $\alpha, 100\bar{p}_1, 100(1 - \bar{p}_k)$.) This revised method always provides an estimate of μ if $\bar{p}_1 \leq 0.5 \leq \bar{p}_k$. In duplicate experiments, if experiment B has greater mortality proportions than experiment A, then the trimmed Spearman-Kärber estimate of μ for B will *never* be greater than the estimate for A as long as $\alpha \geq 100\bar{p}_1$ and $\alpha \geq 100(1 - \bar{p}_k)$ in both bioassays.

Regarding the accuracy and precision of the estimator, the good statistical properties of the conventional Spearman-Kärber estimator are well known (2, 8, 9). The trimmed version of the Spearman-Kärber estimator has equally good properties, but is not as sensitive to anomalous responses as is the conventional version. Equations for calculating an approximate standard error to attach to the trimmed Spearman-Kärber estimator are given in the Appendix.

Because the $\alpha\%$ -trimmed Spearman-Kärber estimation procedure does not fail when $\alpha \geq 100\bar{p}_1$ and $\alpha \geq 100(1 - \bar{p}_k)$ and because the sensitivity of the procedure to anomalous responses decreases as α is increased, it appears that one should choose α as large as feasible. However, the standard error of the estimate increases as α increases. The choice of α then is a matter of judgment. For a group of experiments where the lowest concentrations cause approximately 5% mortality or less, and/or the highest concentrations cause

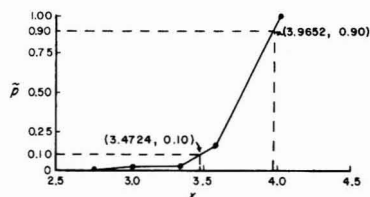


Figure 1a. Estimated cumulative relative frequency polygon for adjusted data from Table III

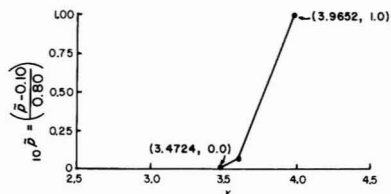


Figure 1b. Estimated cumulative relative frequency polygon of Figure 1a after trimming 10% from each tail

Table V. Hypothetical Sets of Data and Acceptable Results (10)—Percentage Mortality

Tank	1	2	3	4	5	6	C
Concn, $\mu\text{g/L}$	7.8	13	22	36	60	100	Control
No. of test fish	10	10	10	10	10	10	10
Data set							
4A	0	0	10	100	100	100	0
4B	0	0	70	100	100	100	0
4C	0	0	10	40	100	100	0
4D	0	0	20	70	100	100	0
4E	0	0	20	30	100	100	0

approximately 95% mortality or more, we recommend a choice of $\alpha = 10$.

Performance of Estimators on Test Data

The Committee on Methods for Toxicity Tests with Aquatic Organisms (10) has published hypothetical test data and "acceptable ranges" for the associated LC50 estimates and their 95% confidence limits (Table V) to help scientists evaluate estimation procedures. Their report does not contain the criteria by which the "acceptable ranges" were determined. These data have been analyzed by some of the methods mentioned in this paper, and results are shown in Table VI. The Daum (5) probit program did not converge for data sets 4A and 4B; the fact that the estimates produced are acceptable is fortuitous. The BMD (4) probit program did converge but gave negative variance estimates for data sets 4A and 4B. For data set 4A the estimate based on the probit model is not in the acceptable range. For data sets 4C and 4E the estimate based on the probit model equals the lowest acceptable value. For data set 4D the estimate based on the logit model equals the lowest acceptable value. For data set 4C the 10- and 20%-trimmed Spearman-Kärber estimates are larger than the highest acceptable value. We believe that for data set 4C, an estimate as large as 42.4, which is the value found by linear extrapolation from the responses in tanks 3 and 4, is more reasonable than an estimate smaller than 36.0, where the response was 40% mortality. Notice that some of the 95% confidence intervals of all three methods (probit, logit, and Spearman-Kärber) are wider than deemed acceptable. In our

Table VI. Results Calculated by Different Methods for Data of Table V

Data set	Acceptable values	Probit		Logit ^c	Spearman-Kärber, ^d %				
		Daum ^a	BMD ^b		0	5	10	20	
4A	LC50	25.5–27.5	26.4 ^e	24.1 ^f	26.2	26.7	27.2	27.4	27.4
	Lower ^g	21.1–24.0	NC ^h	NC	20.3	22.6	22.5	22.0	22.0
	Upper ^g	28.6–30.8	NC	NC	33.6	31.7	32.8	36.0	36.0
4B	LC50	19.0–21.5	20.0 ^e	21.0	20.0	19.7	19.5	19.4	19.1
	Lower	14.7–19.4	NC	NC	16.6	15.2	14.7	14.3	13.8
	Upper	22.9–24.5	NC	NC	24.1	25.5	25.9	26.2	26.4
4C	LC50	35.5–37.2	35.5	35.5	36.4	36.1	37.0	37.5 ^f	38.2 ^f
	Lower	26.1–30.7	28.8	26.1	27.7	28.7	29.0	29.3	28.1
	Upper	43.4–45.3	44.1	48.4	47.8	45.5	47.2	48.0	51.8
4D	LC50	29.4–30.0	29.5	29.5	29.4	29.5	29.7	29.8	29.7
	Lower	23.5–23.9	23.8	24.3	23.8	23.2	22.8	22.7	23.3
	Upper	36.3–37.4	36.6	35.8	36.5	37.7	38.6	39.1	38.0
4E	LC50	35.4–40.5	35.4	35.4	37.5	36.1	37.1	38.1	40.2
	Lower	28.1–30.8	28.2	26.2	26.5	28.3	28.4	28.7	29.6
	Upper	44.5–46.0	44.5	47.7	52.9	46.1	48.3	50.5	54.7

^a Maximum likelihood estimate based on the probit model (5); confidence interval using the Fieller procedure (7). ^b Maximum likelihood estimate based on the probit model (4); confidence interval end points from $\log_e(\text{LC50}) \pm 2 \times \text{SE}[\log_e(\text{LC50})]$ (7). ^c The minimum transform chi-square estimate based on the logit model. The logit transform suggested by Anscombe (17) was used. ^d $\alpha\%$ -Trimmed Spearman-Kärber estimates; $\alpha = 0, 5, 10, 20$. ^e Probit method did not converge. ^f Indicates point estimates of LC50 which are not in the range of acceptable values. ^g Lower and upper 95% confidence interval end points. ^h NC indicates 95% confidence interval end points are not calculable.

opinion, however, the intervals are narrow enough to be of practical value.

Conclusions

The $\alpha\%$ -trimmed Spearman-Kärber calculations have been programmed in FORTRAN and are performed routinely in our laboratory by use of the Montana State University XDS Sigma 7 computer. The program is integrated with a plotting routine for obtaining plots of toxicity curves, LC50 vs. time. We have analyzed hundreds of bioassay data sets using the $\alpha\%$ -trimmed Spearman-Kärber method, the maximum likelihood method for the probit model, and the minimum transform chi-square method for the logit model. The $\alpha\%$ -trimmed Spearman-Kärber method always provided useful results, but the methods based on the logit and probit models exhibited all of the deficiencies previously described.

Based on our experience with real and hypothetical data and taking into account accuracy, precision, computability, and robustness, we conclude that the $\alpha\%$ -trimmed Spearman-Kärber procedure is overall a better method than the methods based on the probit and logit models.

Appendix

Variance Formulas. Let x_1, \dots, x_k and n_1, \dots, n_k be as defined in the Preliminaries section. Let $\tilde{p}_1, \dots, \tilde{p}_k$ be as defined in the description of the first step in calculating the $\alpha\%$ -trimmed Spearman-Kärber estimate. Let $A = \alpha/100$; $L = \max\{i: \tilde{p}_i \leq A\}$; and $U = \min\{i: \tilde{p}_i \geq 1 - A\}$. Then x_L is the largest \log_e -concentration for which the adjusted proportion response is less than or equal to A , and x_U is the smallest \log_e -concentration for which the adjusted proportion response is greater than or equal to $1 - A$.

Define:

$$V_1 = [(x_{L+1} - x_L)(\tilde{p}_{L+1} - A)^2 / (\tilde{p}_{L+1} - \tilde{p}_L)^2] \times \tilde{p}_L(1 - \tilde{p}_L) / n_L$$

$$V_2 = [(x_L - x_{L+2}) + (x_{L+1} - x_L)(A - \tilde{p}_L)^2 / (\tilde{p}_{L+1} - \tilde{p}_L)^2] \times \tilde{p}_{L+1}(1 - \tilde{p}_{L+1}) / n_{L+1}$$

$$V_3 = \sum_{i=L+2}^{U-2} (x_{i-1} - x_{i+1})^2 \tilde{p}_i(1 - \tilde{p}_i) / n_i$$

$$V_4 = [(x_{U-2} - x_U) + (x_U - x_{U-1})(\tilde{p}_U - 1 + A)^2 / (\tilde{p}_U - \tilde{p}_{U-1})^2] \tilde{p}_{U-1}(1 - \tilde{p}_{U-1}) / n_{U-1}$$

$$V_5 = [(x_U - x_{U-1})(1 - A - \tilde{p}_{U-1})^2 / (\tilde{p}_U - \tilde{p}_{U-1})^2] \times \tilde{p}_U(1 - \tilde{p}_U) / n_U$$

$$V_6 = \{[(x_U - x_{L+1})(1 - A - \tilde{p}_U)^2 / (\tilde{p}_U - \tilde{p}_{L+1})^2] - [(x_{L+1} - x_L)(A - \tilde{p}_L)^2 / (\tilde{p}_{L+1} - \tilde{p}_L)^2] + (x_L - x_U)^2 \tilde{p}_{L+1}(1 - \tilde{p}_{L+1}) / n_{L+1}\}$$

Let $\hat{\mu}$ denote the $\alpha\%$ -trimmed Spearman-Kärber estimate and $\text{V}\hat{\mu}$ denote the estimated variance of $\hat{\mu}$. We are at present using these formulas, which are first order approximations, for $\text{V}\hat{\mu}$:

For $U - L \geq 4$,

$$\text{V}\hat{\mu} = (V_1 + V_2 + V_3 + V_4 + V_5) / (2 - 4A)^2$$

For $U - L = 3$,

$$\text{V}\hat{\mu} = (V_1 + V_2 + V_4 + V_5) / (2 - 4A)^2$$

For $U - L = 2$,

$$\text{V}\hat{\mu} = (V_1 + V_5 + V_6) / (2 - 4A)^2$$

For $U - L = 1$,

$$\text{V}\hat{\mu} = (x_U - x_L)^2 \{[(0.5 - \tilde{p}_U)^2 / (\tilde{p}_U - \tilde{p}_L)^4] \tilde{p}_L(1 - \tilde{p}_L) / n_L + [(0.5 - \tilde{p}_L)^2 / (\tilde{p}_U - \tilde{p}_L)^4] \tilde{p}_U(1 - \tilde{p}_U) / n_U\}$$

We are calculating approximate 95% confidence interval end points for μ using

$$\hat{\mu} \pm 2.0 [\text{V}\hat{\mu}]^{1/2}$$

We have calculated $\text{V}\hat{\mu}$ for more than 32 000 simulated data sets. These calculations indicate that if $U - L$ is greater than 1, $\text{V}\hat{\mu}$ is a conservative estimate of the variance. Consequently, the confidence intervals are wider than necessary to provide 95% confidence.

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Determinative Method for Analysis of Aqueous Sample Extracts for bis(2-Chloro)ethers and Dichlorobenzenes

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■ A method for the identification and measurement of bis(2-chloroethyl)ether, bis(2-chloroisopropyl)ether, and the dichlorobenzenes extracted from aqueous samples at the submicrogram per liter level is presented. The method employs two gas chromatographic (GC) columns, the first a relatively nonpolar pesticide type such as 4% SE-30 + 6% OV-210 on Gas Chrom Q, and the second the highly polar 3% SP-1000 on Supelcoport; and a Florisil column to separate the bis(2-chloro)ethers from the dichlorobenzenes (DCB's) for subsequent GC analyses. By use of the Florisil column, the DCB's are first collected in a 200-mL hexane eluate, after which the bis(2-chloro)ethers are collected in a 200-mL 5% ethyl ether in hexane eluate. Results of the analysis of extracts of finished waters sampled in a 113-city survey for the bis(2-chloro)ethers and the dichlorobenzenes are included to demonstrate the effectiveness of the determinative method presented.

Because they are potential carcinogens, bis(2-chloroethyl)ether (BCEE) and bis(2-chloroisopropyl)ether (BCIE) became the object of a year-long study when they were found in Illinois and Indiana drinking water supplies (1). Likewise, enforcement action was undertaken against another manufacturer when, during the course of the National Organics Reconnaissance Survey (NORS) (2), BCEE was found in the Philadelphia drinking water supply (3). However, during the latter study it was determined through the use of gas chromatography-mass spectrometry (GC-MS) that dichlorobenzenes (DCB's) can interfere with the identification and measurement of the bis(2-chloro)ethers by gas chromatography when using the relatively nonpolar pesticide columns recommended in previously published work (4, 5). Confirmatory test procedures developed to overcome these interferences resulted in a method of accurately identifying and measuring BCEE, BCIE, and DCB's in the same solution. The method consists of using a highly polar second GC column composed of 3% SP-1000 on Supelcoport, 100/120, and a Florisil column separation technique. This determinative method is considered necessary when GS-MS capability is not accessible, or concentration levels do not meet the sensitivity requirements of the latter technique, and is greatly enhanced by the use of a halogen specific detector.

The method as presented here was subsequently applied to the analysis of extracts of finished water samples taken during the 113-city, National Organics Monitoring Survey (NOMS), being conducted as a followup to the NORS and designed to gather data on a number of specific contaminants. Among those investigated were BCEE, BCIE, and the DCB's.

The NOMS is being conducted in a four-part seasonal effort and should be completed by the summer of 1977.

Experimental

Sample Preparation. Samples for the NOMS were collected in 1-gal glass containers and extracted with 15% ethyl ether/hexane using three 60-mL portions of solvent; the extracts were dried by passage through anhydrous crystalline sodium sulfate and concentrated using the Kuderna Danish apparatus and nitrogen blowdown, all as reported in previously published work (5). Although expensive and less convenient to use, a two-chamber micro-Snyder column substituted for the nitrogen blowdown will diminish losses by 10–12% in the final concentration step.

Gas Chromatography. One of the two columns used is a relatively nonpolar pesticide type. The NOMS data (Table II) was obtained using 4% SE-30 + 6% OV-210 on Gas Chrom Q, 80/100, although similar columns have been used successfully (4, 5). The second is the highly polar 3% SP-1000 on Supelcoport, 100/120. Both materials are packed in 180 cm × 4 mm i.d. glass columns, and both columns are operated at 100 °C.

Two detectors are suitable for the analysis, the microcoulometric titration (MCT) system previously described (5), and the Model 310, Hall (the mention of commercial names does not imply endorsement by the Environmental Protection Agency) electrolytic conductivity detector (used in the NOMS) from Tracor Instruments. Both are element selective and are used in a chlorine-specific mode. When using the

Table I. Retention Times for bis(2-Chloro)ethers and DCB's

Compound	Column packing			
	4% SE-30 + 6% OV-210 on Gas Chrom Q 80/100		3% SP-1000 on Supelcoport 100/120	
	Column temp., °C			
	100		100	
	N ₂ carrier flow			
	90 mL/min		90 mL/min	
	R _t , min	RR _t ^a	R _t , min	RR _t ^a
mDCB	2.7	0.96	1.8	0.59
BCEE	2.8	1.00	3.1	1.00
pDCB	2.8	0.99	2.1	0.67
oDCB	3.1	1.15	2.5	0.81
BCIE	4.0	1.42	2.3	0.74

^a Relative to BCEE.

MCT detector, nitrogen carrier flow for each column is 90 mL/min. When using the Hall detector, carrier flow is 75 mL/min. For maximum sensitivity 50 μ L are injected from a sample extract that has been concentrated to 1 mL.

Column Adsorption Chromatography (CAC). A Florisil column procedure is used to completely separate the DCB's from the bis(2-chloro)ethers. The Florisil is the same as that used for pesticide analysis and described in EPA methods (6). It is activated at 130 °C in an open dish overnight and is stored in a closed container at that temperature. The amount used is determined by the standardization procedure based on the adsorption of lauric acid.

The sample is transferred to a Florisil column that is pre-washed at room temperature with about 70 mL of hexane. The column is then eluted with 200 mL of hexane which quantitatively recovers the DCB's. The second elution is done with 200 mL of a solution of 5% ethyl ether in hexane. Both bis(2-chloro)ethers are quantitatively recovered in this eluate. Each eluate is collected in a Kuderna-Danish flask and ampul for concentration to 1 mL and subsequent GC analysis.

The efficiency of the separation procedure was determined by introducing 1 mL of hexane containing 1 μ g of each of the five compounds onto a Florisil column and analyzing at a maximum sensitivity of 0.005 μ g/L for DCB's and a 0.005 μ g/L for BCIE and BCEE, the three consecutively collected eluates, namely, 200 mL of hexane followed by 200 mL of 5% ether in hexane, followed by 200 mL of 50% ethyl ether in hexane.

Results and Discussion

Determinative Method. On the relatively nonpolar type column, 4% SE-30 + 6% OV-210 (Table I), BCEE elutes in 2.8 min, BCIE elutes in 4.0 min, and the meta (m) and para (p) isomers of DCB elute in approximately the same time as BCEE (Figure 1). More information than can be obtained with this column alone is therefore necessary to identify the three compounds. Only ortho (o) DCB (3.1 min) and BCIE are clearly identifiable and quantifiable using this column.

On the highly polar column, SP1000 (Table I), the order of elution is reversed for ethers (itself a very useful piece of

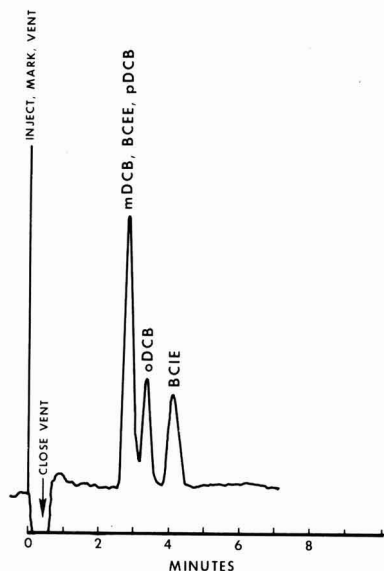


Figure 1. Chromatogram of mixture of BCEE, BCIE, and DCB's, using 4% SE-30 + 6% OV-210 on Gas Chrom Q 80/100, Col T = 100 °C. N₂ carrier flow = 90 mL/min

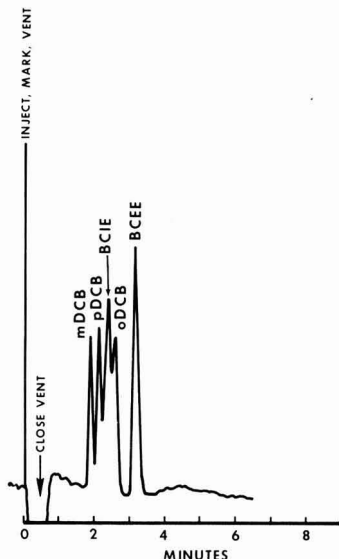


Figure 2. Chromatogram of mixture of BCEE, BCIE, and DCB's, using 3% SP-1000 on Supelcoport 100/120, Col T = 100 °C. N₂ carrier flow = 90 mL/min

Table II. Summary of Confirmed Findings (μ g/L) Reported in NOMS

City	Compound ^a			
	BCEE	BCIE	oDCB	pDCB
17	0.19
18	0.04	0.03
23	0.06
25	0.01
28	0.03
32	0.02
38	0.02
40	...	0.03	...	0.01
43	0.06
49	1.54
53	0.01
56	0.01
60	0.12
61	0.17	0.17
65	0.03	0.03
67	...	0.41	...	0.05
70	0.03
75	0.01
77	0.30	0.17	...	0.01
80	0.06	0.09	...	0.04
88	0.06	0.09
102	0.36	0.55	...	0.06
104	0.41
109	...	0.02
118	0.01	0.01
121	0.02
122	0.01	0.01
50	0.01
Totals	13	8	1	20

^a No confirmed findings for mDCB.

Table III. Sequence of Information Acquired in Process of Finished Water Extract Analyses (NOMS)

Column line	A, analytical information acquired	B, analytical mode	C, BCEE	D, BCIE	E, oDCB	F, mDCB	G, pDCB
1	Negative results	GC (SP-1000)	69	97	111	112	51
2	Tentative identification	GC (SP-1000)	44	16	2	1	62
3	Disproved	GC (SE-30/OV-210)	22	7	1	1	40
4	Qualitative and quantitative confirmation	GC (SE-30/OV-210)	5	3	0	0	2
5	Qual confirmation, quant corrected	GC (SE-30/OV-210)	0	0	0	0	4
6	Inconclusive	GC (both columns)	17	6	1	0	16
7	Disproved	GC after CAC (Florisil)	9	1	0	0	2
8	Qual and quant confirmation	GC after CAC (Florisil)	7	5	1	0	7
9	Qual confirmation, quant corrected	GC after CAC (Florisil)	1	0	0	0	7

confirmatory evidence), and BCEE (3.1 min) is clearly resolved for identification and measurement. However, BCIE (2.3 min) is not clearly resolved from p and o DCB (Figure 2), and accurate quantification using this column is not possible for these three compounds in the same solution. It is useful to note, however, that all of the DCB's are sufficiently resolved on this column for identification and measurement when the bis(2-chloroisopropyl)ether is absent.

To summarize, when DCB's are present in the sample, BCIE is clearly identifiable and quantifiable using the relatively nonpolar column, and BCEE is clearly identifiable and quantifiable using the SP1000 column. This fact is very useful in confirming results because the absence of DCB's is clearly indicated when the quantification of BCEE and BCIE, accurately obtainable for each on one column, is essentially duplicated on the other column.

If the presence of DCB's as well as the bis(2-chloro)ethers is indicated, results must be checked by employing the Florisil column procedure to separate the two classes of compounds. Identification and quantification can then be confirmed or corrected by analyzing the 5% ethyl ether in hexane eluate using the relatively nonpolar column for BCEE and the SP 1000 column for BCIE and by using the hexane eluate and both columns for the analysis of the DCB's.

Studies have shown that the separation of the two classes of compounds is complete using the Florisil column. BCEE and BCIE were detectable only in the 5% ethyl ether/hexane eluate, and DCB's were detectable only in the hexane eluate when analyzing the fortified extracts at a maximum sensitivity of 0.005 µg/L.

Eluting the original extract from the Florisil column with 200 mL of hexane has also removed some unidentified, relatively nonpolar compounds which have interfered with attempts to obtain GC-MS confirmation of BCEE. These compounds are generally nonhalogenated and do not interfere with the analysis of the original extract using the halogen-specific detectors. In other cases a cleanup has been effected by having some halogenated interfering materials retained on the Florisil column.

National Organics Monitoring Survey (NOMS). The NOMS has provided an excellent test of the capability of the method to identify and measure the low-level concentration (0.005 µg/L lower limit of detectability using an electrolytic conductivity detector) of BCEE, BCIE, and DCB's, either alone or in mixture, in the extract of an aqueous sample. Out of the 113 cities monitored for these compounds, positive findings obtained on 28 cities were confirmed. These results are listed in Table II.

Table III presents the sequence of analytical information acquired by the analyst in the course of obtaining these confirmations. For a clearer understanding of how the method

is applied and the effectiveness with which it operates, study the sequence of events in the analysis for pDCB. pDCB (Table III) was tentatively identified in 62 (Column G, line 2) of the 113 samples when using a single GC column (SP1000). By use of the second GC column (SE30/OV210), 40 of these identifications were disproved (line 3); two others were proved to be properly identified (line 4) and free of interference, while in four other cases the compound of interest was isolated from an interference (line 5) that had given a misleadingly high result on the first column; 16 of the tentative identifications were still inconclusive (line 6) and therefore were treated by column adsorption chromatography using Florisil.

Two of these remaining 16 tentative identifications were finally disproved (line 7) by the "Florisil" procedure, and in seven cases pDCB was isolated for identification and measurement (line 8) on both GC columns. For seven others a corrected measurement was obtained (line 9) because an interference had been eliminated. Thus, a total of 14 of the 16 treated by the Florisil procedure was finally confirmed as containing pDCB, bringing to 20 the number of verified results out of the 62 originally reported as tentative.

In nearly every case, concentrations were too low to have been verified by GC-MS even had it been available, but the rigorous determinative procedure—the use of highly dissimilar GC columns in conjunction with a column-adsorption separation and cleanup procedure, and a halogen specific detector—has provided identifications and measurements that possess a very high degree of validity.

Conclusions

The determinative method presented provides for the accurate identification and measurement of BCEE, BCIE, and o, m, and p DCB in extracts of aqueous samples, alone or in mixture. The method produces exceptionally reliable data and is an especially valuable tool in circumstances where GC-MS cannot be applied or is unavailable.

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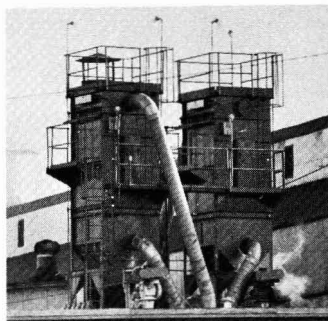
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CIRCLE 13 ON READER SERVICE CARD

INDUSTRY TRENDS

Waste Resources Corp. (Philadelphia, Pa.) said that there is a shareholder suit against it to try to prevent its merger into a subsidiary of Warner Co., that had been previously announced.

The **Dow Chemical Co.** (Midland, Mich.) requested that the EPA restrict registration of pentachlorophenol (PCP) to purified grades only, and said that purified PCP presents far less a hazard than does technical-grade PCP.

The **Kavag Division, Universal Oil Products G.m.b.H.** (W. Germany) has an order for what may be the world's largest thermal incinerators—four units, each 55 metric t—for large industrial complexes to be constructed in the U.S.S.R.

The **Gas Research Institute** (Chicago, Ill.) has applied to the Federal Power Commission to allow pipeline company members to recover payments to the institute from adjustments of rates charged to customers as a "reasonable and proper" operating cost.

Hittman Corp. (Columbia, Md.) is developing a Preventive Maintenance System for the pneumatic trash collection system of Jersey City, N. J. The system should alleviate many operational problems.

Envirotech/Chemico Air Pollution Control has been selected to furnish a coke-pushing emission control system for Bethlehem Steel Corp.'s No. 5 coke oven battery at Bethlehem, Pa.

Trans Union Corp. (Lincolnshire, Ill.) has reached agreement on an exchange ratio for acquisition of the remaining 15% of Ecodyne Corp. shares still outstanding. One share of Ecodyne would bring 0.45 share of Trans Union, subject to various approvals needed.

American Air Filter Co., Inc., announced that the last of six AAF-Elex electrostatic precipitators has been placed on line to control particulate emissions from coal-fired boilers at TVA's Johnsonville (Tenn.) Steam Plant.

Alten Corp. (Mountain View, Calif.) is supplying an automatically controlled solar heating/cooling system—believed to be the first for a privately financed commercial building—for Central California Savings & Loan, Auburn, Calif.

Alyeska Pipeline Service Co. (Anchorage, Alaska) has awarded a one-year maintenance contract for the southern district and the marine terminal at Valdez, to ACV Corp. (Anchorage).

An **FMC Corp.** engineer has reported that hydrogen peroxide is "highly effective" in controlling sulfides in oil refinery wastes while sour water strippers are shut down.

The **Environmental Sciences Division of Brown and Caldwell** is working on a major wastewater monitoring program for a new 0.34-mgd Anheuser-Busch brewery.

Utilities have been invited by **ERDA** to host a 4.8-MW fuel cell power plant. The fuel cell module will be built by **United Technologies, Corp.** Fuel cell delivery is expected in July 1978.

Nalco Environmental Sciences (Northbrook, Ill.) has been requested to measure and document ocean wave activity for Oceanic Contractors, Inc., to help India develop its first offshore oil field.

Neptune International Corp. will acquire Air Pollution Industries. According to the agreement, each AirPol shareholder will receive \$1.50/share, for a total cash consideration of \$870 000.

Arthur G. McKee & Co. was selected by ERDA to furnish technical assistance services in monitoring ERDA's \$80 million coal fluidized-bed combustion demonstration program.

C-E Power Systems and ERDA have signed a \$7.7 million contract for development, fabrication, and testing of a coal-fired industrial fluidized-bed boiler.

Fuller Co. (Cataqua, Pa.) has a \$1.6 million contract from St. Joe Minerals Corp.'s Zinc Smelting Division to recover lead dust generated through zinc smelting. Fuller will install recovery units capable of handling 532 000 acfm.

Reynolds Aluminum Recycling Co. collected a record 112 million lb of aluminum during 1976, and paid the public almost \$17 million. Reynolds now pays 17¢/lb for aluminum.

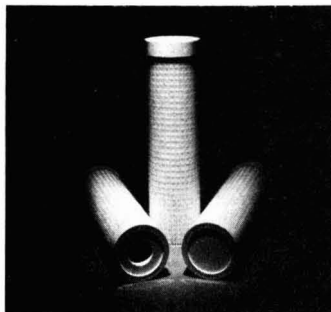
The **Carborundum Co.** (Niagara Falls, N.Y.) has recently signed a \$38 193 contract with Hittman Associates, Inc. for analysis of toxic pollutants in wastes from steam generating plants located throughout the U.S.

Ionics, Inc. (Watertown, Mass.) has a \$600 000 contract to design and construct a 100 000-gpd seawater desalting plant, using electrodialysis technology for the U.S. Department of the Interior's Office of Water research and technology.

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Fluidized bath

New fluidized bath, Model SP-54, is a bed of aluminum oxide particles fluidized by low-pressure air. Maximum operating temperature is 600 °C. Has application in uniform heating of coal slurries for liquefaction with no clogging of tubes. Excellent heat-transfer medium. System is 24 in. in diameter and 36 in. deep, and has other industrial uses. Techne **120**

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Chemical feed system

Proportional chemical feed system uses principle of proportional feeding by direct injection into main stream, with feeding metering by pulse generator and flowmeter installed in main line. System can handle solutions and slurries. The Dymax Group **124**

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New liquid cationic polyelectrolyte acts as a primary coagulant, coagulant aid, and sludge conditioner. Polymer is highly effective in centrifugation and vacuum filtration; it increases efficiency of clarifiers, thickeners, and sludge drying beds. Effective over wide pH range for many municipal and industrial sludges. Dearborn Chemical (U.S.) **125**

Drip watering kits

These distribute water slowly and precisely to an individual plant at 20–40 gph. This maintains soil oxygen, reduces water use by more than 50%, reduces plant stress, cuts weed growth, and increases yields. Flow-control valves and anti-siphon devices are included. GRO-MOR **126**

Control valves

Complete line of compact, bellows-sealed regulating and shut-off valves can contain hazardous, toxic, or expensive fluids in applications such as high-purity systems, high or low temperature systems, and high vacuum. NUPRO **127**

Clamps, hooks

Clamps, hooks, snap hooks, toggles, and the like, are made of stainless steel for use in pollution treatment equipment, aerators, and maintenance. They withstand severe and corrosive environments. Transmar **128**

Portable flowmeter

Compact flowmeter measures industrial effluent; handles discharge rates as high as 34 mgd. Reads in U.S., Imperial, or metric units, and reads true flow even when effluent channel width is non-standard. No electrical contact with effluent; no moving parts. Quantum Science **129**

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NEW LITERATURE

Liquid level gauging. Application Guide AG-2 presents information about unique level-gauging products and their effective application. Metritape, Inc. **153**

Corrosion protection. Bulletin T676 tells how to achieve longer boiler life, higher operating efficiency, and lower maintenance costs by eliminating corrosion and pitting during down-time. Metropolitan Refining Co., Inc. **154**

Analytical aids. Pub. No. 43-5952-5747 describes supports, phases, packings, test mixes, and other items for gas and liquid chromatographs. Hewlett-Packard **155**

Filter cartridges. "The HDC Filter Guide" fully describes pleated all-polypropylene filter cartridges. Applications are electroplating solutions, makeup and rinse water, and many others. Pall Corp. **156**

Oil recovery. Bulletin PC-1 tells how treatment of oily wastewater and wastewater emulsions improve oil-water separation, recover oil, minimize sludge

volume, and improve effluent quality. Nalco Chemical Co. **157**

Carcinogenesis. NIOSH Occupational Carcinogenesis Program, First Year Report. HEW Publication No. (NIOSH) 77-111. Single copies. Publications Dissemination, NIOSH, 4676 Columbia Parkway, Cincinnati, Ohio 45226 (write direct).

Soil conservation. "More Than A Green Thumb." Discusses soil and water conservation. Kansas Association of Conservation Districts, 1101 Orleans, Topeka, Kans. 66604 (write direct).

Resource issues. Booklet, "What Mining Means to Americans," explains how the U.S. is becoming dangerously dependent upon foreign sources for resource supplies. American Mining Congress, Ring Building, Washington, D.C. 20036 (write direct).

Waste management. Report, "Waste Management in OECD Countries." OECD News Division, 2, rue André Pascal, 75775 Paris Cedex 16, France (write direct).

Solar energy. Feature article has title, "Israel Moves Toward a New Solar Society." Consulate General of Israel, 800 Second Ave., New York, N.Y. 10017 (write direct).

Food supply protection. Report CED-77-30. "To Protect Tomorrow's Food Supply, Soil Conservation Needs Priority Attention." Report to the Congress. Comptroller General of the United States, Washington, D.C. 20548 (write direct).

Land disposal pollution. Technical Report No. 89 is entitled, "Nitrogen and Metal Contamination of Natural Waters from Sewage Sludge Disposal on Land." Water Resources Research Center, Purdue University, West Lafayette, Ind. 47907 (write direct).

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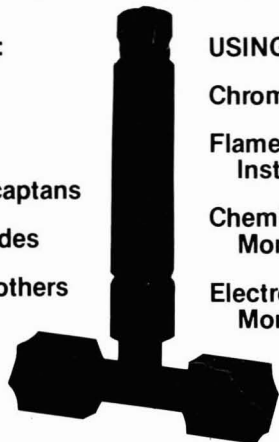
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Energy from the Wind/Supplement I. Barbara L. Burke and Robert N. Meroney. Colorado State University, Engineering Research Center, Foothills Campus, Fort Collins, Colo. 80523. 1977. \$10, loose-leaf.

Prepared in the same format as the basic volume, the supplement contains over 1100 new references to books, conference proceedings, articles, and technical reports on wind power; most of these new references were published between 1973-77. A cumulative author and subject index is included.

Proceedings of the IOI's Forum on Ozone Disinfection. International Ozone Institute, Merrill Lane-Skytop Complex, Syracuse, N.Y. 13210. 1977. \$30, hard cover.

This collection of papers from the June 1976 meeting held in Chicago, Ill., covers such topics as wastewater disinfection and ozone/UV oxidation of chlorinated compounds in water. The volume will be useful to engineers, managers, chemists and health effects personnel.

Deep Well Injection of Industrial Wastes: Government Controls and Legal Constraints. William R. Walker and William E.

Cox. 176 pages. Virginia Water Resources Research Center, 225 Norris Hall, VPI & SU, Blacksburg, Va. 24061. 1977. \$8, paper.

With more stringent water quality requirements, the disposal of liquid wastes is becoming more troublesome. Deep-well injection as a disposal method is economically and technically feasible, but environmental and legal and institutional problems have been cited. The book discusses the ramifications of these various problems.

Basic Industrial Hygiene. Richard S. Brief. 245 pages. American Industrial Hygiene Association, 66 S. Miller Rd., Akron, Ohio 44313. 1977. \$10.75, paper.

This is a basic training manual on the principles and procedures of industrial hygiene. It is suited for plant managers and engineering personnel who are not professional industrial hygienists.

Proceedings of the Symposium on Sources, Effects and Sinks of Hydrocarbons in the Aquatic Environment. 582 pages. American Institute of Biological Sciences, 1401 Wilson Blvd., Arlington, Va. 22209. \$5, paper.

The Proceedings, in effect, is a review of current knowledge on the cycling of hydrocarbons in aquatic environments. Especially covered are the behavioral, physiological and morphological effects of these compounds on aquatic species.

Air Pollution from Pesticides and Agricultural Processes. Robert E. Lee, Jr., Ed. 265 pages. CRC Press, Inc., 18901 Cranwood Parkway, Cleveland, Ohio 44128. 1977. \$49.95, hard cover.

To assess the environmental impact of man's agricultural activities, this monograph speaks to the chemical and physical ramifications of pesticide sources, concentration, transport, atmospheric transformations, and toxicity. Analytical procedures and techniques are documented, and available legislative controls are assessed.

Toxic Substances Law and Regulations 1977. 208 pages. Government Institutes, Inc., 4733 Bethesda Ave., N.W., Washington, D.C. 20014. 1977. \$25, paper.

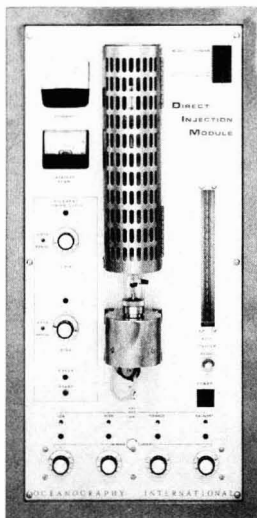
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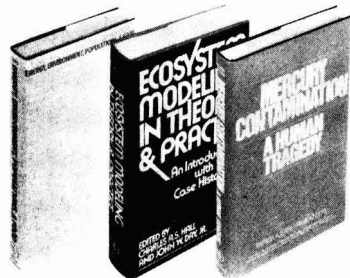
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An Assessment of Environmental Regulation. Engineering Foundation
Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

July 17-22 Rindge, N.H.
Critique of the OSHA Program. Engineering Foundation
Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

July 24-27 Seattle, Wash.
Nuclear Power Financial Considerations. Atomic Industrial Forum, Inc.
Write: Atomic Industrial Forum, Inc., Conference Office, 7101 Wisconsin Ave., N.W., Washington, D.C. 20014

July 24-29 Geneva, N.Y.
1977 Symposium for Innovation in Measurement Science. Instrument Society of America
Environmental topics will be discussed.
Write: Peter Vestal, Instrument Society of America, 400 Stanwix St., Pittsburgh, Pa. 15222

July 31-August 1 Rindge, N.H.
Clean Combustion of Coal. Engineering Foundation
Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 1-5 Schenectady, N.Y.
Fourth National Conference on the Effects of Energy Constraints on Transportation Systems. Union College and the Energy Research and Development Administration
Write: Office of Graduate Studies and Continuing Education, Wells House, 1 Union Ave., Union College, Schenectady, N.Y. 12308

August 1-6 Boulder, Colo.
Conference on Air Quality Meteorology and Atmospheric Ozone. American Society for Testing and Materials/Committee D-22 on Methods of Sampling and Analysis of Atmospheres
Write: Alvin L. Morris, president, Ambient Analysis, Inc., P.O. Box 4056, Boulder, Colo. 80306

August 3-5 Denver, Colo.
26th Annual Conference on Applications of X-Ray Analysis. University of Denver and Denver Research Institute
Write: Mrs. Mildred Cain, Denver Research Institute, University of Denver, Denver, Colo. 80208

August 8-9 Lewisburg, Pa.
Ninth Mid-Atlantic Industrial Waste Conference. Bucknell University, University of Delaware, Drexel University,

Johns Hopkins University and Pennsylvania State University
Write: Dr. Michael D. LaGrega, Civil Engineering Department, Bucknell University, Lewisburg, Pa. 17837

August 10-12 College Station, Tex.
Coastal and Ocean Engineering; Environmental Engineering in the Coastal Zone. Texas A&M University and American Society of Civil Engineers/Brazos County Branch
Write: American Society of Civil Engineers, 345 E. 47th St., New York, N.Y. 10017

August 14-19 Henniker, N.H.
Considerations for an Expanded Coal Industry. Engineering Foundation
Write: Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

August 15-19 New Hampton, N.H.
Environmental Sciences: Air. Gordon Research Conferences
Write: Alexander M. Cruickshank, director, Gordon Research Conferences, Pastore Chemical Laboratory, University of Rhode Island, Kingston, R.I. 02881

August 18-19 Washington, D.C.
Energy Conservation in Industrial Plants. New York University of Continuing Education
Write: Ms. Heidi E. Kaplan, Information Services Manager, New York Management Center, Dept. 14NR, 360 Lexington Ave., New York, N.Y. 10017

August 21 East Lansing, Mich.
Environmental Aspects of Industrial Fermentation Processes. Society for Industrial Microbiology
Write: Ms. Ann Kulback, Society for Industrial Microbiology, c/o American Institute of Biological Sciences, 1401 Wilson Boulevard, Arlington, Va. 22209

August 21-26 East Lansing, Mich.
Annual Meeting of the American Institute of Biological Sciences. American Institute of Biological Science
Topics will include the ecological effects of power production, and biological control of pest organisms. *Write:* Ms. Carol H. Chisolm, coordinator of meetings, American Institute of Biological Sciences, 1401 Wilson Blvd., Arlington, Va. 22209

August 22-23 Washington, D.C.
The Solar Energy Business: Opportunities and Outlook. The Energy Bureau
Write: Robert W. Nash, Executive Director, The Energy Bureau, 101 Park Ave., New York, N.Y. 10017

August 22-24 Durham, N.H.
International Biannual Workshop on Nitrosamines. University of New Hampshire
Write: Dr. Robert E. Lyle, Dept. of Chemistry, North Texas State University, Denton, Tex. 76203

August 27-31 Boston, Mass.
Second Conference on Light Rail Transit. Transportation Research Board
Write: W. Campbell Graeb, Engineer of Public Transportation, Transportation Research Board, 2010 Constitution Ave., N.W., Washington, D.C. 20418

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174th American Chemical Society National Meeting. American Chemical Society

Write: A. T. Winstead, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036

August 28–September 2 Washington, D.C.

Twelfth Intersociety Energy Conversion Engineering Conference. American Nuclear Society, American Chemical Society and others

Write: Glen A. Graves, general chairman, National Science Foundation, 1800 G St., N.W., Washington, D.C. 20550

August 29–September 1 New Orleans, La.

Second Symposium on Stationary Source Combustion. U.S. Environmental Protection Agency/Industrial Environmental Research Laboratory-RTP

Write: Betty Farley, symposium coordinator, Acurex Corp./Aerotherm Division, 485 Clyde Ave., Mt. View, Calif. 94042

August 29–September 2 Berkeley, Calif.

Fifth Annual Conference on Environmental Issues in Electric Power Generation. University of California—Berkeley/

College of Engineering and Continuing Education in Engineering

Advance registration is required. *Write:* Continuing Education in Engineering, University of California Extension, 2223 Fulton St., Berkeley, Calif. 94720

August 31–September 2 South Lake Tahoe, Nev.

15th Annual Seminar and Equipment Show. Governmental Refuse Collection and Disposal Association

The exhibit will display a wide range of solid waste systems. *Write:* Bob Lawrence, City of San Leandro, 835 E. 14th St., San Leandro, Calif. 94577

Courses

July 9–August 27 Washington, D.C.
Practical Energy Conservation Techniques—Commercial Buildings Application. George Washington University

Course meets for 8 Saturday morning sessions. Fee: \$170. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, D.C. 20052

July 17–30 Fort Collins, Colo.
Eighth Westinghouse International School of Environmental Management. Westinghouse Electric Cooperation/Environmental Systems Department

Fee: \$2900. *Write:* Dr. James H. Wright, general manager, WESD, P.O. Box 1899, Pittsburgh, Pa. 15230

July 25–29 Nashville, Tenn.
Pollution Control: Meeting EPA and OSHA Standards Through IR and GC Techniques. Fisk Institute/Fisk University

Fee: \$250. *Write:* Director, Fisk Institute, Box 8, Fisk University, Nashville, Tenn. 37203

July 26–28 New Brunswick, N.J.
Community Noise Control. Rutgers/Cook College Dept. of Environmental Science

Fee: \$150. *Write:* Donald A. Deieso, Instructor, Dept. of Environmental Science, Rutgers University, Cook College, P.O. Box 231, New Brunswick, N.J. 08903

August 2–4 New Brunswick, N.J.
Ambient Air Monitoring. Rutgers University/Cook College

Fee: \$165. *Write:* Robert E. Hague, Instructor, Dept. of Environmental Science, Rutgers University, Cook College, P.O. Box 231, New Brunswick, N.J. 08903

Call for Papers

July 15 deadline
Symposium on Advanced Ozone Technology. International Ozone Institute

Conference will be held November 2–4, 1977, at Toronto, Ontario, Canada. *Write:* Dr. Ahron Netzer, Head, Physical Chemical Processes, Wastewater Technology Center, Canadian Center for Inland Water, P.O. Box 5050, Burlington, Ontario, Canada

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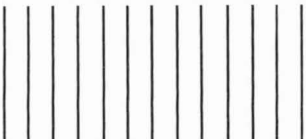
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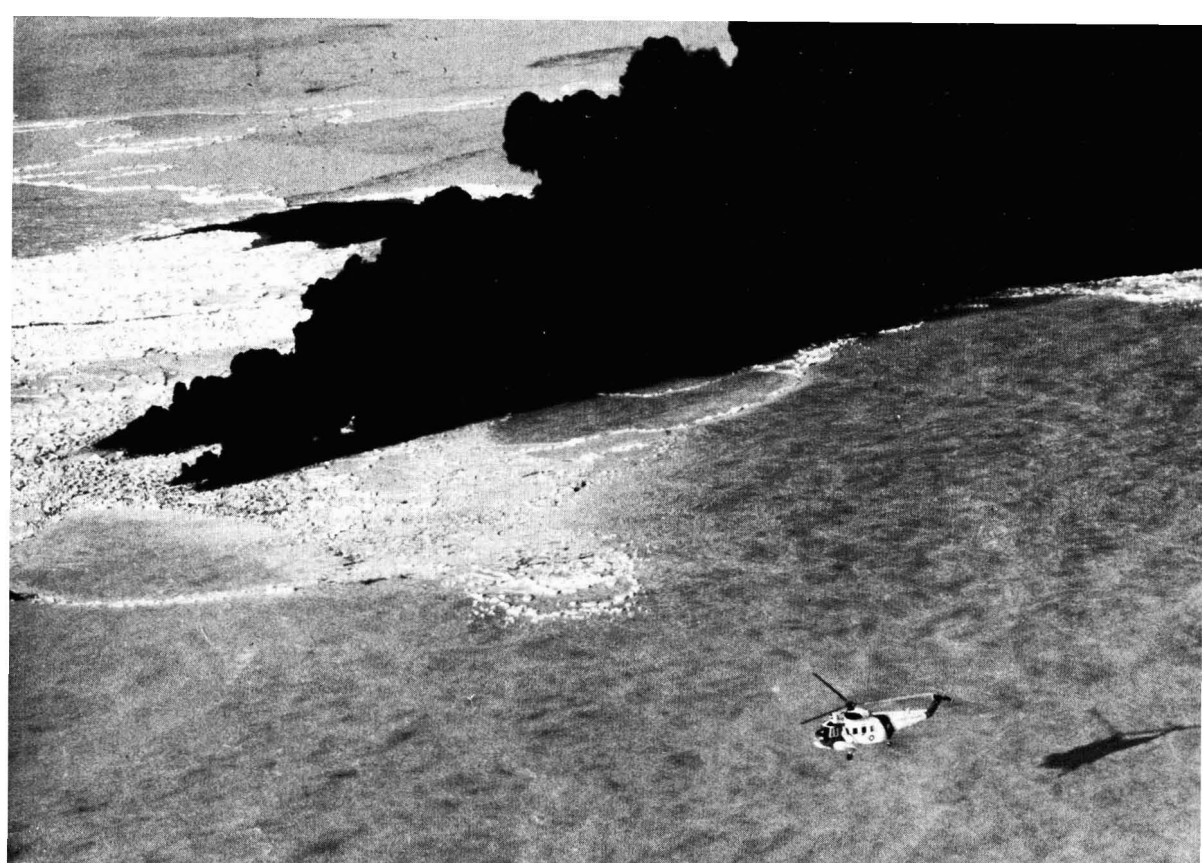
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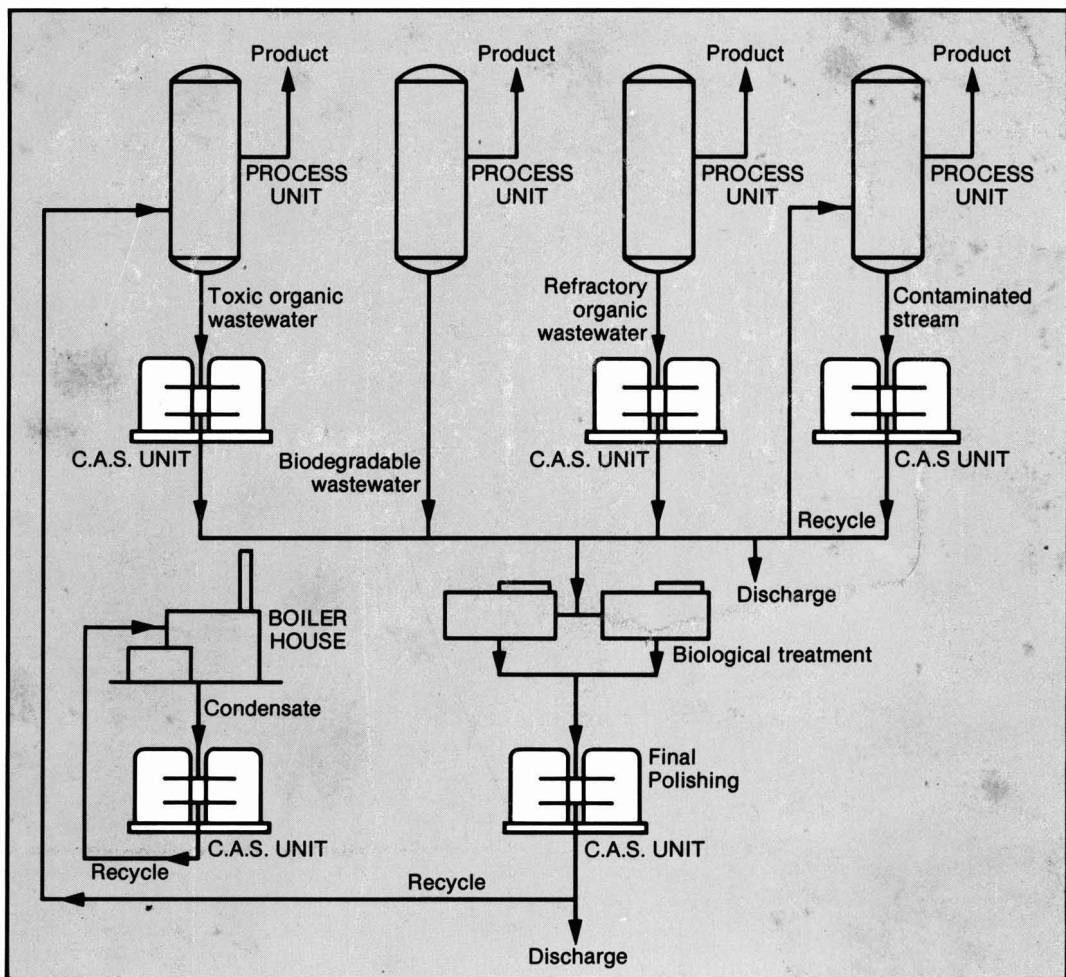
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