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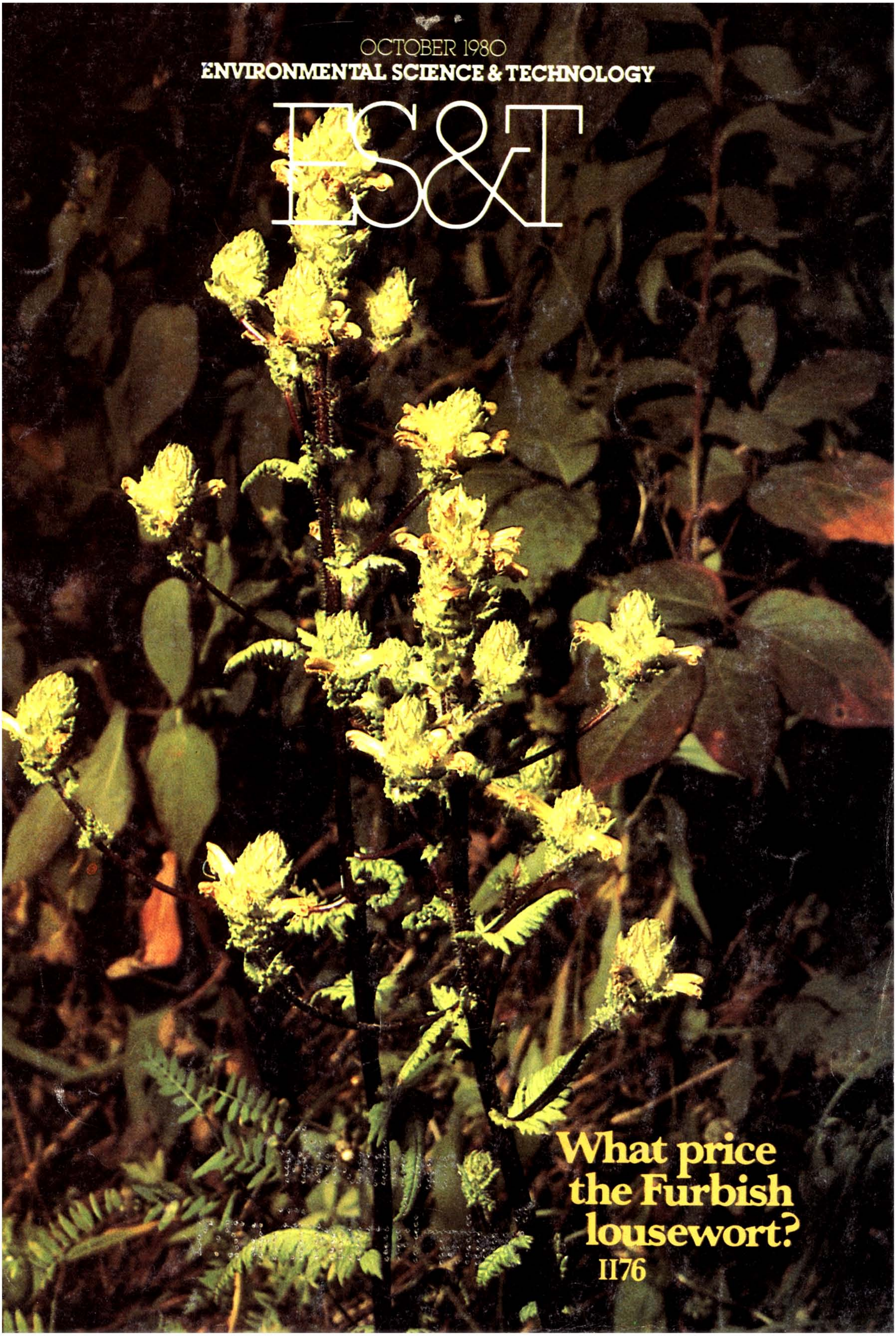
ES&T



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1176

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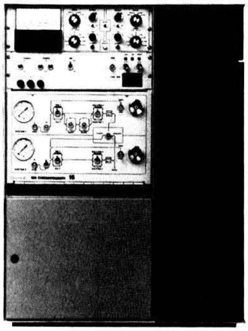

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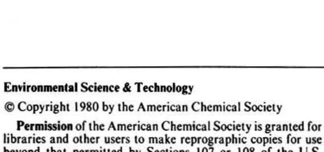

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* To whom correspondence should be addressed.
■ This article contains supplementary material in microform. See ordering instructions at end of paper.

## DEPARTMENTS

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ES&T
EDITORIAL

# Clean, not healthy

Today's relatively antienvironmental mood contains the bothersome notion that our national well-being, in terms of productivity, and environmental quality are dichotomous. Plenty of evidence reinforces this mood: widespread economic uncertainty, current congressional efforts to scuttle environmental legislation, campaign rhetoric regarding downward trends in U.S. productivity, and suggestions in the popular press that declines in the U.S. work ethic are somehow related to the shackling of our industry by federal regulation. Oddly, even the absence of proper scientific tools or reliable scientific data is cited as an additional reason for environmental retreat.

Clearly, the notions of environmental regulation and industrial productivity are related, perhaps even antagonistic where useful by-product options do not exist or inflation/unemployment effects prevail. In reality, a continuum of options for decision making exists, and the tendency to dichotomize environment and production must be seen as a poor rationalization of generalized anxiety. The requirement for unassailable scientific proof of harm before regulation and the elimination or substantial weakening of present environmental legislation are acts of choice consistent with our traditional value system which prizes industrial output and discounts the rights of future generations (and the future generally). Unfortunately, this choice places present technology in the outrageous position of supporting increased contamination in order to afford the cost of cleaning up.

That's the point. We have chosen, so far, a clean environment, not necessarily a healthful one. There is some tyranny of words here, and the tendency to dichotomize these issues is encouraged by ambiguity in word pairs such as "clean/healthful" and "cost/benefit."

Actual implementation of water legislation has improved scenic/aesthetic features of waterways and probably has made them safer for fish. No serious progress has been made with regulation of human toxicants. In air quality legislation, we have focused on urban smog and ignored global threats from carbon dioxide. We have many more laws and regulations than we had 10 years ago and the estimated costs of these are not trivial. But we have bought *clean,* not *healthy.*

Cost and benefit are essentially defined by this perception. The option for a healthful environment involves quite different choices and portends economic costs and adjustments to our lifestyle which we as a society are currently not willing to make on the basis of potential hazards.

In this sense, the issues of environmental health and industrial productivity are, at least presently, dichotomous. We do not believe that the costs of stopping protective policies that are ultimately shown to be unnecessary are inherently less than the costs of potential suffering. This mood is reflected in most current efforts to soften present laws, many of which have differing definitions of "hazards," "degree of protection," or "burden of proof."

So our traditional decision-making system is working. It is reducing complex issues involving the public weal to traditional terms (cleanliness) with traditional results (don't tread on me or my pocketbook). There is comfort in tradition, but unfortunately very little security, as we have not faced up to the ethical issues of public health protection.

R F Christman

# ES&T
# LETTERS

### July editorial

Dear Sir: It was with great interest that I read the editorial "The protection quandary" in the July issue of *ES&T,* for I too wish to be protected from harm. However, if I extend the thoughts expressed by the editor in the opening paragraphs, the best of all possible worlds would be one in which there were no facts and I would *know* nothing, *believe* nothing, and have no *worries.* This state of blissful ignorance is in keeping with the belief that the "federal Goliath" can protect me "from any contaminant that *may have* an adverse effect on my health."

I *know* that there are possible adverse effects, not only from contaminants, but also from consumption of many common chemicals. It is well-known that excessive consumption of any chemical, even sodium chloride or sucrose, will provide undesirable effects. The undesirable effects can be controlled by regulation of dosage, because for all materials there is a dose–response relationship which must be considered in evaluating the potential degree of adverse effect.

Suggesting that EPA should offer protection "from any contaminant that *may have* any adverse effect on my health" is asking for the impossible. It is impossible to prove absolute safety. It is possible to make risk assessments that are based on both exposure and toxicity.

The editorial calls for studying the hazards "continuously." Neither the manpower, financial resources, nor the need exist to study all potential hazards "continuously." It is, of course, prudent to reevaluate risk judgments whenever circumstances indicate such an action. It would not be prudent, however, to study all hazards on a continuous basis.

It would be well to be guided by assessment approaches being developed by such bodies as OECD, EEC, and EPA for the evaluation of human and environmental safety of chemicals. I do not want "some specialists" who believe that some hazard might exist to forestall the introduction of a new chemical until *all* questions have been answered. I do not want those "specialists" to have the power to decide to remove man-made (and natural) chemicals from the environment completely (i.e., zero residual) until all questions have been answered.

It would seem more reasonable for these issues to be settled on the basis of scientific facts which are used by open-minded scientists who can deliberate and decide whether the risks involved are acceptable or unacceptable. In this way society would have the benefit of chemicals that are judged to be acceptable, based upon a sufficient amount of scientific data which deal with the particular questions raised by each chemical. The potential for hazard needs to be addressed with the best resources available, but the probability of injury needs to be the factor which controls decision making.

As for me, I *know* that chloroform (and other chemicals) are in my drinking water; I *know* that the relevant chemistry of chloroform (and other chemicals) is complex; I *know* that chloroform (and other chemicals) can be hazardous; but I *don't worry* about such matters without factoring in the amounts of the chemical which might be ingested and the reasons for having that chemical in the environment. One should worry only when the information is not available to make a risk assessment.

**Herbert E. Allen**
Professor
Pritzker Dept. of Environmental
Engineering
Illinois Institute of Technology
Chicago, Ill. 60616

### Bioenergy effects

Dear Sir: Your article on the environmental effects of biomass use ("Bioenergy: the lesson of wood burning?" *ES&T,* July 1980, p. 769) clearly presents some important concerns about the use of firewood for residential heating. In generalizing from residential wood combustion to other biomass energy options, however, your article presents a very misleading picture.

As your article states, the most serious environmental problem with the direct combustion of wood is particulate emissions. The formation of particles is especially high in decentralized applications (in which incomplete combustion conditions are preferred), and also particularly hard to control in such cases. Thus when it comes to burning wood, the decentralized systems are indeed the dirtiest. But is the same true for converting biomass materials to liquid and gaseous fuels, or for producing biomass residues?

Biomass can be converted to synfuels via thermochemical or biological pathways. Most thermochemical conversion technologies are economically infeasible at small scale, so scale is not an issue in assessing their environmental impacts. The bioconversion technologies, which use microorganisms to convert biomass into methane or ethanol, are practical for a broad range of system scales. In many cases, small-scale operations may lead to significantly reduced waste (or by-product) handling problems for these technologies.

The waste sludge resulting from the biogasification of biomass is rich in nutrient and soil-building values. In applying the sludge to agricultural fields it is important to disperse it over a wide area, preferably over the entire area that produced the original biomass feedstock. This is recommended in order to avoid a buildup of toxic materials in fields treated with sludge. Small-scale conversion operations clearly help to avoid such problems by facilitating adequate sludge redispersal. Similarly, stillage handling after alcohol fermentation may be simpler

*(continued on page 1158)*

and cheaper for small-scale conversion systems where the stillage needs only minimal drying before it can be used.

The most serious environmental liabilities associated with the use of most forms of biomass are the environmental costs of producing the biomass residues. Collecting crop residues that are currently returned to the soil will exacerbate some of the environmental problems currently plaguing agriculture, such as erosion and the loss of humus and nutrients from agricultural soils. Intensive production of biomass will have all of the environmental liabilities of intensive agriculture. It is difficult to relate the scale of a biomass farm to its environmental costs, except that more dispersed operations will allow the environment's natural defenses to function more effectively. It is interesting to note that some of the adverse impacts of collecting field wastes and of producing intensively grown biomass could be substantially mitigated by coupling biomass production operations with decentralized biogasification facilities.

When it comes to utilizing standing-forest biomass for energy, large-scale users will exert a tremendous pressure for high-density harvesting of wood, probably by clear cutting. Decentralized users, by contrast, may be able to harvest their wood by selective harvesting operations. Selective cutting is considerably more environmentally benign, and can even be used to upgrade the timber quality on many woodlots.

Thus while wood combustion produces substantially greater combustion emissions when used at small-scale decentralized facilities, it cannot be generalized that the environmental liabilities of biomass energy utilization are greater when decentralized systems are used. In many cases, the opposite is true. Biomass energy options span a broad range of technologies and applications, each with its own unique environmental characteristics. The scale of a particular biomass energy enterprise is not indicative of its environmental impact.

**Gregory Morris**
Energy and Resources Group
University of California
Berkeley, Calif. 94720

**Corrections**

November 1979, p. 1351, col. 3. The quantity "3.8 × $10^8$ metric tons/y" should read "3.8 × $10^6$ metric tons/t" (21st line from the top). Also, the phrase "18–78 grams of $SO_6^{-2}$/ha/y" should read "18–78 kg/ha/y" (42nd line from top).

November 1979, p. 1353, Figure 2. "Sulfate loading to lake water (g $SO_4^{-2}$/ha/y)" should read "Sulfate loading to lake water (kg $SO_4^{-2}$/ha/y)."

August 1980, p. 885. The name of the first author of the correspondence entitled "Accumulation of polychlorinated biphenyls in surficial Lake Superior sediments" is incorrectly reported. The correct name is Roger R. Greenburg.

August 1980, p. 904. A study of non-point-source particles in the atmosphere was incorrectly attributed to John Cooper and co-workers at the Oregon Graduate Center. The work was performed by Douglas W. Cooper and co-workers at the Harvard University School of Public Health.


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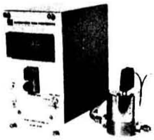

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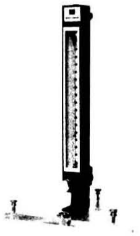

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## Acrylic Purge Meters, 7260 Series

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## 150mm Four Tube Flowmeter Units, 7400 Series

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# CURRENTS

## INTERNATIONAL

**Canada has passed a new Transportation of Dangerous Goods Act** which is aimed at controlling international and interprovincial shipment of hazardous wastes. Canadian Environment Minister John Roberts expressed hopes that eventually a nationwide manifest system would be developed to assist federal and provincial governments in the overall management of hazardous wastes. Also, Canada and the U.S. signed a Memorandum of Intent for cooperative efforts in dealing with acid rain and other forms of air pollution crossing the Canada-U.S. border. These efforts will entail both regulatory and scientific research tasks.

## WASHINGTON

**Government spending on pollution control increased to $11.9 billion** in 1977-78, the last year for which figures are available, the U.S. Bureau of the Census reported. Water quality control accounted for $8 billion of the total, land quality control for $3 billion, and air quality control for $0.4 billion. The bulk of the spending, $10.8 billion, was at the state and local level, though this figure includes $4 billion in federal grants-in-aid. The Census report also found that revenues from current sewage charges at the local level amounted to $2.8 billion, compared with $6.8 billion in direct expenditures.

**The EPA is studying the risks and benefits of the fungicide captan.** Evidence suggests that captan is carcinogenic and mutagenic; the investigation will determine whether the risks to farm workers and consumers posed by its use are severe enough—in relation to its benefits—to warrant a restriction or ban on the substance. Captan is widely used to protect fruits and vegetables from fungi. Agricultural workers may be exposed to high concentrations if they are present in fields during or after spraying.

**A reduction in the 1-h CO standard has been proposed by the EPA.** The action would set the limit at 25 ppm, down from the current 35 ppm. The proposed change is based on revised criteria which take into account the effect of CO on moderately exercising "sensitive" individuals. The original criteria did not take into consideration the effect of exercise. Also proposed is a change from the "deterministic" standard that calls for no more than one exceedence per year. The new standard would be enforced on the basis of "expected exceedences"; under this method, data from more than one year would be considered, to allow for statistical fluctuations that could, for example, result in 2 or 3 exceedences in one year but no exceedences in 2 other years. No change was proposed in the 8-h standard, which will remain at 9 ppm. Comments must be filed by Nov. 10. The complete proposal was published in the *Federal Register*, Aug. 18, 1980 (45 *FR* 55066).

*Sen. Tsongas (D-Mass.)*

**The Senate has struck a compromise on a bill to settle the fate of Alaska's federal lands,** but differences must still be worked out with the House, which has already passed its own version of the bill. The compromise was quickly approved after Sen. Mike Gravel (D-Alaska) lost a key test vote and gave up his attempts to delay action on the matter. The compromise was introduced by Sen. Paul Tsongas (D-Mass.) as a substitute to a much more pro-development bill reported out by the Senate Energy Committee. Tsongas's version calls for 54 million acres to be set aside as wildlife refuges, would turn over 60 million acres to Alaska, and would allow exploration for oil and gas in the Arctic coastal plain. The House version sets aside 80 million acres for refuges and forbids any oil or gas exploration in the coastal plain.

**The National Commission on Air Quality is studying the effects of increased coal use.** "This study will provide needed comparative information on the cost-efficiency and environmental judiciousness of several national energy strategies," said research committee chairman Edwin D. Dodd, who is also chairman of the board of Owens-Illinois, Inc. "The commission hopes Congress will find this information useful in drawing up a balance sheet on the pros and cons of potential energy plans." In addition to examining the air quality effects of coal use, the study will attempt to determine the extent to which Clean Air Act regulations will affect the penetration of coal into the energy market.

**State management of environmental programs is often impeded on the federal level, a GAO study has found.** State environmental officials told the General Accounting Office that late issuance of federal regulations is "the single greatest obstacle to the management of their programs." They also cited inflexible regulations, detailed grant conditions, and mandatory federal policy "guidance" as obstacles to effective implementation. The GAO recommended that the EPA establish a formal program of consultation to seek the states' views before action affecting state implementation is taken, and that joint EPA–state committees for each program be established to identify problem areas.

## STATES

**Connecticut may sue the EPA over its decision to permit use of high-sulfur oil in New York City** utility boilers. ConEd was granted special permission to burn the 1.5%-S fuel at 3 plants in Manhattan for 1 y.

*CT DEP Commissioner Pac*

The test will determine whether ConEd will be allowed to switch to coal at these sites. Connecticut's Department of Environmental Protection charges that the EPA failed to follow proper procedures in granting the variance; in particular, the EPA failed to hold a hearing requested by Connecticut and which the state claims is required by the Clean Air Act before a variance that has the potential to cause an interstate air pollution problem may be granted. DEP Commissioner Stanley J. Pac has requested EPA Administrator Costle to stay the variance. "Failure to immediately stay your final action will force the state of Connecticut to seek immediate judicial relief," he wrote in a letter to Costle.

**California faces a loss of $850 million in federal funds after failing to adopt automobile inspection** and maintenance legislation demanded by the EPA. The EPA took formal action to cut off the federal highway and sewer construction assistance Sept. 2, the day after the CA legislature failed to meet yet another deadline for passage of the needed bill. The cutoff is not likely to go into effect before the end of the year, however, and there are indications that the legislature will act on the unpopular measure once the November elections are over with. The state may also mount a legal challenge to the EPA's action. The EPA is requiring mandatory inspection and maintenance programs for automobile emission-control equipment in regions that appear to be unable to meet ambient air standards by 1982.

**The states of the Ohio River Valley participated during September in a fish-sampling program** aimed at measuring progress in water pollution control. Samples of fish flesh are being analyzed by the U.S. Food and Drug Administration for trace metals and selected organics, including commonly used pesticides. Fish population studies were also carried out and should provide an integrated measure of pollution, since certain species thrive in polluted water while others are sensitive to pollution. Population data will be available shortly; the tissue analyses will be completed early next year.

**Pennsylvania has protested the EPA's plan to impose large fines** on firms not in compliance with the Clean Air Act by Jan. 1. Under new rules, the EPA can levy a penalty equal to the cost of needed pollution control equipment that was not installed. In a letter to EPA Administrator Costle, PA Secretary of Environmental Resources Clifford L. Jones wrote, "I am gravely concerned that the imposition of large financial penalties may, in fact, interfere with ongoing control activities and could divert resources from productive control effort into legalistic posturing. . . . Regulatory actions such as this can severely damage our efforts to forge links to industry and build support for a strong national Clean Air Program."

## MONITORING

**Computer models for predicting air pollutant concentrations** in mountainous terrain are to be developed under a $700 000 contract that EPA awarded to Environmental Research and Technology, Inc. (Concord, MA). Models will be developed through comprehensive studies conducted in the field, and will be supplemented by laboratory experiments with scaled physical models. One important aspect is to use "realistic" laboratory simulations of field experiments, followed by laboratory extensions of field data, to demonstrate the practical usefulness of laboratory work in air pollution modeling.

## TECHNOLOGY

**More emphasis will be placed on passive solar energy**—the type that uses no active collectors and associated equipment—through a pro-

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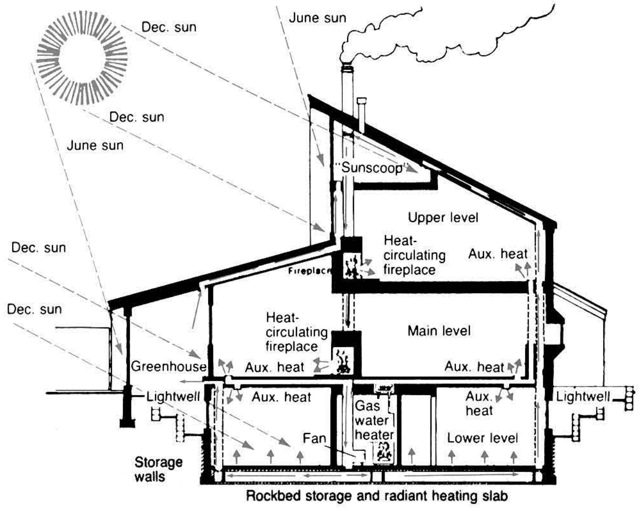

**Source:** Design by Downing Leach and Associates gram of housing construction in Metro Denver, CO, sponsored by the Colorado Office of Energy Conservation and others. Houses will range about 1000–2700 ft$^2$, and $55 000–129 000, with five for $60 000. They will feature energy conservation designs, passive solar heating/cooling, and daylighting. The Solar Energy Research Institute (Golden, CO) will provide prototype funding, and numerous technical, review, and publicity services. In selected instances, state financing at less than 9% annual simple interest may be available for prospective buyers.

**PCBs may be rendered harmless with sodium naphthalide,** which would strip chlorine away from PCB molecules and "salt out" sodium chloride. Another product would be a sludgelike polymer that could be filtered out and burned in a conventional incinerator, according to Dane Parker of Goodyear Tire & Rubber Co. (Akron, OH), who developed this process. The sodium compound might be used, for instance, to decontaminate valuable heat-transfer liquids, now worth more than $10/gal. Bringing down PCB concentrations to 10 ppm—EPA's standard is 50 ppm—would allow approved land disposal or conventional incineration. Otherwise, elaborate, very high temperature burning will be required.

**Demonstration of flue gas desulfurization with aqueous carbonate** will be a $55-million project at a Niagara Mohawk power plant (100 MW) in Tonawanda, NY. It will feature production of elemental sulfur as a by-product. This alleviates the need for costly, unwieldy scrubber sludge management and disposal, especially in view of increasingly stringent waste regulations and decreasingly available disposal sites. EPA is contributing $9.5 million to the project.

**Repelling cotton boll weevils with far less synthetic chemical pesticides** may be possible with the methyl ester of alpha-eleostearic acid, a derivative of tung tree oil. This development arises from many years of research by U.S. Dept. of Agriculture (USDA) scientist Martin Jacobson, who noted that tung oil is now commercially available for about $10/gal. Thus, this approach need not be inordinately costly. USDA's Boll Weevil Research Laboratory in Mississippi plans further tests of the tung oil derivative on cotton buds in U.S. and Mexican fields.

**Ultraviolet rays may be a nemesis for fiercely toxic dioxin.** First, the dioxin is solvent-extracted from chemical waste in batches. Normally, about 1500 gal of solvent would handle 160-gal waste batches. The dioxin solution is then exposed to UV rays for 20–40 h to cleave the dioxin molecules. The process was developed by IT Enviroscience (Knoxville, TN) and tried by Syntex Agribusiness on 4300 gal of waste. EPA estimated the cost for that cleanup at $2–3 million, but Syntex said that this figure was overstated. However, both companies are not giving out much information on the results of this effort.

## INDUSTRY

**One of the better approaches to meeting Clean Water Act goals** would be to establish the degree of water quality that provides for protection and propagation of fish, shellfish, and wildlife in U.S. waters. That is what Kenneth Macek, manager of EG&G Bionomics (Wareham, MA), suggested to a House subcommittee. He observed that valid, reproducible laboratory techniques exist for measuring, estimating, and predicting acute and chronic toxicity of chemicals as they affect aquatic organisms. He also recommended that these techniques be used on an "effluent-by-effluent" basis, since a "pollutant-by-pollutant" approach could be so time-consuming and costly and would defeat the purpose.

*Macek of EG&G Bionomics*

**A $50-million continuing nuclear insurance program** to cover expenses of utilities in case of a prolonged nuclear power outage is being established by the American Public Power Association (Washington, DC). The program would cover principal/interest on financial obligations, as well as continuing and ongoing maintenance and security costs in the event of physical loss or damage of nuclear units. Radioactive contamination would be included. Maximum coverage would be $50 million, or 730 times the per diem recovery rate.

**With the EPA deregistration action on the herbicide TOK, the maker,** Rohm and Haas Co. (Philadelphia, PA), has stopped sale of the material and is recalling all stocks known to exist. Generically known as nitrofen, TOK has been found, from company-supported and other studies, to be mutagenic, teratogenic, and carcinogenic, according to evidence developed. TOK varieties had been used in certain vegetable-growing and plant nursery applications, though not residentially. Earlier, the state of California restricted TOK use and forbade women of child-bearing age from mixing, loading, or applying TOK.

**To monitor pollution levels in water, air, and soil, GCA Corp.** (Bedford, MA) will be prime contractor to EPA to the tune of $5.4 million. This probably will be the most extensive monitoring project ever conducted in the U.S., and will cover Love Canal near Niagara Falls, NY. Love Canal has been declared a Federal Emergency Area. GCA will use an integrated approach, use subcontractors' services, and deliver to EPA appropriate data to determine the extent of risk brought about by substances found during the monitoring project.

**The "bubble" concept must be unrestricted to be effective,** the American Iron and Steel Institute (AISI, Washington, DC) says. That concept places an imaginary "bubble" over an industrial plant and allows some components to emit more pollution. This is offset by reductions in other parts, so that the plant meets overall emission standards. AISI complains that EPA's definitions of the concept are "too rigorous," and gives as an example separate requirements for containment of fugitive emissions. The institute suggests that even if some fugitive emissions escape, road dust control could offset them.

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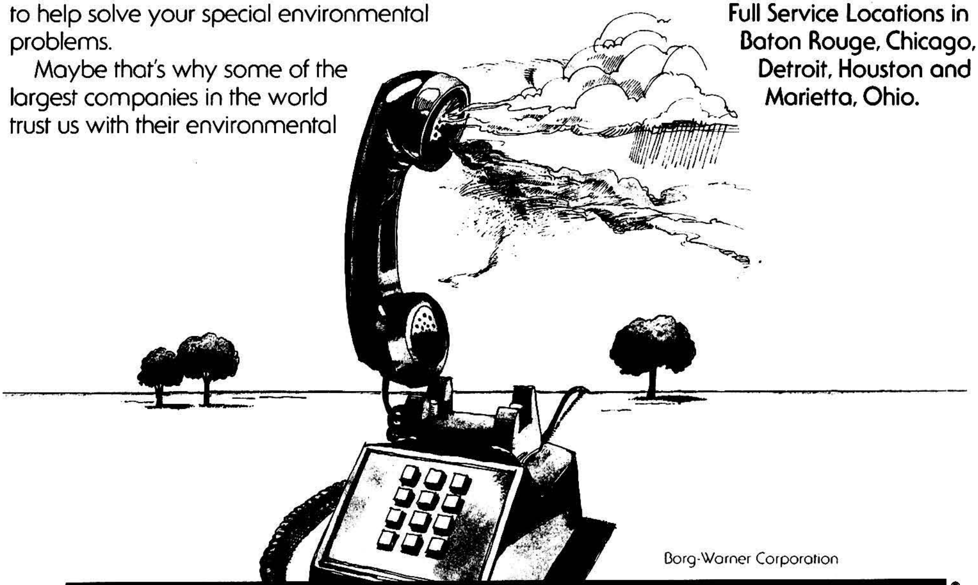

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# Forest pesticides: an overview

*Their use may comprise only a small fraction of total pesticide application, but large territorial areas are covered. And human and nontarget species exposure, as well as certain chemicals involved, are subjects of concern and rather intense debate*

At first glance, the ongoing controversy concerning the use of chemical pesticides in forest management may be somewhat surprising. After all, forest pesticide use is normally only about 1-5% of total pesticide use. (The U.S. total in 1978, for all needs, was about 1.7 billion lb.)

The amount of controversy may become more understandable when one considers the following:

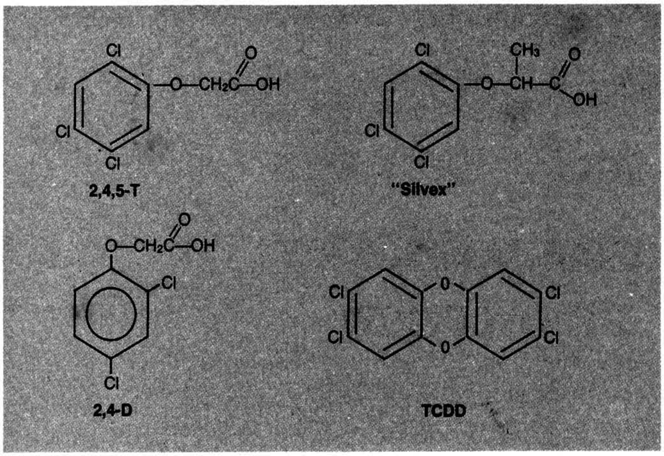
- Forest applications of pesticides can cover large areas, particularly to control insect epidemics in commercial forest-growing parts of the Northeast, Southeast, upper Midwest, and Pacific Northwest; thus, there is growing concern about human and nontarget species exposure and about pesticide drift after spraying. EPA is considering regulations which would require public warning concerning drift before a broad-scale spraying operation is undertaken.
- Although insect control spraying operations cover large *areas,* they involve far less chemicals by weight; about 80-90% of forest pesticide applications involve herbicides, such as 2,4-D, 2,4,5-T, and "Silvex" (a 2,4,5-T ester). However, use of the latter two substances in forests, pastures, and rights-of-way was temporarily suspended by EPA in February 1979, pending an administrative hearing. Debate now swirls around 2,4-D.
- Widely viewed television programs speculated about extensive toxic effects of the military defoliant "Agent Orange," an approximately 1:1 blend of 2,4-D and 2,4,5-T, heavily used during the Vietnam war. Some experts in the pesticides field ascribe adverse health effects to 2,4,5-T's impurity, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD).
- There were accounts of incidents of alleged increases in spontaneous human abortions in areas where 2,4-D and 2,4,5-T were used for weed control (Ark., Calif., Mont., Okla, Ore., Wash.); these have been widely reported on television and in newspapers.

In addition, controversy concerning 2,4-D was heightened in the West when an article appeared in the *Los Angeles Times* in late June. It stated that the California Department of Health Services (CDHS) issued a "hazard alert" to warn the public about nerve damage and carcinogenicity attributable to this herbicide. The CDHS denied that it issued a "hazard alert," although it did warn of possible nerve damage to people who have skin contact with 2,4-D and fail to wash it off. The department also clarified its press release, pointing out that tests regarding 2,4-D carcinogenicity in animals were suggestive, perhaps, but *inconclusive,* so far.

### A chemical use study

Whatever the public controversies may be, thorough scientific evaluations of forest pesticides are called for. Thus, several federal agencies (such as EPA, USDA, VA, and Health and Human Services) and user organizations (the National Forest Products Association (NFPA, Washington, D.C.), the American Farm Bureau, National Agriculture Aviation Association, and others) are engaged in and are funding such studies and evaluation programs.

One program is the Forest Use Chemical Project (FUCP), started last December and aimed at developing comparative risk/benefit analyses for major chemical and nonchemical pest control measures used in forest management. One reason for this emphasis on forest management is the amount of public attention (and controversy) directed toward the use of forest chemi-



cals. The herbicide 2,4-D is of particular interest, although various insecticides, which comprise most of the remaining percentages of forest chemicals used, will be studied.

FUCP involves a departure from EPA's traditional approach of reviewing all of the uses associated with a *single* pesticide. The agency's Special Pesticide Review Division is managing the program; Michael Dellarco is project manager.

The project's scope will entail actual management of growing trees for harvest. Areas covered are to be:

- California, western Oregon, and western Washington (Douglas fir)
- eastern Oregon and eastern Washington (pine)
- Great Lakes states (mixed conifer)
- northeastern states (mixed hardwood, spruce, balsam fir)
- southeastern states (pine).

The areas and trees chosen were selected because of their geography, managed tree species, and economic importance. Project completion is planned for April of next year.

One thrust will be herbicide exposure monitoring. This will cover the impact of exposure of humans, wildlife, and nontarget plant species to chemicals and other pest controls used in timber management. Direct exposure resulting from pesticide application and from spray drift from the target site will be assessed. Additionally, attempts will be made to evaluate exposure by indirect routes, such as ingestion of chemical residues in edible fish and game taken from a sprayed forest, chemical residues in drinking water supplies from watershed runoff, and reentry of chemicals used for forest pest control into the ground.

Most data would be acquired from results of available studies and literature searches. Still, if analysis of data reveals that there may be substantial human hazards associated with one or more pest control methods, human exposure studies would then be conducted to develop a quantitative risk assessment. However, before any such studies were initiated, the FUCP would develop study protocols and submit them for peer review.

### The 2,4-D debate

Another research effort involves a reassessment of the hazard, if any, in continued use of the herbicide 2,4-D as a forest pesticide. Recently, considerable pressure has been brought to bear on EPA, from various environmental advocacy and citizens' groups, and the like, to cancel the registration of this herbicide on the grounds that it may have carcinogenic, teratogenic, and other adverse human effects. So far, however, the agency has not concluded that 2,4-D is unsafe.

Edwin Johnson, EPA's deputy assistant administrator, pesticide programs, told *ES&T* that research to fill in data gaps, particularly with regard to any 2,4-D toxicity, will be conducted. It may take up to several years to determine what chronic effects there may be.

It is normally up to the companies registering pesticides to demonstrate toxicity, or lack of it. However, if a severe toxicity problem should crop up, the EPA and other federal agencies may conduct related research. Also, "contracts could be let to universities to assess effects upon those who come into frequent direct contact with a pesticide," Johnson said.

### A cooperative initiative

EPA is not alone in conducting 2,4-D studies, or requesting them. The NFPA and USDA, in the meantime, have retained SRI International (Menlo Park, Calif.) to carry out research concerning human spontaneous abortions. A future study of neural tube defects (anencephaly, hydrocephaly, meningomyelocoele) is under consideration. Areas covered would be those in which 2,4-D, 2,4,5-T, and 2,4,5-TP ("Silvex") were heavily used. However, studies of 2,4,5-T and "Silvex" may be hampered somewhat, according to SRI, because:

- There is relatively much more exposure to 2,4-D than to 2,4,5-T and "Silvex," even prior to effective suspension of the use of the latter two.
- If 2,4,5-T and "Silvex" studies are delayed much longer, more of the affected people would move away from areas of interest; records would be lost and memories would fade; thus, study quality could be impaired. Studies, by the way, are not restricted to the chemicals mentioned just above, but to phenoxy herbicides in general.

Generally, the study populations would comprise farm groups; private, state, and federal forest workers; pesticide applicators; and others, as deemed appropriate. For spontaneous abortion studies, the plan is to analyze data to select 100 cases and 200 controls. Preferably, for any neural tube studies that may be conducted, families with affected children born in 1977–79 would be examined—the idea being that 2,4,5-T and -TP were in use until March 1979, and if they were indeed teratogens, they could have acted very early in a pregnancy. Thus, effects could show up to at least the end of 1979.

Exposures to phenoxy herbicides are to be classified as "low, medium, and high." "Low" would mean that there was no herbicide use by husband or wife, no aerial spraying within 0.5 mi during the first three months of the wife's pregnancy, and no contaminated clothing brought home. "Medium" would entail exposure within 0.5 mi of aerial spraying during the first three months of pregnancy, or the husband's use of herbicides, with no contaminated clothing brought home. "High" would involve application, mixing, or handling phenoxy herbicides by husband (at home) or wife during the first three months of pregnancy, or laundering contaminated clothing during that interval.

### The 2,4,5-T suspension

The controversy surrounding 2,4-D heats up by several more degrees when the subject changes to that of 2,4,5-T. As mentioned earlier, EPA suspended the registration of 2,4,5-T for most uses in March 1979. On March 13 of

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this year, the agency began an administrative hearing to review all risk and benefit information. It then will determine whether suspended and nonsuspended uses of 2,4,5-T and "Silvex" should be entirely cancelled. EPA apparently believes that those two compounds are dangerous and leans toward cancellation. The Dow Chemical Co. and other makers of the herbicide, as well as major user groups, maintain that they are safe if used in accordance with label instructions.

One major difference between 2,4-D and 2,4,5-T, other than the obvious ones of structure and physical/chemical properties, is that TCDD is a side reaction product in the manufacture of trichlorophenol, the feedstock for the latter herbicide. (TCDD, incidentally, is the extremely toxic substance that figured in the ICMESA debacle at Sèveso, Italy, several years ago. Although herbicides were not made there, the chemical originated from manufacturing trichlorophenol as a feedstock for other products.)

Vietnam veterans and Vietnamese nationals exposed to "Agent Orange" complained that this exposure caused cancer, loss of sex drive, personality changes, and hitherto unexplained weaknesses in the limbs. Then, in 1978, in the vicinity of Alsea, Ore., and certain other areas where 2,4,5-T was used as a forest pesticide, it was charged that this chemical was related to spontaneous human abortions. Two studies—Alsea I and II—were made; after Alsea II, EPA decided that there was a significant cross-correlation between these abortions and 2,4,5-T use patterns during the period May 1973–March 1978. Accordingly, in early 1979, the agency took an emergency suspension action against certain uses of 2,4,5-T.

In Britain, despite heavy public pressure, 2,4,5-T has so far not been banned. Since 1957, that country has had a Pesticide Safety Precautions Scheme to clear pesticides as safe or to forbid their marketing and use.

### TCDD tests

At the center of the 2,4,5-T/"Agent Orange" controversy is TCDD, which is reported to have carcinogenic characteristics. These characteristics were tested and described in 1978 by R. Kociba and his associates at Dow (Midland, Mich.). The Dow scientists gave rats two-year diets of 0.1, 0.01, and 0.001 $\mu$g/kg body weight·d of TCDD. That translates to 2200, 220, and 22 parts per trillion (ppt), respectively. At 0.1 $\mu$g/kg·d, or 2200 ppt, there was increased incidence of hepatocellular and squamous-cell carcinomas of the lung, hard palate, nasal turbinates, and tongue. Interestingly enough, incidence of tumors of the uterus, pituitary, adrenal glands, and the pancreas was reduced. However, there were other histopathological changes.

At 0.01 $\mu$g/kg·d, or 220 ppt, there was lesser toxicity which showed itself through urinary porphyrin excretion (females), liver and lung lesions, and certain other symptoms. Ingestion of 0.001 $\mu$g/kg·d, or 22 ppt, of TCDD "caused no effects considered to be of any toxicologic significance," according to the Dow scientists.

At the Illinois Institute of Technology Research Institute (IITRI), 50 rats and mice of each sex were fed 0.01, 0.05, and 0.5 $\mu$g/kg·d (male) or 0.4, 0.2, and 2.0 $\mu$g/kg·d (female) of TCDD in a food mixture with corn oil and acetone, for 2 d/week, over 104 weeks. Higher-dosed males suffered retarded weight gain, and 22 of them contracted thyroid tumors. Three male rats in the mid- and high-dose groups developed thyroid cancer. Nine females—seven in the mid- and high-dose groups—contracted thyroid tumors; also, females seemed prone to liver cancers and neoplasms. Sixteen females got liver neoplasms, as opposed to three males. Generally, cancer risk appeared proportional to TCDD doses. Also, 48 of the rats, all but two on the high-dose TCDD diet, developed toxic hepatitis. Moreover, skin application led to fibrosarcomas in 21 of 30 females tested.

Results of the IITRI tests were revealed earlier this year. The tests were run under contract to the National Cancer Institute (NCI). Meanwhile, agricultural groups and manufacturers of 2,4,5-T have expressed their belief that dioxin toxicity of the herbicide is shown by test results to be insufficient to warrant restrictions in its use. On the other hand, some environmental advocacy groups call for permanent deregistration of 2,4,5-T and 2,4-D, as well. EPA's Johnson told *ES&T* that 2,4-D registration will be continued in the foreseeable future, unless results of tests under way show that it carries more risk than presently estimated. He does not, however, envision any "rehabilitation" of 2,4,5-T.

### Other pesticides

Partially to replace 2,4,5-T, EPA has expedited the registration of glyphosate for controlling brush, particularly in northeastern forests. Glyphosate is marketed by Monsanto under the trade name "Roundup."

Pesticides are used also against insect pests, such as gypsy and tussock

### EPA's views on 2,4-D

At present, EPA believes that available information on potential adverse health effects of 2,4-D does not warrant a regulatory action to remove its products from the market. The agency also does not see an imminent hazard or unreasonable health effects when 2,4-D products are used according to label instructions and precautions. However, EPA plans to obtain better toxicological information on 2,4-D. To support the foregoing conclusions, the agency submits that:

- No available evidence indicates that 2,4-D contains TCDD or any form of dioxin; none have been found, despite thorough chemical analyses.
- Studies pertinent to any 2,4-D oncogenicity were deemed to be inadequate and inconclusive.
- Animal tests with even large doses of 2,4-D did not appear to bring about life-threatening reproductive effects.
- Present evidence does not indicate human health effects from the potential human exposure.
- While many 2,4-D products, registered for use since the 1940s, underwent scientifically valid tests, some of the tests do not meet today's standards for testing; thus, there may be significant information gaps regarding toxicity.
- Pursuant to a new Section 3(c)(2)(B) of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), EPA can and, in this case, apparently will require 2,4-D registrants to develop information where gaps exist; registrants have 90 days to show compliance and can have their registrations suspended if they fail to meet the agency's conditions. Data requirements will be sent to registrants after they are reviewed by the FIFRA Scientific Advisory Panel.

In addition, EPA plans:

- to conduct reproductive toxicity tests on several derivatives of 2,4-D in order to have a good basis for comparison with data from registrants
- to continue its ongoing review of forest pest control practices, including evaluation of all chemical and nonchemical controls
- to review all new data as they come in, to determine whether changes in regulatory positions are warranted, especially any new animal tests and human exposure data
- to continue to support 2,4-D field tests.

For more detailed information, those concerned with 2,4-D should contact EPA's Office of Pesticide Programs and ask for the "2,4-D Fact Sheet."

moths, spruce budworms, bark beetles, and the like. One "workhorse" is carbaryl ("Sevin"); another is "Dimelin."

But forestry weapons other than chemicals also are being researched. One is *Bacillus thuringiensis,* a nemesis of numerous insect pests. Another is the use of parasitic wasps, such as *Tryptogamma.* And in Norway and Sweden, where spruce bark beetles take a heavy toll, sex pheromones are being tried as a means of controlling pest populations through chemical interference with the mating process. For this effort, the Scandinavian countries will spend a total of about $23 million this year. The idea is to lessen dependence upon potentially harmful chemicals.

Another thrust will be integrated pest management (IPM, *ES&T,* November 1979, p. 1335), which would use combinations of biological, chemical, and cultural strategies, singly or together, as deemed appropriate. The federal interagency IPM Coordinating Committee finds forest IPM progressing well in insect and disease control. However, the committee feels that vegetation control still relies almost completely on chemical herbicides and that improved, integrated ways must be found to combat severe pest infestations.

Possible future research avenues could include developing viruses such as those which suddenly decimate tussock moth populations in the Northwest. Also, microorganisms might break pesticide residues down; Battelle Laboratories (Columbus, Ohio) researchers appear to have developed bacteria that metabolize 2,4-D and render it innocuous.

### An Alsea II critique

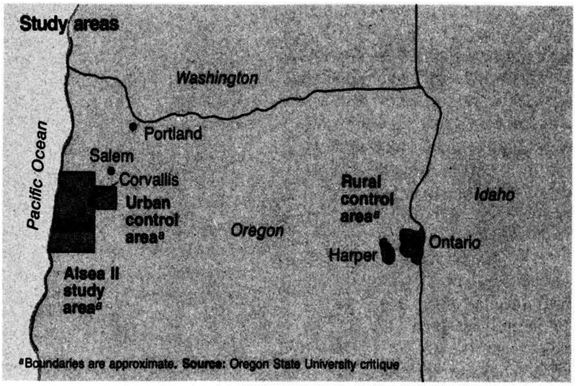
Last year, six scientists, from the Environmental Health Sciences Center of Oregon State University (Corvallis) and other organizations, challenged EPA's Alsea II findings through the medium of a scientific critique. The Alsea studies were conducted after women living in the western Oregon area noted an apparently temporal relationship between seasonal use of 2,4,5-T and spontaneous abortions. At the close of Alsea II, EPA reported:

- The abortion rate was higher in the study area than in either rural or urban control areas.
- There was a seasonal four-month cycle of abortions in the study area with an outstanding peak in June.
- There was a significant cross-correlation between the spontaneous abortion index and 2,4,5-T use patterns in the study area.

In arguing with EPA's findings, the six scientists, led by Sheldon Wagner of Oregon State (a physician and toxicologist), submitted that conclusions were erroneous because of:

- failure to account for differences in characteristics between the study area and the rural and urban control areas
- inaccuracies in collection of spontaneous abortion data
- failure to account for "marked" differences in the medical practice among areas
- incomplete and "inaccurate" data on 2,4,5-T use
- failure to recognize that the magnitude of the monthly variations in hospitalized spontaneous abortion rates in the study, and the rural and urban control areas is no greater than would be expected from random variations.

The scientists said that when corrections to some of their objections were applied, spontaneous abortion rates in the study area "did not appear to be related to the use of 2,4,5-T."


Study areas

^a Boundaries are approximate. **Source:** Oregon State University critique

### "Zero risk" not assured

Perhaps the crux of the forest pesticide controversy is the debate about the achievability of "zero risk," and whether, as some advocacy groups charge, the forest products industry puts more priority on profits than on public health. The NFPA's William McCredie told *ES&T* that his industry has a very great self-interest in protecting public health in general, as well as the health of its employees. He said that NFPA plans to expand support of, and cooperation with, all efforts to continue monitoring epidemiological and health effects studies and risk assessments. To carry out these plans, NFPA proposes cooperative roles with government, and sponsorship of studies such as the SRI project described earlier. Health and risk evaluations would be conducted in keeping with "the most rigorous scientific methods."

For its part, EPA plans to take whatever further enforcement actions may be necessary—reducing pesticide spray drift and improved product labelling could be among such actions—to minimize exposure and commensurate public health risk. However, as EPA's Johnson told a joint meeting of the American Paper Institute and the NFPA, held in Washington, D.C., in June, his agency "is *not* administering a 'zero-risk' pesticide regulatory statute." He also pointed out that "EPA does *not* give assurances of absolute safety regarding pesticide use in broad-scale spraying programs."

What the agency does, rather, is to operate on the premise that citizens have the right to know which chemicals they may be exposed to. EPA is exploring ways to require advance public notice and other protective measures during publicly conducted or funded spraying programs, and is advising the forest products industry to do the same voluntarily, not to wait for federal regulatory action. Also the agency is encouraging efforts to enhance public awareness of the risks and benefits stemming from "judicious pesticide use," with respect to preservation of public health, as well as the productivity of forests and croplands. —Julian Josephson

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# The great kelp controversy

*Despite a series of failures and charges of incompetence, General Electric is receiving an additional $4.4 million from the Energy Department for a project aimed at growing kelp on "ocean farms" for conversion to methane gas*

From the start it was big project, involving big money, big names like General Electric, the U.S. Navy, and the American Gas Association, and a big idea: growing kelp, for conversion to methane gas, on millions of acres of floating platforms over the deep ocean. But while proponents continue to point to a potential energy supply of 1 quad a year by the year 2000, critics call the project a mismanaged boondoggle that is wasting millions of federal dollars without producing a single piece of useful data.

At the very least—and there is general agreement here—the project has had a checkered past. Some early efforts, under the direction of the Navy and with funding at various times from the National Science Foundation, the Energy Research and Development Administration (ERDA), and the American Gas Association (AGA), were not notable successes. By 1975, two attempts had been made to grow kelp in ocean facilities; both times the plants died.

At this point a plan was developed to supply nutrients to the plants by pumping up deep water. Howard A. Wilcox, a nuclear physicist with the Naval Underseas Laboratory, and Ab Flowers, a metallurgical engineer with the AGA, came up with the idea of testing this scheme on a "quarter-acre module"—a wire and rope lattice, suspended from a buoy, on which the plants would be attached and which would use diesel pumps to bring up water from a depth of 1500 ft.

Funding for the module came from the Department of Energy in 1978, to the tune of $1.2 million. (By this time General Electric had replaced the Navy in the project, and was being funded by the AGA. DOE, and ERDA before it, had separately been funding studies by Wheeler North at CalTech on kelp growth.) A hundred plants provided by North were set out on the module in December 1978; two months later, all were dead. DOE last year approved an additional $4.4 million for GE to modify the structure to provide adequate protection for the plants, a program that began last month.

Those involved in the project, while admitting past failures, argue that the setbacks do not detract from the soundness of the concept or the need to continue the work. Larry Raymond, program manager of the project at the Energy Department's Solar Energy Research Institute (SERI), attributed the most recent failure to a "freak" storm. "They had a series of very rough storms that simply tore the plants off the structure." And, he argued, "a fair amount of money has gone into this to date. To have the program interrupted at this point would be totally unjustified to the taxpayers."

### Early warnings ignored

But others see the failures as part of a larger pattern of incompetence that more money is not likely to alter. Many warnings against rushing into the project and not first obtaining basic data on kelp growth were apparently ignored. In a letter to Wilcox dated March 25, 1976, North spelled out some of his "misgivings about the QAM [quarter-acre module] operation":

> 1. . . . there may be physical problems with the QAM that need to be solved. . . .
>
> 2. There is not 100% control over the dispersal of the upwelled water. As I see it, we will not be able to state with much precision the exposure [to pumped-up nutrients] received by a given plant on the QAM. . . .
>
> 4. Biological hazards [to the plants] may appear. . . .
>
> 5. There may be adverse effects from long-term exposure to upwelled water among our plants. I have definite worries about this.
>
> 6. According to my calculations, the plants will have to accumulate 4% of the total nutrients that we upwell in order to grow at approximately normal rates. The likelihood that they can do this is not at all clear to me. . . .

Furthermore, the DOE branch responsible for biomass recommended against funding the QAM proposal. Roscoe F. Ward, then the branch chief of the Fuels from Biomass Program, wrote a memo in March 1978 setting out his position:

> The staff of the Fuels from Biomass Branch does not feel that the AGA quarter-acre module should be supported. However, we do feel strongly that we need additional data on kelp growth rates and nutrient requirements. This data cannot be obtained by the quarter-acre module experiment. We believe the growth studies under well-controlled conditions can be performed readily on land-based aquatic test sites.

The project was nonetheless approved on orders from Assistant Secretary Robert D. Thorne.

Shortly after the plants were set out, in December 1978, North wrote a memo warning of modifications that were needed in the test farm:

> 1. Protection against current is extremely important. We need a curtain around the entire farm. The curtain should remain in place at all current velocities. . . .
>
> 2. One-way valves are needed in the exhaust hoses of the upwelling system to prevent flow reversals when one or two pumps shut down. Flow reversals have happened and nearby plants have become sucked into the ports, seriously damaging them. At least six plants have been badly defoliated by this process. . . .

Both factors apparently contributed to the destruction of the entire crop within two months.

### Question of competence

The suspicion that those pushing the strongest for the test module—and those most immediately involved in its design and operation—had the least expertise in marine biology is reinforced by a controversy that developed over potential yields of the kelp plants. While GE was projecting yields of 25–100 dry, ash-free tons per acre per year, the marine biologists consulted by DOE argued that maximum theoretical yields were more like 30–50. John H. Rhyther of the Woods Hole Oceanographic Institution, concerned over these "extravagant" projections, wrote Ward in February 1978: "With the certainty and conviction that comes from complete and utter ignorance, the kelp farm proponents have stipulated and projected yields and other characteristics of their proposed operation that are wholly unrealistic and unreasonable."

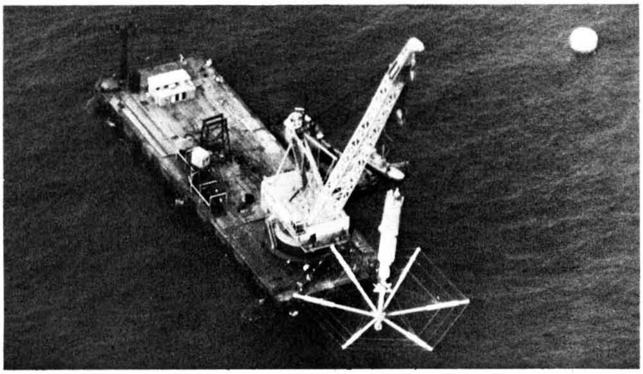
Joel Goldman, also of Woods Hole, explained, "They were talking about yields for these plants higher than any yields ever recorded"—possibly even higher than thermodynamically possible. "The last I've heard, they're still talking about tremendous yields."

Goldman has been a strong critic of the ocean farm project, in part because he sees it as a diversion of funds needed for the more basic studies that he and others are pursuing under DOE contract. He sees a "tremendous mismanagement of a program and a tremendous waste of money. My major criticism is that they didn't have the right kind of people involved. They've never taken the advice of people who were knowledgeable in this area." And as a result, he said, "There is not one piece of data on anything done in the ocean. I don't think we've learned anything."

Another critic is Ward, the DOE branch chief who advised against funding the QAM project. "The total project didn't make sense," he said. "There were lots cheaper ways to run these experiments." And he emphasized the issue of competence: "GE has really no expertise in the area of aquatic biomass or structures." (Goldman put it this way: "I have as much competence in building electrical devices as GE has in growing biomass in the oceans.")

Ward also asserts that GE did not live up to its contract obligations to prepare progress reports, and that the final report was, in the words of a memo Ward wrote on April 18, 1979, a "series of disorganized items hastily thrown together"; there were "no data, discussions of results, conclusions or recommendations of how to solve the problems." An outside reviewer asked to examine one section of the report agreed: "I found the information to be identical to that received from General Electric in March of 1978 [before the QAM experiment began]. There does not appear to be any new information in the document."

Ward believes that his opposition to this and other projects that he felt were of questionable scientific value led to attempts to force him out of DOE. (Ward is now at the United Nations, on a two-year leave from the department.) Whether Ward is a persecuted whistle-blower or simply an employee who irritated his superiors is uncertain; there is some evidence for the former, and there is unmistakeable evidence that he was put under extreme pressure at DOE. Ward was removed from his position as branch chief in May 1978, two months after recommending that the GE proposal be turned down. An investigation by the inspector general (IG) of DOE found that Ward's supervisor had been told "that Robert Thorne wanted Roscoe Ward removed from his position as branch chief. Ward supposedly lacked sufficient political judgment, even though he knew his business and was competent from a professional standpoint."



**Expensive experiment?** *Wire-and-rope-lattice test farm is lowered into the Pacific*

The following spring, the new branch chief, Sanford M. Harris, took a series of steps clearly aimed at getting rid of Ward. According to another IG investigation, Harris in fact sent a note to the division director saying, "I suggest that, on the basis of uncommon activity on his part, we find a place for him temporarily on assignment right out of here and with him officially relieved of all present duties until the new assignment is completed (or he is removed)." Although a letter of reprimand that Harris issued Ward in April 1979 was removed on the order of a grievance examiner, and an attempt to suspend him was overruled by the division director, other actions against Ward went through. The IG report found that his travel was restricted, that he was denied access to information related to his responsibilities, and that he was gradually relieved of responsibility for programs he had been managing.

### 'Went beyond his authority'

Leslie Levine, a DOE official who at one point was acting branch chief of the biomass program, maintained that it was just a personnel problem: "Roscoe Ward would decide what should be done and what shouldn't be done. He insisted on making policy and implementing policy in a way that went beyond his authority."

And Levine strongly defended the methane-from-kelp project and the decision to invest the additional $4.4 million: "I believe that aquatic biomass has the potential of being a real winner in the long run. There's the potential for high yields; there's the potential for specialized products; and there's the potential for growing biomass in facilities that do not compete with farmland in the U.S."

Both Levine and Raymond at SERI insist that the decision to provide additional funding was not so much their doing as the House Appropriations Committee's doing. "We got direct congressional language that said, 'You will fund it,'" explained Levine. "Those kinds of directions are not the equivalent of law, but they're very close to it."

But DOE made no attempt to oppose that direction, despite the finding of the IG that "the support for the follow-on effort by GE . . . is questionable," in particular since the initial $1.2 million grant was for a "discrete one-time effort" with GE responsible for all cost overruns. The new money will go to modifying the structure to provide the protection against current that North pointed to a need for in his memo of December 1978.

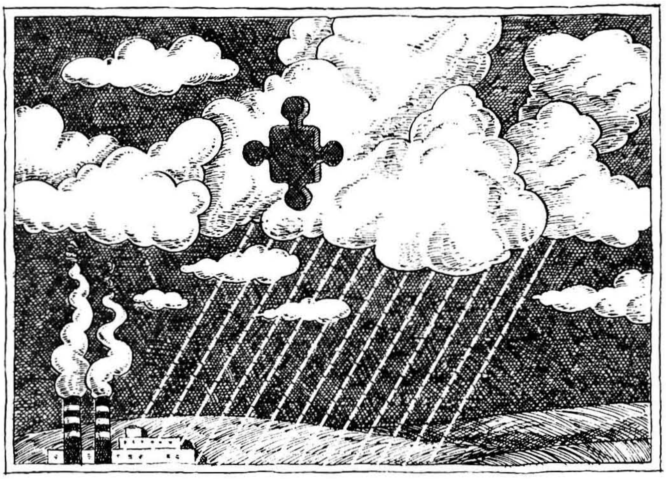
Raymond argues that the additional $4.4 million—once again termed a "one-time" grant—is justified since it will provide the basis for getting the essential data. "There are no facilities available at this time that would not cost at least as much that would provide the answers." And while admitting that "there are very, very strong arguments against" the scheme, he believes that we need to spend the money to get the data and settle the argument.

Critics are not so confident that anything will be settled. "I think a year from now it will be another $4 million down the tubes," said Goldman

—Stephen Budiansky

# Acid rain and the missing link

*The chemical pathways in the atmosphere that convert $SO_2$ and $NO_2$ to the acids that eventually fall in rain are poorly understood*



It is a fact, often stated, that oxidation of sulfur and nitrogen oxides leads to the formation of acid rain. But just how that oxidation occurs is largely unknown—a mysterious missing link in the chain that stretches from power plant stacks and automobile exhaust pipes to sterile lakes and damaged crops.

"We know the gross reaction, but we don't know the details in between," said John Jansen of the utility-supported Electric Power Research Institute (EPRI). Many theoretical reaction mechanisms have been proposed, but few have been confirmed experimentally, either in the laboratory or in the atmosphere. And the experimental confirmation that is available provides scant insight into the relative importance and rates of the various reaction mechanisms.

Available atmospheric evidence does suggest that the overall oxidation process is a complex mix of many different reaction pathways. A. Paul Altshuller of the EPA's Environmental Sciences Research Laboratory in Research Triangle Park explained that observations of atmospheric sulfate indicate that the relatively well understood gas-phase photochemical oxidation steps cannot account for the total sulfate production. If photochemistry were the only oxidation process that converts $SO_2$ to sulfate, he said, "sulfate should drop off dramatically in winter"—by something like a factor of 10—because available sunlight is reduced. "But the concentrations do not drop more than a factor of two."

The conclusion is that other processes, particularly heterogeneous reactions, are playing a part. Liquid-phase reactions are thought to occur when $SO_2$, an oxidizing gas such as oxygen, ozone ($O_3$), or hydrogen peroxide ($H_2O_2$), and possibly a trace metal catalyst diffuse into a cloud droplet. Reactions may also occur on the surface of carbonaceous or metallic particles.

Simply invoking heterogeneous chemistry, however, does not instantly solve any problems. Altshuller pointed out that both $O_3$ and $H_2O_2$ themselves drop off in winter, implying that the heterogeneous oxidation rate should fall along with the gas-phase oxidation rate in winter. On the other hand, so long as the detailed mechanisms are unknown, it is impossible to say just what the controlling factor in the reaction rate is. If metal catalysts are required to carry out the liquid-phase oxidation, for example, the abundance of the catalyst might be a more important controlling factor than the concentration of the oxidizing species.

### Realistic conditions needed

Jansen summed up the current state of affairs saying, "We feel that the aqueous-phase chemistry is unknown." Altshuller agreed. Although some work has been done, it is generally inconclusive, he said. "If you read the literature, you find quite a bit on heterogeneous reactions, but the problem is to get people to agree on the numbers"—that is, the rate constants.

Both Jansen and Altshuller emphasized that the key to future work must be the use of more realistic conditions in laboratory studies in order to tackle the "whole, largely unknown aspect of what happens to $SO_2$ in cloud droplets," as Altshuller put it. According to Jansen, the work to date has concentrated on reactions in bulk solutions rather than in droplets. "That doesn't represent the atmosphere," he said. "People have been looking too much at bulk reactions."

EPRI is supporting a study at the Desert Research Institute which, though it will still be looking at the "gross" chemistry, will attempt to simulate atmospheric conditions more truly. Reactions will be studied in a cloud chamber in which temperature, pressure, and humidity can be controlled. Ultimately, EPRI hopes to have data on sulfate formation as a function of such variables as condensation nuclei size, $SO_2$ concentration, and buffering capacity of the droplets. The EPA is tackling the problem through some detailed laboratory studies and through a field measurement program in conjunction with the National Science Foundation and the National Center for Atmospheric Research. Acids, oxidizing gases, and acid precursors are sampled from an instrumented aircraft before a cloud forms; acids are then measured in the cloud water.

A parallel effort is the development of models of sulfate formation and transport. But this effort, according to Altshuller, is hindered by a lack of detailed information on $H_2O_2$ concentrations in the atmosphere and by the difficulty of incorporating such detailed, small-scale data into a large-scale model. "You have to have a model that concurrently deals with large-scale and long-time transport *and* the details in the pollution layer."

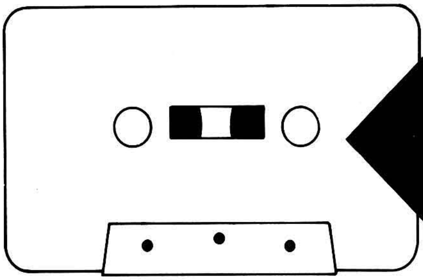
If knowledge of the transformation of sulfur is spotty, it approaches the nonexistent for nitrogen. While the smog photochemistry of nitrogen, which can lead to the formation of nitric acid, has been extensively studied, the heterogeneous chemistry is a complete blank. Part of the reason for that is a measurement problem. Ammonium nitrate, the common particle form of nitrate, is quite volatile, easily lost from filter media. Inert media that retain all of the ammonium nitrate also trap nitric acid, thus obscuring the information that could help to distinguish between the heterogeneous and homogeneous pathways.

### Control strategies

Determining the relative contribution of these pathways, for both sulfur and nitrogen, may be important in developing methods to control acid rain. Different control strategies may be dictated depending on whether already-formed sulfate aerosols get into water droplets, or whether $SO_2$ gets into the droplets and then reacts to form sulfate. Jansen also stressed the importance of discovering if there is a limiting species—such as a metal catalyst— in the conversion; if so, a control strategy could logically be aimed at that limiting species.

Subsequent reactions that sulfate and nitrate undergo in the atmosphere could also hold implications for control strategies. For example, reaction with atmospheric ammonia could result in a partial neutralization which reduces the acidity of the rain that ultimately reaches the ground. But Altshuller cautioned that control strategies must be evaluated in terms of the ultimate effects at the earth's surface; atmospheric chemistry is only one piece of the picture. If the rain gets into the soil, for example, "it doesn't really matter whether the sulfate comes down as ammonium sulfate"—the product of the neutralization reaction with ammonia—"or sulfuric acid," he said; the effects are probably the same since deamination occurs rapidly in soil.

—Stephen Budiansky



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# Superfund:
# The debate drags on

**Michael R. Deland**
*ERT, Concord, MA*

EPA's recent promulgation of regulations implementing the Resource Conservation and Recovery Act of 1977, provides the mechanism, albeit cumbersome and controversial, to control from "cradle to grave" the disposal of hazardous wastes now being generated. Still lacking, however, after two years of congressional discussion, is legislation which addresses the vast quantity of hazardous waste which has been accumulating for years in dump sites throughout the country, many of them now abandoned. Thanks in part to the wide publicity given Love Canal, there is a chance for passage this session of the long awaited "superfund" legislation.

Support for some version of remedial legislation is broad, ranging from a plank of the Democratic Party platform calling for a "major effort to clean up hazardous waste dump sites of which there are thousands throughout the country," to the more qualified endorsement of Irving Shapiro, chairman of DuPont, who recently cited abandoned hazardous waste sites as a "particularly vexing problem" and backed a proposed House bill as the "best answer" to cleanup.

### Congressional debate

There are currently three separate superfund bills being debated in Congress, H.R. 7020, H.R. 85 (which is limited to discharges into navigable waters), and S. 1480. Of these, the Senate bill is the most comprehensive, calling for the establishment of a $4.085 billion fund over six years; the House proposals establish a range from $600 million to $1.2 billion over four years. Still being debated is the size of industry's share: likely to be 75–80% of the total, funded by a "front-end fee" approach.

Environmental and labor groups understandably endorse the Senate approach, while industry, feeling some bill is inevitable, is lobbying for the House version. Lawyers for the chemical industry have fundamental objections to S. 1480, namely, that it is "unduly broad in scope, lacking in meaningful statutory standards, ambiguous and uncertain as to its intent and effect, and impermissibly vague and burdensome." Their more specific criticisms include the notification requirements, the removal of remedial provisions, and liability questions.

The Senate bill currently requires notification, both for sites at which hazardous substances are stored or disposed of and for "releases" of hazardous materials to the environment. This reporting duty extends to virtually anyone having any present, past, or conceivable future association with the site. The remedial and removal orders are similarly broad, giving the EPA administrator authority to establish such requirements as he "deems appropriate" to protect public health, welfare, and the environment.

The question of assignment of liability is likely to remain among the most controversial. S. 1480 contains stringent liability provisions based on several factors, the key of which is the assumption that those "who have been generically associated with such problems in the past and who today profit from products and services associated with such substances" should bear the brunt of the cost of cleanup. This approach results in the establishment of absolute liability for generators of hazardous waste, regardless of any intervening role played by third parties. The only defenses to this are an act of God or of war. Industry argues that this unfairly creates "a retroactive liability for events which have occurred in the past and for which the enterprises bearing the liability have no casual responsibility whatever."

### Ultimate resolution?

While few question that something must be done to "defuse" the abandoned waste sites, characterized by Administrator Costle as "ticking time bombs," a concensus on a sensible approach remains elusive. Crystallized within the debate over the "superfund" are disturbing questions which will continue to confront us in the 1980s. New discoveries have shown long-accepted practices to be an insult to our environment and a threat to our health. How many more Love Canals are there? Will the cost to "cure" the next one fall within EPA's estimated range of $3.6 billion to $44 billion or be closer to CEQ's estimates of $28.4 billion to $55 billion? Given such disparity, do those estimates serve a useful purpose?

Science has advanced sufficiently to unearth new problems, but their resolution, or even accurate risk assessment, must await further progress. Meanwhile, Congress, in the face of technical uncertainty, is left to find political solutions, subjecting the process to new strains and taxing the patience of a public justifiably awaiting results.

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# What price the Furbish lousewort?

*This keynote address on a new kind of cost–benefit analysis was given at the Fourth Conference on Environmental Engineering Education sponsored by the Association of Environmental Engineering Professors and the American Academy of Environmental Engineers, held in Toronto, Canada, on June 19–21, 1980*

**Eric Ashby**
*Brandon, Suffolk, England*

Before you embark on the technical papers for this conference, let me tell you two stories, each with a moral. For the first I take you back 88 years and transport you from Toronto to London. In the British Parliament the Lord Stratheden and Campbell is introducing, for the tenth time in six years, a bill to abate smoke in London. It has been a winter of dense sulphurous fogs; visibility is reduced sometimes to no more than a yard; traffic is paralysed; even walking along the streets is at times impossible. The stuff seeps into theatres so that audiences cannot see the stages.

No one in the Parliament of 1892 is ignorant of the facts about fog. The politicians often had to grope their way through fog to get there. They had learnt from dozens of speeches what causes the fog, what damage it does, how it could be prevented. They are now going to be asked to pass a law to abate it.

Industrial smoke from boilers generating steam was already controlled by law in the metropolis; these London fogs were caused mainly by domestic fires from nearly a million homes burning high-sulphur coal. The damage was obvious: Smoke corroded metal and stonework and it killed as many people as were killed in outbreaks of cholera, a death less dramatic only because it was insidious and delayed. During three weeks in the winter of 1880, more than 2000 Londoners died from ailments attributable to the fog. The smoke could be prevented, simply by giving up the use of soft coal in open fires and heating homes by closed stoves burning coke or anthracite coal. This was the way homes were heated on the Continent, though in some countries it was easier to do because there was a plentiful supply of wood, which could be used instead of coke or hard coal.

The hazards of smoke were evident; the nuisance of it blighted the city; the cure was at hand. But (I now take you back into the Parliament of 1892) Lord Stratheden and Campbell again fails to get his bill approved. Worse than that, he is ridiculed by the Prime Minister, Lord Salisbury. The bill proposed to make it an offense for a householder to allow opaque smoke to issue from his home. "How," says the Prime Minister, "do you define the word 'opaque'?" Defining it would "give infinite pleasure, amusement, and occupation to Her Majesty's Courts of Justice. I do not know whether my noble friend thinks he would ever get Parliament to pass such a measure as this, or whether he would get the English people to obey it if it were passed. It would condemn Londoners to live in homes where they would never see a fire with a flame in it. I do not think that, for the sake of avoiding an occasional inconvenience, grave as it is [not a very felicitous way to describe dying from bronchitis] for a certain number of days in the winter, people would condemn themselves to

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a flameless fire all the winter through." He continues his ridicule: "Conceive of an inspector going to every house in London and seeing that the grate was properly fitted in order not to emit smoke. The burden . . . would be worse than the London fog."

The bill was rejected. The British people, through their legislature, had done an implicit cost-benefit analysis. For the benefits of what one journal described as an "open, pokeable, companionable fire," they were prepared to pay the cost of a higher death rate, the long drawn out misery of respiratory diseases, blackened and crumbling stonework, dirt on windows and curtains, a "daily increasing sacrifice of daylight to dirt" (*1*).

Why do I tell you this story? In it lies a high-priority problem in environmental engineering education. I have no doubt that engineers who have to make policy decisions about the environment are well qualified in the technology of conservation and pollution control. They know how to build flood barriers, abate smoke, treat sewage, and design power plants and reservoirs. They know about the hazards to the environment that arise from exploitation by man: acid rain, rivers bereft of oxygen, impoverished vegetation and wildlife. They also know about the hazards to man that arise from abuse of the environment: soil erosion, threats to the ozone layer, accumulation of noxious substances like DDT residues and mercury. In these areas, I believe education is by and large adequate, though this conference may well improve it. What is lacking from education is analysis of that intangible entity we call public opinion, and of the impact of public opinion on policy making. How do people do this cost-benefit calculation between a companionable open fire and a menacing pea-soup fog? How do they distinguish between acceptable and unacceptable risks? How is it that prejudice so often overrides common sense? Confronted by public attitudes such as this, how can the trained environmental engineer best put his expertise at the disposal of society?

### The second story

Before I answer this last question, here is my second story. This one takes place in the 1970s, and much nearer home. It is familiar to some of you already.

The U.S. Army Corps of Engineers plans to build a $1.2 billion hydroelectric dam on the St. John River in Maine. It is not a region of virgin wilderness; it has been lumbered for timber since the 1840s. Pulp mills and potato farms lie along the river. But on the steep banks of the river, precariously perched between white spruce and downy alder, there grows a rare plant, discovered by an amateur botanist, Kate Furbish, in 1880—just 100 years ago—and named after her, the Furbish lousewort.

If the Corps of Engineers builds the dam, the Furbish lousewort is likely to become extinct. At any rate, that is what conservationists say. Under the Federal Endangered Species Act, President Carter was obliged to halt progress on the dam; the decision was recorded in the eighth annual report of the Council for Environmental Quality for 1977 (*2*).

This is not an isolated freak incident. There is also the much publicised triumph of the snail darter, a little fish which held up the building of the Tellico dam in Tennessee. And in Britain in the 1960s, both houses of Parliament were engaged in a long controversy to decide whether or not to allow a reservoir to be built in a remote valley in Teesdale. The benefit was to be an impressive expansion of industry at the Tees estuary in an area blighted by unemployment. The cost was that the dam might endanger the relics of an alpine flora, including a rare plant called the Teesdale sandwort. The dam was built, but only after delay and bitter controversy (incidentally, the Teesdale sandwort still flourishes there) (*3*).

> ***In these areas, I believe education is by and large adequate, though this conference may well improve it. What is lacking from education is analysis of that intangible entity we call public opinion, and of the impact of public opinion on policy making.***

A century or so ago, when the railroads were driven through the land and industry sprawled into the countryside, the idea of pitting the snail darter, the sandwort, and Miss Furbish's lousewort against a major engineering project would have been regarded as crazy. Not so today. The title of this address—"What price the Furbish lousewort?"—stands for a new kind of cost-benefit analysis.

On one side of the balance are masses of quantitative data, technology assessments, computer outputs, scale drawings, and blueprints. On the other side are unquantified symbols of another life style: a companionable open fire, a rare plant, a marsh visited by migrating birds. And, to the dismay of some engineers and administrators, the unquantified symbols sometimes tip the scale. To study how and why this happens is, in my view, an essential ingredient in the education of environmental engineers. It is clear that environmental engineers are already well aware of this. In all four position papers circulated to us there is reference to the problem. Let me quote from one of them, the paper by Aulenbach and Brezonik's work group: "The finest technical solution to a problem is worthless if it cannot be explained or sold to the public and consummated."

Now I shall draw the morals from these two stories. I begin by offering you a sobering string of negatives. In applying his expertise to environmental problems, the engineer cannot rely on persuasion by hard data; quantification isn't enough. He cannot assume that the response to his carefully argued case will be rational; logic penetrates the head, but not the heart, and many of these issues are settled by the heart. He had better not hope for consensus. Most environmental issues are conflicts between one kind of good and another kind of good; they are not simple duels between good and bad. We lack efficient institutions for the management of this kind of conflict. And—as though this were not a forbidding enough list—the Furbish lousewort (representing nature) has a lesson to teach the environmental engineer (representing industrial man), which industrial man continues to disregard at his peril.

### Quantification is not enough

There was a time—it's over now—when cost-benefit analysis was regarded as a reliable technique for making choices in such matters as the siting of airports, highways, power plants, and reservoirs. Economics is about the logic of choice, and cost-benefit analysis is a favourite tool of economists. Imponderables, such as noise, disruption of the skyline, the hazards of smoke, and the amenities of wilderness—none of these dismayed the economist. He found ingenious ways to quantify them. How much would you pay to put in double glazing to cut out the racket of trucks, or, for that matter, how much would you pay to move away from the noisy neighbourhood altogether? What is a reasonable compensation for having to repaint your home once a year, or for enduring the inconvenience of bronchial attacks brought on by smoke and sulphur dioxide? What price the risk of your death on a highway without crash barriers? What price the preservation of the Furbish lousewort?

To all these questions economists are willing to supply ingenious (but, in my view, utterly implausible) answers. Thus, for a huge dam proposed for the Delaware River at Tocks Island, the benefits were reckoned to amount to $29 million a year (of which over a third was an estimate of the profits from tourists at $1.35 per tourist-day); the cost, including discount, was computed at about $18 million a year. So—provided you attach no importance to the intrinsic beauty of the river at Tocks Island, no importance to the fact that the Delaware River is the only river on the Eastern seaboard not to have been disfigured in this way, and no importance to the stress caused to the people who would be displaced from their homes—the cost-benefit analysis promises annual profits of $11 million a year. The advice, therefore, was: Build the dam.

In any event, there is no dam at Tocks Island, nor is there likely to be one, for two reasons. The minor reason is that the cost-benefit analysis is wrong. Neglected factors, such as road building to the site, change in discount rate, and so on, make a nonsense of the original arithmetic. But that's only a minor reason. The major reason is that the imponderables tipped the scale when this political decision had to be made. We now know the reason for this.

It isn't just that cost-benefit analysis is unreliable when it involves projection into the future (though this is true); it is also—and this is the decisive educational point—an *inappropriate* technique. It sets out to answer the question: What is *efficient* for society? But this is not what the public asks about environmental issues nowadays; they ask: What is *good* for society? And the most precious kinds of good cannot be quantified without distortion.

There is another reason why quantification is not enough and indeed is sometimes counterproductive: namely, the way it may drive the public into disillusion and resentment. In Britain, the procedure for public participation over environmental issues is through the Town and Country Planning Acts. The relevant minister conducts a public enquiry at which any citizen, without having to engage a lawyer, can give evidence. The trouble about these enquiries is the risk that they will be "David-Goliath" affairs. The proponent of the scheme has access to expertise and cash. At the enquiry he smothers the public with highly sophisticated evidence that mystifies and ultimately enrages them. Over setting the route for a motorway, for instance, the transport authority flourishes a cabalistic number called COBA, which is derived from a string of variables fed into a computer. The COBA value identifies the optimum route for the motorway. But—and I come back to the importance of studying how public opinion evolves—the reaction to COBA has been vigorous protest, which reduced some public enquiries to a dogfight. Why? Because you find that COBA, once you insist on dissecting it, hides assumptions repugnant to the ordinary citizen. When you enquire exactly what data are fed into the computer for traffic density, time saved, risk of accidents, noise, disturbance of the landscape, and so on, you find the following sort of thing. First, if route A compared with route B saves one second, then it is assumed that 3600 drivers, each saving one second, are the equivalent of one driver saving one hour. Second, the estimate of the cost of a death saved is $94 000, a figure resting on the flimsiest of evidence. Despite inflation, Englishmen are, apparently, cheaper than Canadians (where the assumed cost of a fatal accident is about $134 000), and even cheaper than Americans (where it is about $160 000) (*4*).

***It isn't just that cost-benefit analysis is unreliable when it involves projection into the future (though this is true); it is also—and this is the decisive educational point—an inappropriate technique.***

The seminal question is this: In making environmental impact assessments, is it better to restrict economic analysis to values that are unquestionably quantifiable, leaving the decision maker to integrate the imponderables into the decision by subjective means? Or is it better to stretch economic analysis to cover values that have to be stripped of their human meaning in order to quantify them? The education of an environmental engineer should bring him face to face with this issue.

### Rationality is not enough

On the top floor of the Athenaeum Club in London—the Valhalla of intellectuals—there are bedrooms where members can stay overnight. The bedroom between no. 12 and no. 14 is labeled 12a, even though some of the members are scientists or engineers. I have never seen evidence that there is a higher mortality or morbidity rate among persons who are born on the 13th of the month, or who travel on the 13th, or who sleep in a room numbered 13, but the highly intelligent members in this temple of rationality are taking no chances. It's a pretty reminder that man does not live by rational thought alone. So the engineer who gets involved in policies for the environment has to take account of a second difficulty. Not only are policies likely to be influenced by unquantified variables (e.g., the tranquillity and clarity of water in a river may be reckoned more important than its *coli* count or its acidity or its phosphate content), but even quantified variables are not interpreted rationally by the public.

There was an example of this recently in Britain. The Medical Research Council published in the last week of March 1980 the most thorough investigation ever made in Britain of the impact of lead on health. This, combined with a study on lead emissions from automobiles, published in 1978 by the Atomic Energy Authority, gives a clear quantified picture of the sources of lead and their pathways into human beings (*5*). I'll not digress to give you the details of this; it's enough to say that lead from the air accounts for only 11% of an adult's total intake of lead and that the most dangerous sources of lead in Britain are from water carried to homes in lead pipes and from lead in paint. So a rational policy would be to give a higher priority to abating lead pollution from these sources than to the reduction of lead additives in gasoline. But even on the day the report was issued and before critics had had time to read it, the anti-lead lobby produced a broadsheet denouncing this authoritative scientific study as a "cover-up" and a "political document." The scientists in the Medical Research

Council were labeled "establishment figures" who had succumbed to pressure from the oil lobby. These critics don't disprove the quantitative data; they don't even dispute them. They simply reject the evidence because it doesn't support the popular prejudice.

So here is another desirable ingredient in the education of the environmental engineer: a critical study of irrationality in public opinion. Fortunately there is plenty of material for study. A lot of work has been done on the mismatch between the statistical assessment of risks and the public perception and evaluation of the same risks. It is common knowledge that people attach much more importance to the severity of a hazard than to its frequency of occurrence. The question, Would you average only one major accident every 10 years, with only half a million deaths?, would be regarded as lunatic. But half a million deaths once a decade is only the extrapolation for 10 years of the annual carnage on the roads of America, which is accepted with practically no protest. If you put, in rank order, judgments of the social cost of death you get a surprising result, with nuclear power (which has killed scarcely anyone to date) at the head of the list, and alcoholic beverages, smoking, and motorcycling near the bottom (*6*).

The problem is made more subtle because of inconsistencies between the opinions of people about risks and the way they behave. Because infrequent hazards with severe consequences (e.g., air disasters and dam collapses) arouse public disquiet much more than do frequent hazards with less severe consequences (even though on an actuarial basis the resulting risks are the same), public policy decisions to avoid these infrequent hazards may entail great expense. But individuals in their private capacity, whatever fuss they make in public about the dangers from nuclear accidents, air crashes, and the like, behave in a different way when they come to choose insurance premiums for themselves and their families. Their evaluation of the very serious hazard is "It will never happen to me." They are much more interested in insurance against high-frequency, low-consequence events, such as being burgled or losing their baggage, than they are in insurance against low-frequency, high-consequence events such as floods and earthquakes. Two persons may well agree about the statistical probability of some environmental hazard; what is unpredictable is how they perceive and evaluate the hazard.

This is why the subject of risk-benefit analysis is so important for environmental engineers; political decisions vitally important in your profession are determined largely by this unpredictable factor. Engineers have to accept the unpalatable fact that the subjective assessment of a risk is, for most people, more *real* than the objective statistical assessment of the risk.

**The management of conflict**

Perhaps I should break off for a moment to apologise to you for proposing two extensions to the core curriculum in the environmental engineer's education: the first, knowledge of how to incorporate unquantifiable values into the decision equations for environmental policies, perhaps taught through a course on environmental ethics; and the second, knowledge of how to reconcile the technologist's judgment about an environmental issue based on hard data (lead levels in air, smoking and lung cancer, probabilities of nuclear accidents) with popular judgment, which may have no rational relation to the hard data, taught maybe through a course on risk-benefit analysis. It's reassuring to read, in the position paper by Gloyna and Cooper, that the AAEE are willing to allow an average of 17% of curriculum time to be given to humanities and social sciences. That's where this knowledge could be included. But, at the risk of choking you with suggestions, I have more to add. Since the environmental engineer will inevitably become involved in controversy, he must know something about the management of conflict.

***Engineers have to accept the unpalatable fact that the subjective assessment of a risk is, for most people, more real than the objective statistical assessment of the risk.***

The adversaries in environmental conflicts are often ill-matched. In the British county of Leicestershire, a great controversy is presently going on between the National Coal Board, which proposes to sink mines in the Vale of Selvoir, and the villagers and farmers who live there. It is a conflict between one good (a massive addition to Britain's energy supplies) and another good (the preservation of a placid stretch of countryside.) The Coal Board's case is supported by a brigade of engineers, geologists, and economists, and the money to pay lawyers. The inhabitants of the Vale are hard put to raise money for the most modest expert advice. Although British law does provide machinery for public participation, the public are very poorly equipped compared with their opponents. The media describe it as a David-Goliath encounter.

The significant thing about the original David-Goliath encounter was that David won; and the interesting thing is that in many environmental conflicts today, the Davids are winning. Thirty or 40 years ago this would have been inconceivable. The public interest lobby was no match for the experts. Today, public interest lobbies are so vigorous that you can't propose to build a dam or power plant or extend an airport or bury radioactive waste without being absolutely certain of massive, implacable organised opposition. Advocacy runs roughshod over fact. The conflict becomes emotive and unproductive because the arguments hurled from each side are incommensurable. By what calculus *can* you measure the benefits of assured energy against the benefits of a serene landscape? Certainly not by the bogus economic trick of "shadow pricing" the landscape. And the politician, mindful that there are more votes in emotion than in logic, is tempted to trade long-term benefits for short-term approval from his constituents.

This rising tide of public participation, going to the length in Austria and Sweden of national referenda on whether or not to use nuclear power, may be good news for conservationists, but it has a danger, especially for environmental engineers. If participation is wrongly managed, it creates distrust between two categories of people who—in the public interest—ought to have confidence in one another. In a recent symposium on engineering and the environment, the opening speaker talked about the intervention of the "citizen activist" in the U.S. as "little short of a nightmare." Militant conservationists throw words like "vandalism" and "desecration" at engineers who are only doing what society expects of them: directing (in Tregold's words) "the Great Sources of Power in Nature for the Use and Convenience of Man."

Conflicts end in decisions, one way or the other, but a decision is only one of the outcomes and indeed sometimes not the most critical outcome of a conflict. The most critical outcome, if the affair is mismanaged, may be a serious weakening of confidence in the institutions of government. A decision that does not command consent may wither on the vine. What matters just as much is the process by which the decision is reached. The only way to prevent polarization between those whose job is to exploit nature in the public interest and those who, also in the public interest, elect themselves to defend nature, is not to *avoid* conflict (that would be unrealistic), but to *manage* conflict. So here is a third extension to the education of an environmental engineer: He needs to have some understanding of the management of conflict.

All pluralistic democracies like our own find themselves in a dilemma over the machinery of public participation. The tradition is that we elect representatives who faithfully look after our interests, and that they are advised about technical matters by a staff of faithful public servants, also trying to look after our interests. Confidence in this tradition has been greatly weakened since the war, for reasons difficult to diagnose. Active minority groups, claiming to represent public opinion more accurately than their elected representatives or the civil service, now demand to be drawn into the process of decision making. Their influence is magnified by the media because protest and dissent are "news"; consensus and compromise are not "news." So we are at present in a stage of very interesting experimentation. The first steps in public participation were to publish consultative documents and to seek comments on decisions virtually taken already. This sort of cosmetic treatment is nowadays dismissed as "mere tokenism." The next step was to equip the objectors with all the necessary information and even to finance them to prepare their case. This is what the famous Berger Commission did for the enquiry about the Mackenzie River gas pipeline in northern Canada (*7*).

The Berger Commission adopted a model strategy in other ways, too. It didn't just sit in Ottawa, listening to the sort of people who can come to Ottawa to give evidence. It took to the road—or rather to the Mackenzie Valley itself—and held hearings on Indian reservations, in village halls, tents, and hunting camps. And it created confidence not only in the integrity of the commission itself, but (a much more important result) in the Canadian *process* of decision making. One decisive value judgment it made was to show respect for the Indians' concept of land ownership. "The land," said one witness, "belongs not only to the people presently living, but it belongs to past generations, and the future generations that are yet to be born."

The San Diego Gas and Electric Company went one step further when they had to decide on a site for a new power station in southern California. They called a general meeting of the interested parties and got the citizens themselves to set up a committee, which they financed and serviced. Then the company backed out and left the committee to tour the area and hold its own hearings. The committee came up with a recommendation for a site, which the company adopted (*8*).

***The only way to prevent polarization between those whose job is to exploit nature in the public interest and those who, also in the public interest, elect themselves to defend nature, is not to avoid conflict (that would be unrealistic), but to manage conflict.***

These are examples of tentative experiments to devise a fresh machinery, suitable for the age of TV documentaries, investigative journalism, phone-ins, and citizen forums, to secure public confidence for major decisions that will permanently affect the environment. They are experiments that must not be left to lawyers and politicians: The environmental engineer is a key figure in this developing drama. (It *is* a drama. The future of our environment depends on how the plot develops.) Many problems still need to be resolved: Who (for instance) is eligible to participate? How can participants all have equal access to the necessary data? And how can they be educated—without the education being rejected as propaganda—to understand the data if it is disclosed to them?

Environmental engineers can make a great contribution to this process of social innovation, particularly in the art of interpretation of highly technical issues. For an excellent example of this, you do not need to go more than a few blocks from this room. The Ontario Royal Commission on Electric Power Planning published in 1978 a report on nuclear power in Ontario that is (in my view) a masterpiece of popularisation without propaganda (*9*).

### The lesson of the Furbish lousewort

Finally I come to what I think may be the most unexpected point in this address, and it's the most difficult point to make. Put bluntly, it is that the Furbish lousewort—symbolising nature—holds a secret essential to the survival of industrial society, which man has not yet unravelled. And environmental engineers are the sort of people qualified to try to unravel it.

Natural ecosystems such as forests, prairies, and lakes are the projects of millennia of evolution. Let me enlarge upon something I wrote about last year that is relevant to environmental engineers.

Natural systems have their networks of symbiosis, their food chains from plankton to mammals, their recycling plants (aptly summarized by Hamlet: "We fat all creatures else to fat us, and we fat ourselves for maggots"). Man-made ecosystems have similar networks of symbiosis. Recollect what happens when you switch on the light, flush the toilet, put waste in the trash bin, stop to fill up at a gas station, make a phone call. These are signals to fellow members of the ecosystem; after every signal you expect and depend upon a response. If the expected responses were to fail widely for all five of these signals, city life would collapse. Already some failures are quite common due to technical faults, human errors, or deliberate anarchy. A power failure in New York, a strike among sewage workers in London, sabotage by a gang of urban guerrillas in Belfast—all these have happened; all these are examples of the vulnerability of cities.

The ugly fact is that man-made systems lack a fundamental quality found in natural ecological systems: They have none of the built-in stability that preserves or restores equilibrium in forests, lakes, and oceans. The reason for the difference is that, in nature, equilibrium has evolved alongside diversity and complexity. Instabilities in natural ecosystems are eliminated by natural selection. In man-made systems, we have evolved the diversity and complexity (networks of transport, power, and sewage disposal) without introducing—indeed without having even invented—the corresponding stabilisers to keep man-managed systems in equilibrium. In taking a shortcut to a materialist's utopia, we have failed to include the linchpin of natural ecosystems: their extraordinary resilience (*10*).

Last summer, I saw in the Canadian Rockies a sober reminder of this. The railroad track through the Rockies is one of the engineering wonders of the world. There is one place where the route has been changed. The old route ascended to a high valley floor, close to some splendid mountain peaks. So a grand hotel was built there; alpine guides were brought out from Switzerland; and the place was developed for tourism. Then, for some reason, a better route for the railroad was found, and the track and the hotel were abandoned. That happened not so many years ago, but the forest has taken charge again. Among the dense undergrowth you can, here and there, see turf-covered remnants of the grand hotel, and there is a narrow bush-covered clearing between the trees where the track ran. In a few decades the pretentious man-made ecosystem has vanished, and the natural ecosystem has colonised it all again.

How is it that the evolution of man-made ecosystems has not produced its own fail-safe stabilisers, such as natural ecosystems possess? I think it may be because the need for stabilisers in man-made systems is comparatively recent. In the days before mass aggregation into cities and mass transport and mass communication, *space* was the great stabiliser. If you lived in a community of, say, 5000 people in the Midwest, the tensions of Washington, not to mention the tensions of Tehran and Calcutta, were too far away to matter.

Today, space no longer isolates a community from the perturbations of Western society. The days are over when an industrial dispute in the local mill could be settled by negotiation between employer and employee; a settlement now has to be nationwide, and—as we have learnt in the last 10 years—the settlement can be upset and the equilibrium of society tumbled by shock waves generated by a meeting of a dozen Arabs in a parched and desert country thousands of miles away.

There are other, more subtle, dangers of aggregation in cities. The stability of communities depends upon unwritten social contracts of courtesy and neighbourliness. It is difficult to sustain these in the man-made ecosystem of a city, where you eat and drink among strangers, and where the cocktail party with 50 acquaintances has to take the place of a quiet drink with a couple of friends because it saves time. The urban environment we have created makes it more and more difficult for people to be concerned with one another and equally difficult for them to get away from one another. There are, in short, *social* limits to growth, and the dangers of exceeding these limits are, it is my conviction, more ominous than are the well-publicised dangers of exceeding material limits.

The remedy pressed upon us by some writers is an atavistic retreat to the simple life. To expect industrial society to undergo what biologists would call de-differentiation into a "small-is-beautiful" social order is simply not on. There is no retreat from a technological society, and the only way cities are likely to be abolished is by nuclear war. So we are saddled with a daunting problem. How can we build, into rapidly evolving technological ecosystems, components to confer stability, fail-safe systems of the kind which preserve natural ecosystems from extinction? It is, I believe, the top priority problem for our generation. We haven't even designed the components that need to be built in yet, let alone decide how to build them in. It's a problem that needs collaboration with political scientists, social psychologists, and the like. But is it not, perhaps, the supreme challenge to environmental engineers? Engineers have created the nuts and bolts of the man-made ecosystem; environmental engineers are very active in protecting the natural environment from overexploitation. Should they not take on the task of stabilising the human ecosystem itself?

***How can we build, into rapidly evolving technological ecosystems, components to confer stability, fail-safe systems of the kind which preserve natural ecosystems from extinction? It is, I believe, the top priority problem for our generation.***

You may not ever travel to Maine to see the Furbish lousewort. But the weeds in any patch of natural vegetation issue the same challenge. We have survived, say the weeds, since the Cretaceous. Man is a mere novice in evolution compared with us. He hasn't yet learnt the secret of the weeds: how to create fail-safe communities.

### Acknowledgment

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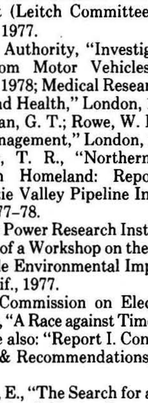

**Lord Ashby** *is a British botanist and university administrator, Baron (Life Peer) of Brandon, Suffolk, England, and is listed in "International Who's Who".*

# The geochemical control of seawater (Sillen revisited)

*The current view of how seawater composition is regulated emphasizes the balance between inputs and outputs*

**Russell E. McDuff**
**François M. M. Morel**
*Massachusetts Institute of Technology*
*Cambridge, Mass. 02139*

Sillen's 1961 discussion of the physical chemistry of seawater (and its subsequent elaboration in 1967) is a seminal publication in the field of chemical oceanography. Yet one is pressed to find more than a handful of present-day chemical oceanographers who actually subscribe to Sillen's thermodynamic view of ocean chemistry. Current models for seawater composition emphasize the dominance of balances between the various inputs and outputs; balance sheets have become more important than solubility relationships in explaining oceanic chemistry. The difference between these divergent views is not just a matter of mathematical and chemical formalism. In one case, one would expect a very constant composition of the ocean and its sediments over geological time; in the other, historical variations in rates of exogenic processes should have caused changes in ocean composition and may be reflected in the sedimentary record.

A principal aim of Sillen's classic paper was to provide an explanation for the low alkalinity of the ocean compared to its ionic content; as Sillen noted, the acids and bases of the oceans are almost balanced: "We are about 0.5% from the equivalence point."

In the historical view of Goldschmidt, the major ion composition of the oceans is the result of a one-way reaction:

$$\text{600 g Igneous rock} + \text{1 kg Volatiles} \rightarrow \text{600 g Sediments} + \text{1 kg Seawater}$$

The almost perfect balance of acids and bases during this process is an unlikely situation. (Comparison of material fluxes to the oceans over geological time with estimates for the masses of dissolved and sedimentary material provides, of course, an even more compelling reason to doubt that a one-way process is responsible for the present-day ocean composition.)

In the modern view of a steady-state balance between inputs and outputs for major ions, the low oceanic alkalinity seems just as precarious: Relatively small changes in anionic fluxes compared to cationic fluxes could result in large historical excursions in seawater alkalinity. Unless some rather tight feedback mechanisms are provided, the remarkable acid-base balance of the oceans still appears as an unlikely coincidence. Sillen provided a chemically satisfying solution to this problem by proposing a heterogeneous equilibrium (over geological time, not necessarily locally or over observable intervals), for example involving reactions such as:

$$\underset{\text{Kaolinite}}{1.5\ Al_2Si_2O_5(OH)_4(s)} + K^+ \rightleftharpoons \underset{\text{K-mica}}{KAl_3Si_3O_{10}(OH)_2(s)} + 1.5\ H_2O + H^+$$

$$\underset{\text{Calcite}}{CaCO_3(s)} + 2H^+ \rightleftharpoons CO_2(g) + Ca^{2+} + H_2O$$

There is but one problem with this elegant model: The existence of the necessary authigenic silicate phases in sufficient quantities has yet to be demonstrated in oceanic sediments. The problem before us is to reconcile the Sillenian concept of a heterogeneous chemical control of seawater alkalinity with the modern ideas of the processes actually controlling the major ion concentrations in the oceans.

Let us first consider the question of input and output balances for the major seawater ions whose concentrations and inventories are summarized in Table 1, columns 1 and 2. A variety of processes are involved in transfers of material in and out of the oceans (Figure 1). Our objective here is to identify the dominant sources and sinks in the oceanic balance sheet.

## Ins and outs

The fluvial inputs of materials (Table 1, column 3) are calculated from the mean river concentrations estimated by Livingstone (1963) and the average of the annual discharge estimates of Lvovitch (1973) and Kozoun (1974), $4.55 \times 10^{16}$ L/y. The principal uncertainties are associated with the concentration estimates; effort needs to be devoted to a thorough revision of Livingstone's summary. Residence times, in millions of years, are readily calculated by dividing column 2 by column 3.

For chloride, two sinks are of importance: atmospherically recycled sea salt and deposited evaporites. Seafloor hydrothermal activity may also be significant (Edmond et al., 1979a). The deposition of evaporites is related to tectonic activity and as such is difficult to quantify. Certainly, no important deposits are forming today. Conversely, the residence time is so large (~ 100 My) that an imbalance between input and output rates has little influence on oceanic concentration over periods less than tens of millions of years. Finally, about half of the chloride at the earth's surface is stored in the sea (Garrels and Mackenzie, 1971), placing well-defined limits on its concentration excursions. For these reasons, we will assume that the chloride cycle is closed, recognizing that for the contemporary ocean this is almost certainly not the case.

Other elements cycle with chloride. This component is usually represented

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FIGURE 1
**Transfer processes**

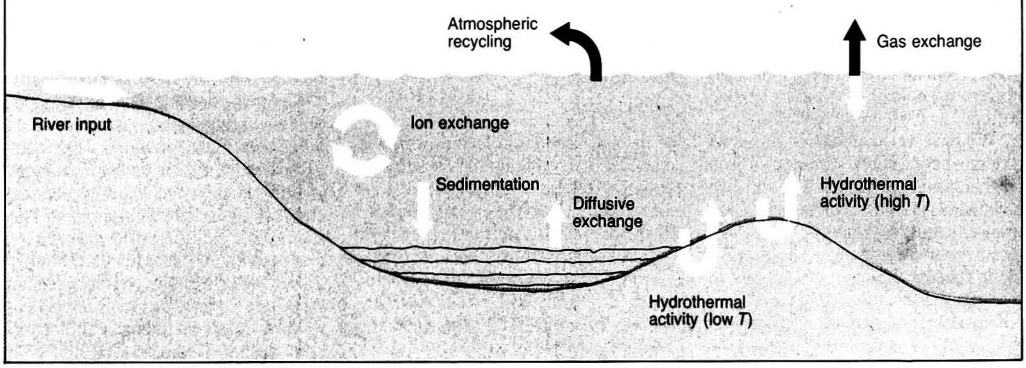


TABLE 1
**Input–output balance for major seawater ions and alkalinity**

| | Concentration (mmol/kg) | Ocean inventory ($10^{18}$ mol) | River input | Atmospheric/ evaporite cycling | Ion exchange | Hydrothermal activity | Low-temperature basalt weathering | Carbonate deposition | Net |
|---|---|---|---|---|---|---|---|---|---|
| | | | ($10^{12}$ mol/y) | | | | | | |
| Cl | 545 | 710 | 10.0 | (−10.0) | | ? | | | .0 |
| Na | 468 | 608 | 11.8 | −9.3 | −1.9 | ? | | | 0.6 |
| Mg | 53 | 69 | 8.0 | −0.5 | −1.2 | −7.8 | | | −1.5 |
| $SO_4$ | 28 | 37 | 3.7 | −0.5 | | −3.8 | | | −0.6 |
| K | 10 | 13 | 3.2 | −0.1 | −0.4 | +1.3 | −4.0 | | .0 |
| Ca | 10 | 13 | 17.1 | −0.1 | 2.6 | +3.1 | +2.0 | −24.7 | .0 |
| Alk | 2.4 | 3.1 | 47.8 | | 0.5 | −0.4 | | −49.4 | −1.5 |
| $\Sigma C$ | 2.3 | 3.0 | 43.7 | | | +0.5 | | −49.4 | −5.2 |

as atmospherically cycled sea salt (Garrels and Mackenzie, 1971). Some workers have recently suggested, however, that evaporitic contributions are of substantial importance (Holland, 1978; Stallard, 1980). While sea salt cycling through aerosols is in seawater proportions, evaporitic cycling is not; $CaSO_4$ and NaCl are preferentially enriched in evaporite deposits. To estimate fluxes, we assume a 1:2.5 mixture of these respective pathways (Holland, 1978). Sea salt proportions are assumed for the aerosol component (normalized to chlorine), and Na/Cl = 1 and Ca/Na = .021 (the seawater value) for the evaporitic component. The use of the seawater Ca/Na value may underestimate $CaSO_4$ cycling. The resulting fluxes are summarized in Table 1, column 4.

The detrital load of rivers has a substantial cation-exchange capacity ($\sim 4 \times 10^{12}$ eq/y; Russell, 1970; Sayles and Mangelsdorf, 1977). Upon entering the sea, exchange reactions with this material can alter the primary fluxes of the various cations. Sayles and Mangelsdorf (1977, 1979) have investigated the exchange characteristics of detrital material. Based on their exchange coefficients, fluxes can be estimated (Table 1, column 5). The important effect is in the sodium balance, its cycle being approximately balanced.

In the past decade, ridgecrest hydrothermal metamorphism has been recognized as playing an important role in several geochemical cycles. Two vent systems have been sampled to date, one on the Galapagos Rift at 86° W and the other on the East Pacific Rise at 21° N. The chemistry of the exiting fluids at these locations reflects dilution of a high-temperature end member (generated by reaction of circulating seawater with newly formed basalt) with seawater entrained during ascent of the hot fluid. The high-temperature end member is remarkably uniform: ~ 350 °C, free of magnesium and sulfate, alkalinity depleted, potassium and calcium enriched, and variably enriched or depleted in sodium and chloride. Because the mixing is conservative, the elemental fluxes are in well-defined proportions; hence, knowing the global flux of one allows estimates of the global fluxes of all. Helium provides this opportunity. In the exiting fluids, the $^3He/^4He$ ratio is about 7.8 times the atmospheric (and thus "normal" oceanic) ratio. Injection of these fluids into the ocean results in a prominent mid-depth anomaly in the $^3He/^4He$ ratio. Maintaining this anomaly requires a global flux of $^3He$ of 1000 mol/y (Craig et al., 1975). Elemental fluxes can thus be estimated from their ratio to $^3He$ in the vent waters (Edmond et al., 1979a). This reasoning was originally applied to estimating the flux of heat from such systems (Jenkins et al., 1978). The vent analyses give a heat/$^3He$ transfer of $5 \times 10^{13}$ kcal/mol, implying a heat flux of $5 \times 10^{16}$ kcal/y, in good agreement with independent geophysical estimates ($4–6.4 \times 10^{16}$ kcal/y). The elemental fluxes summarized in Table 1, column 6 provide a strikingly good balance for the magnesium and sulfate cycles. Potassium and calcium are added to the sea. The chloride and sodium mass/$^3He$ ratios exhibit too much variability to define their fluxes. However, their mass/$^3He$ ratios show a nearly 1:1 correspondence and so the net hydrothermal fluxes could be accommodated as were atmospheric and evaporitic recycling. It is important to remember also that the fluxes estimated assume that the observations to date are representative. In this regard, the agreement of results from two very different geologic settings is encouraging.

We have yet to consider fluxes for the most commonly accepted sinks of K, Na, and Mg: reconstitution of degraded clays and authigenesis of aluminosilicates. Attempts to identify the occurrence of these processes have had little success. Holland (1978) has reviewed the various studies and concludes that the fluxes are small at best. Sayles (1979) amplifies this point; the K and Mg contents of marine sediments simply aren't large enough to accommodate the dissolved river flux.

Where then does potassium go? Although few firm data are available, uptake during low-temperature alteration of basalt is a plausible sink. Seafloor basalts subjected to low-temperature alteration show potassium enrichment, particularly in the secondary minerals (Thompson, 1973; Seyfried et al., 1978; Hart and Staudigel, 1978). The extent of uptake is difficult to assess, however, as both the amount of basalt altered and the average uptake are not well known. We assume quantitative removal to close the cycle. What balances the charge? Laboratory studies of basalt alteration at low temperatures (Seyfried and Bischoff, 1979) and interstitial water studies of deep drill cores (McDuff, 1980) suggest that the charge balance is maintained principally by the release of calcium. Magnesium and sodium may be involved in minor ways, however even the signs of their fluxes are not clear. The resulting fluxes are given in Table 1, column 7.

The only significant, documented, oceanic alkalinity sink is calcium carbonate deposition:

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3(s) + CO_2(g) + H_2O$$

This process balances the final three components (including the $CO_2$ flux to the atmosphere; Table 1, column 8). Surface productivity transfers material in excess of the river flux to the deep sea. Dissolution is sufficiently rapid below the calcite saturation horizon to create a situation near equilibrium.

The most striking aspect of the cycle portrayed here is the exchange of sodium, magnesium (less sulfate), and potassium for calcium (Figure 2). The importance of this kind of exchange has been noted previously in the context of ridgecrest hydrothermal metamorphism (Edmond et al., 1979b); on the basis of this analysis, we suggest it is common to other removal processes. After all—and to make engineers happy—alkalinity is calcium carbonate, ultimately.

**Steady state**

In our discussion so far, we have concentrated on obtaining a reasonable balance for the fluxes of major ions and alkalinity in the oceans, but we have not explicitly accounted for their actual (steady-state) concentrations. In particular, we are able to account for an alkalinity loss by calcium carbonate precipitation to balance the alkalinity input from rivers, but we have yet to explain why the alkalinity of the ocean is what it is.

Consider the charge balance condition for the major seawater ions:

$$2[Ca^{2+}] = [Cl^-] - [Na^+] - [K^+] + 2\,[SO_4^{2-}] - 2\,[Mg^{2+}]$$

(Other ions, including $HCO_3^-$, are initially neglected.) On the basis of the previous discussion, the concentrations of all the ions on the right side of this equation are determined by the relative rates of chemical weathering, physical weathering, and flow-through hydrothermal systems. For example, since magnesium and sulfate are completely stripped from seawater by reaction during hydrothermal circulation, their steady-state seawater concentrations are simply proportional to the ratio of the rates of chemical weathering and hydrothermal flow.

For potassium, the situation is not quite as simple. However, if the dominant removal process is scavenging by basalts during low-temperature circulation on the ridge flanks, then $K^+$ must be controlled by the same geochemical processes as $Mg^{2+}$ and $SO_4^{2-}$ (i.e., the ratio of weathering rate to hydrothermal flow rate) although the functionality may be more complicated.

A similar steady-state analysis for sodium and chloride shows that the concentrations are controlled by the relative rates of chemical weathering, physical weathering (rate of formation of detrital clays), and rate of evaporite formation. Although the steady-state analysis may be particularly bad for these two elements, it is worth recalling that their high seawater concentrations preclude any large historical variations.

Finally, the calcium concentration is obtained from the charge balance, making it a complicated function of the various geochemical processes (equivalent to considering the various input and output processes individually):

$$[Ca^{2+}] = f(\text{chemical weathering rate, physical weathering rate, hydrothermal flow rate, rate of evaporite formation})$$

So far the oceanic chemistry model that we have presented is strictly non-Sillenian: Concentrations are controlled by input and output balances and ultimately by geological processes, not by chemical properties. The chemistry (and the buffering) are introduced in our oceanic model simply by considering the heterogeneous carbonate equilibria. Following Sillen, we take the ocean to be in equilibrium both with atmospheric $CO_2$ and with sedimentary $CaCO_3$ over geological time:

$$\frac{[Ca^{2+}][HCO_3^-]}{[H^+]} = \frac{K_s}{K_{a2}} \; (\simeq 10^{3.3})$$

$$[HCO_3^-][H^+] = K_{a1}K_H P_{CO_2} \; (\simeq 10^{-7.4}\, P_{CO_2})$$

The constants are selected for an "average" ocean. Making the assumption that the $CO_2$ content of the atmosphere is controlled at a $P_{CO_2}$ of $10^{-3.5}$ atm by other processes (as discussed later), we now have a complete model for the alkalinity of the ocean. Solving the above equations leads to:

$$pH = 5.35 - 0.5 \log P_{CO_2} - 0.5 \log [Ca^{2+}]$$

$$Alk = [HCO_3^-] = 10^{-2.05} \frac{(P_{CO_2})^{0.5}}{[Ca^{2+}]^{0.5}}$$

(A more complete derivation appears in the accompanying box.)

### An expanded model

**More complete expressions for pH and alkalinity can be derived including $HCO_3^-$ in the charge balance. Let $[Ca^{2+}] = \lambda + [HCO_3^-]/2$, where $\lambda$ is the sum of the other terms of the balance. $[H^+]$ is found by solving the cubic equation:**

$$[H^+]^2 - 10^{-10.7}\, P_{CO_2} (\lambda + 10^{-7.9}\, P_{CO_2}/[H^+]) = 0$$

**Since $\lambda \gg 10^{-7.9}\, P_{CO_2}/[H^+]$, the approximate expression for pH is:**

$$pH = 5.35 - 0.5 \log P_{CO_2} - 0.5 \log ([Ca^{2+}] - [HCO_3^-]/2)$$

**The error introduced by neglecting the bicarbonate term is less than 0.02 pH units. Inclusion of carbonate in the alkalinity expression leads to:**

$$Alk = 10^{-2.05}\, P_{CO_2}^{0.5}/[Ca^{2+}]^{0.5} + 10^{-5.7}/[Ca^{2+}]$$

In this model, the alkalinity of the oceans is low simply because $CaCO_3(s)$ is reasonably insoluble. Note that the actual value of seawater alkalinity is rather insensitive (exponents of 0.5) to the externally controlled partial pressure of $CO_2$ and calcium concentration. However, the concentration of calcium itself is probably quite sensitive to individual variations in weathering rate or flow rate through hydrothermal systems. The interdependence among the principal geochemical processes may well have to be invoked to explain the apparent historical constancy in ocean chemistry. For example, the continental weathering rate and the hydrothermal flow rate are both ultimately dependent upon tectonic activity and are therefore likely to be covariant (Holland, 1978).

In order to be viable, our model has to satisfy steady-state conditions for all geochemical compartments, not just the oceans. The major difficulties that we have created so far concern carbon: If $CaCO_3$ is the only alkalinity sink in seawater, the return flux of $CO_2$ to the atmosphere is insufficient to balance the atmospheric budget (Table 2). For example, the alkalinity, contributed by the weathering of sodium and potassium silicate phases and eliminated after cation exchange by $CaCO_3$ precipitation, must result ultimately in an atmospheric carbon drain. Therefore carbon recycling mechanisms must exist in order to buffer the carbon dioxide content of the atmosphere.

The most obvious mechanisms for recycling and buffering of $CO_2$ in the atmosphere are metamorphic reactions of carbonate rocks into silicate rocks as proposed by Urey (1956), e.g.:

$$CaCO_3(s) + SiO_2(s) \rightleftharpoons CaSiO_3(s) + CO_2(g)$$

In other words, a direct corollary to our simplistic alkalinity model is that all major reverse weathering reactions (outside of $CaCO_3$ precipitation) and concomitant $CO_2$ regeneration take place as metamorphic, not sedimentary, processes.

(An examination of thermodynamic data shows that carbonates and silicates of magnesium, rather than those of calcium, may provide the most suitable buffering mechanism. Magnesium carbonates are, after all, more soluble than calcium carbonates and hence provide a better source of $CO_2$. See Holland, 1978.)

Many authors consider that atmospheric $CO_2$ is controlled by biological rather than geochemical processes. The reason is apparent if we consider Table 3. It seems intuitive that pro-

FIGURE 2

**Exchange of various solutes for calcium**

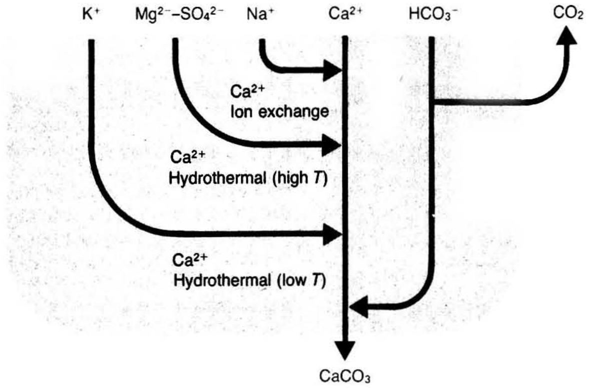


TABLE 2

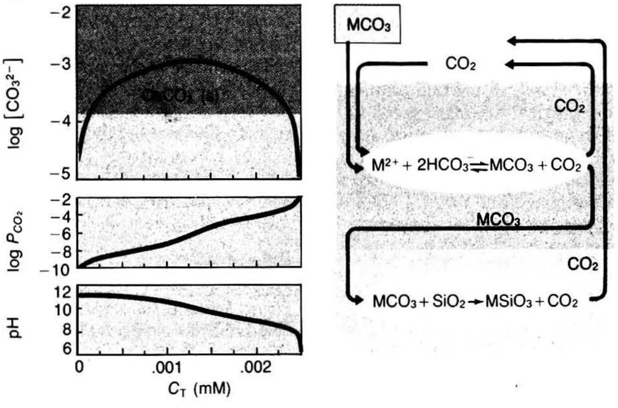
**Oceanic fluxes of carbon**

| | Flux | Atmospheric demand |
|---|---|---|
| River input | 43.7 | |
| Derived from atmosphere | 35.0 | −35.0 |
| Derived from carbonates | 8.7 | |
| Hydrothermal input | 0.5 | |
| Carbonate deposition | 49.4 | |
| Deposited as carbonates | 24.7 | |
| Lost to atmosphere | 24.7 | +24.7 |
| Net atmospheric demand | | −12.4 |

Units: $10^{12}$ mol/y

FIGURE 3

**The role of carbon**



The left side of the figure shows the effect of carbon fixation on carbonate solubility, $P_{CO_2}$, and pH. Calcium and alkalinity are fixed at $[Ca^{2+}]$ = 10 mM and Alk = 0.0025 eq/L. Uptake of $CO_2$ from solution leads to carbonate precipitation, until $P_{CO_2}$ decreases to ~ $10^{-9}$ atm and pH increases to ~ 11. The right side of the figure illustrates the important pathways for regeneration of atmospheric $CO_2$.

TABLE 3

**Carbon reservoirs and fluxes**

| Reservoirs | $10^{18}$ mol |
|---|---|
| Atmosphere | 0.054 |
| Biosphere | 0.4 |
| Ocean | 3.2 |
| Sediments | 6100 |
| $CaCO_3$ | 4200 |
| $MgCO_3$ | 900 |
| $CH_2O$ | 1000 |
| **Fluxes** | **$10^{12}$ mol/y** |
| Air–water exchange | 8000 |
| Photosynthesis and respiration | 5400 |
| Fossil fuel burning | 365 |
| Sedimentation | 27.2 |
| $CaCO_3$ | 24.7 |
| $CH_2O$ | 2.5 |
| Net organic storage[a] | 0.5 |

[a] Calculated from (reservoir mass/2 billion years).

**Sources:** Table 1, Garrels and Perry (1974), and Garrels et al. (1973)

cesses with larger fluxes should provide better buffering mechanisms than those with smaller fluxes. Note however that the partial pressure of $CO_2$ in the atmosphere does not appear particularly well buffered against relative changes in photosynthesis and respiration rates. Corresponding seasonal and geographical $P_{CO_2}$ variations are readily measurable. In fact, atmospheric $P_{CO_2}$ appears rather poorly buffered against changes in an even smaller flux, that of fossil fuel oxidation. One may suggest that it is in the very nature of photosynthesis and respiration to be almost exactly in balance. It is only the very small photosynthetic excess (on average, some 0.01% of photosynthetically fixed carbon) stored in organic sediments over geological time that needs to be compensated by a geochemical supply of $CO_2$ (in excess of the carbonate deposition), according to the Urey reaction (Garrels and Perry, 1974). We can write the total reaction as:

$$(Ca,Mg)CO_3 + SiO_2 + H_2O \rightleftharpoons (Ca,Mg)SiO_3 + CH_2O + O_2$$

(Most of the oxygen is consumed oxidizing iron and sulfur.) As observers it is hard for us to see the important small net flux—the storage of refractory organic carbon—compared to the geochemically unimportant large fluxes of photosynthesis and respiration, much as it is hard to see the flow of a small river into an estuary with a large tidal exchange.

The geological storage of organic carbon is worth considering further in order to understand the $CO_2$ buffering mechanisms. The original carbon source has to be carbonate rocks since other reservoirs are simply too small (Table 3). However, it is impossible that carbon was transferred to the oceans by simple dissolution of the carbonate. Before $CaCO_3$ dissolution could have replenished the atmospheric $CO_2$ consumed by excess photosynthesis, the partial pressure of $CO_2$ would have had to plummet to nanoatmosphere levels and the oceanic pH would have had to exceed 10.5. As noted by many authors, the present-day increase in $P_{CO_2}$ should ultimately be reflected in dissolution of carbonates. Vice versa, a hypothetical decrease in $P_{CO_2}$ could only result in an increase in carbonate deposition or a decrease in carbonate weathering. Carbon would then be further lost from the atmosphere and the hydrosphere rather than being regenerated. The carbon dioxide in the atmosphere, continuously depleted by the weathering of silicates, the deposition of carbonates, and (marginally) the synthesis and storage of refractory organic carbon, must then be replenished by metamorphic processes as symbolized by the Urey reaction. Thus, while seawater alkalinity is directly controlled by the formation of calcium carbonate as its major sedimentary sink, it is also controlled indirectly by carbonate metamorphism which buffers the $CO_2$ content of the atmosphere.

There is little that is very novel in this discussion of the geochemical control of seawater alkalinity. Modern data on elemental fluxes in the ocean have been coupled to the most classical of equilibrium carbonate chemistry. The picture which emerges is one of an ocean composition dominated by geophysical rather than geochemical processes. The acid-base chemistry reflects, however, a fundamental control by heterogeneous chemical processes. That thought, more than the detailed chemistry, is in fact the major message of Sillen.

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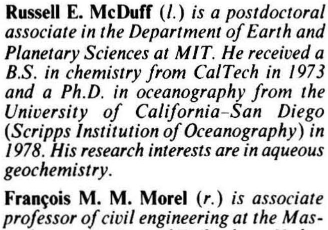
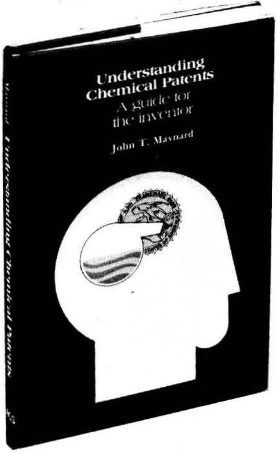


**Russell E. McDuff** (*l.*) *is a postdoctoral associate in the Department of Earth and Planetary Sciences at MIT. He received a B.S. in chemistry from CalTech in 1973 and a Ph.D. in oceanography from the University of California–San Diego (Scripps Institution of Oceanography) in 1978. His research interests are in aqueous geochemistry.*

**François M. M. Morel** (*r.*) *is associate professor of civil engineering at the Massachusetts Institute of Technology. He has been a member of the* ES&T *advisory board since 1978; this spring he was named associate editor of the research section of* ES&T. *Dr. Morel's principal research interest is in interactions of chemical pollutants and microbiota in aquatic systems.*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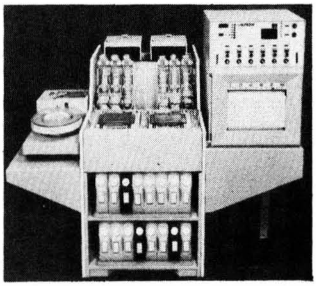

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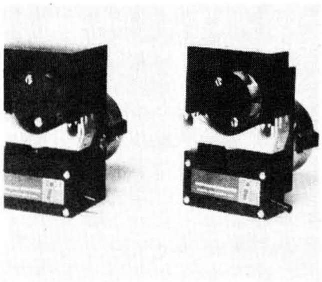
At least 8 h of continuous sampling is possible. The portable pump may be carried in a shirt pocket or clipped to a belt. Two flow ranges are provided: 5-200 mL/min and 5-20 mL/min. A 2.4-V, 2-cell rechargeable nickel-cadmium battery pack provides 600 operating hours. Mine Safety Appliances **108**

**Gas leak detector**
Unit senses $10^{-8}$ cm$^3$/s halogens and $10^{-11}$ cm$^3$/s $SF_6$ tracer gas. Response time is 0.5 s and recovery time is 1 s. A hand-held probe is attached to the console by a 4-m cable. The probe provides audio and visual indication of leak rates exceeding preselected limits. A calibration plot on the console permits direct leak-rate reading. Power is supplied by standard ac line or by a rechargeable 6-V gel pack, which provides up to 8 h of operation. Ion Track Instruments **111**

**Portable level detector**
Hand-held gun detects liquid or powder levels. The probe is lowered into the tank, and an alarm sounds when contact is made with liquid or powder. Markers on the probe indicate distance to the surface. A high-intensity infrared LED shines across the probe gap and a solid-state circuit is used to differentiate between air and liquid or solid. Markland Specialty Engineering **112**



**Small peristaltic pump**
Self-contained unit propels fluid through its own tubing. Flow rate is continuously regulated by a spring-loaded shoe that compensates for pressure variations in the tube. Delrin rollers are driven by a standard 30-rpm electric motor. The pump may be mounted on a post or panel. Instrument Industries **113**

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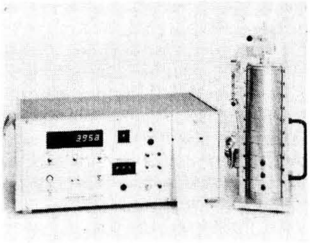
*Need more information about any items? If so, just circle the appropriate numbers on one of the reader service cards bound into this issue and mail in the card. No stamp is necessary.*

***Companies interested in a listing** in this department should send their releases directly to Environmental Science & Technology, Attn: Products, 1155 16th St., N.W., Washington, D.C. 20036*

**Groundwater hydrocarbon monitor**
A $^{1}/_{2}''$ depth of oil on the water table level will cause the oil-water interface sensor float to rise and activate an above-ground alarm. Installation involves inserting a 12″-diameter noncorrosive pipe screen in the ground. The entire system is explosionproof and may be installed in hazardous areas. McTighe Industries **114**



**Aerosol particle analyzer**
Quartz crystals are used as impactors to achieve a range of 0.05–25 $\mu$. The 10-stage cascade separates the particles into as many size groups; the particles are then weighed electronically and the information sent to a built-in hard-copy printer. Output is in the form of a bar chart and list of mass concentrations for each size range. The instrument measures concentrations of 10–60 mg/m$^3$. The particle samples collected remain undisturbed for subsequent analysis. California Measurements **115**

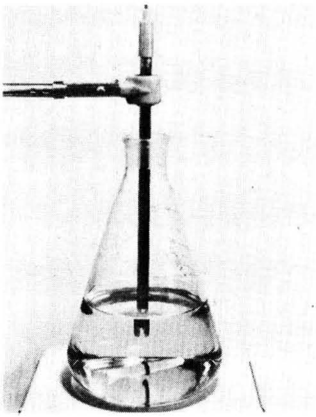
**Absorbance standards for UV/vis**
Set of 9 filters provides absorbance calibration for UV/visible spectrophotometers. Checks up to 3Å are possible. The effect of reflections is compensated for by providing a clear glass filter for zeroing. The filters are mounted in frames that put no physical stress on the filters. Sargent-Welch Scientific **116**

**Unattended chart recording**
Instrument inserted between laboratory equipment and chart recorder automatically switches the recorder attenuation setting to prevent the pen from going off scale. As full scale is approached, the unit switches upward through the ranges ×1, ×10, ×100, and ×1000 as needed; when the signal falls back toward the baseline, the range is reset. This allows the recorder to be set for highest sensitivity for the weakest signals. Peak height and peak shape are retained for all analytical components. Output is for 0–1-V analog recorders. Barringer Research **110**

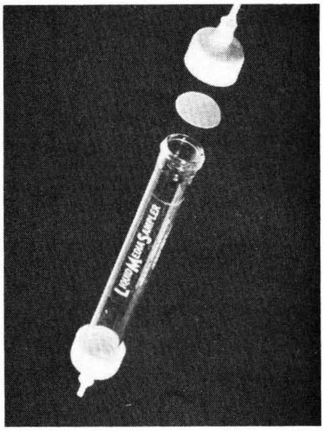
**HPLC electrochemical detector**
Detector can use solid electrodes as well as dropping mercury electrodes, allowing operation in the reductive mode for detection of esters and aldehydes and in the oxidative mode for detection of catecholamines and aromatic hydrocarbons. Sensitivity is typically $10^{-12}$ M and the linear range is 4–5 decades. Reproducibility is better than 2% for solid electrodes and better than 4% for dropping mercury electrodes. The cell can withstand pressures of up to 100 psi. The design of the cell allows the electrodes to be placed in various configurations. Astra Scientific International **117**

**Soil sampler**
Sampling tube is pushed into the ground by foot pressure; depths of 46″ can be sampled in the basic configuration, and deeper samples can be had with the use of 26″ rod extensions. A "moisture meter tube" can be used to remove a core leaving a hole of the exact size needed for implanting moisture sensing devices. Clements Associates **119**

**Suspended solids monitor**
Device is insensitive to particle size or sample color. A self-cleaning sample system allows for long-term unattended operation. Determination of mean particle volume diameter is possible as an option. Microtrac **120**



**Flask-sized pH electrode**
Combination pH and reference electrode is designed for use in tall laboratory vessels. The 9.5-mm-diameter probe has an overall length of 300 mm—twice that of standard electrodes. The reference electrode features a gel-filled sealed construction that eliminates the need for refilling. A variety of connectors to fit most pH meters is available. Sensorex **118**



**Liquid media sampler**
Designed for field use, sampler can be substituted directly for midget impingers or bubblers in most personal monitoring procedures using an aqueous solution as the sampling media. A "leakproof" design eliminates the need for liquid transfers or rinsings in the field. The unit can easily be disassembled for cleaning or decontamination. Industrial Hygiene Specialties **123**

**Wind monitor**
Self-contained system gathers and analyzes wind speed and direction data. The electronics may be programmed to calculate and store data on wind run above, below, or between specified limits; averages; gust frequency, duration, and energy content; and speed, energy, and power profiles with reference to time. Data may also be sorted by direction. Results are displayed on a 6-digit LED output. Natural Power **124**

**Air sampling pumps**
Pumps are electric-motor-driven diaphragm type. Available flow ranges are 30 cm$^3$ to 5 L/min at back pressures to 40″ $H_2O$. Voltage requirements are 1–12 V dc. An integrated pulsation damping system can be provided in some designs where pulsation of free air is required, such as when using a close-coupled flowmeter. Gilian Instrument **125**

**Stack gas analyzer**
Monitor measures smoke opacity, NO, $SO_2$, $CO_2$, and CO. Features include alignment insensitivity, which permits operation even when the monitor is improperly positioned, and a thermal management system that reduces problems associated with widely varying stack gas or ambient temperatures. Environmental Data **126**

ES&T

# LITERATURE

**Flowmeters.** Literature packet provides information concerning ultrasonic flowmetering. Applications include the wastewater field. MAPCO Inc. **151**

**Chromatographic phases.** Wall chart assists the chromatographer with the proper selection of OV® stationary phases, and gives physical, chemical, and chromatographic properties of the current product line. Foxboro Analytical **152**

**pH electrodes.** Bulletin 4134C provides a guide to pH electrodes, and glass, metallic, and process reference electrodes, as well as thermocompensators. Certain reagents are also discussed. Beckman Instruments, Inc. **153**

**Conductivity.** Data sheet describes Hall Electrolytic Conductivity Detector for specific analysis of halogen-, nitrogen-, or sulfur-containing compounds. Varian Instrument Group **154**

**Vapor recovery.** Literature depicts the DYNA 3 Solvent Vapor Recovery System which uses patented water purge regeneration to recover adsorbed solvent vapors from activated-carbon bed. DCI Corp. **155**

**Organics removal.** Bulletin No. 27-31 describes mobile quick-response portable activated-carbon system for removing organics from water, and spells out which organics can be removed. Calgon Corp. **156**

**GC/MS systems.** Information explains how to make use of gas chromatography/mass spectrometry (GC/MS) systems to conduct analyses to meet EPA regulations. Also helps with consolidated permit regulations. Finnigan Corp. **157**

**Cleanup with bacteria.** Data sheet describes Type A DBC Plus™ dried bacterial cultures that can control grease accumulations in waste-water treatment and sewage collection systems. Flow Laboratories, Inc. **158**

**Emergency cleanup.** Technical data material explains SPILL/CLEAN, an all-purpose gelling agent which contains most acids, caustics, flammable solvents, and other hazardous liquids. United States Testing Co., Inc. **159**

**Deuterium products.** Catalog lists deuterium products and research chemicals, some of which have environmental applications. KOR Inc. **160**

**Air protection.** Brochure describes NIXTOX® disposable filters for controlling air emissions and discusses meeting air requirements for workplaces, according to EPA and OSHA regulations. Tigg Corp. **161**

**Reverse osmosis.** Brochure describes reverse osmosis (RO) equipment capable of processing 10 000–100 000 gpd of brackish water and seawater; gives explanatory and technical information. Ajax International Corp. **162**

**GC products.** Catalog lists many new products and columns which meet needs of gas chromatographers. Carle Instruments, Inc. **163**

**Air pollutant analysis.** Bulletin 101 describes corporate capabilities for gathering and analyzing air pollution data for environmental and industrial hygiene applications, using new licenses technique. Energy Technology Consultants, Inc. **164**

**Flame ionization.** Bulletin 783 outlines a step-by-step approach to clean flame-ionization detectors; tells how to get better results with a GC and how to clean a dirty flame-ionization detector properly. Supelco, Inc. **165**

**THM analysis.** Paper by Norman Kirshen tells how to determine trihalomethanes (THM) in drinking water by a liquid/liquid extraction technique comprising EPA method 501.2. Varian Instrument Group **166**

**Water monitoring.** Publication 825 WPM A discusses water monitoring, substances in wastewaters, volatile solids, bacteria measurement, and other pertinent topics. Whatman Inc. **167**

**Sulfur removal.** Brochure describes Buell/Anhydro (dry-process) system to remove $SO_2$ and fly ash from exhaust gases in coal-fired boilers. Envirotech/Air Quality Control Group **168**

**Liquid chromatography.** Catalog lists many accessories for high-performance liquid chromatography (HPLC). Scientific Systems, Inc. **169**

**HPLC.** Literature describes 7500 Liquid Chromatograph for many analytical applications. Micromeritics Instrument Corp. **170**

**Solvents.** Handbook lists references, offers guidance concerning solvents for chromatography and other research work, and discusses physical, chemical, and safety data. Burdick & Jackson Laboratories, Inc. **171**

**HPLC simplification.** Technical Note 3 explains how low-pressure switching valves can simplify HPLC analysis procedures in 8 different ways. Rheodyne, Inc. **172**

**Organics disposal.** Brochure, "Process Waste Disposal Systems," tells how to properly dispose of organic wastes, including PCB, vinyl chlorides, contaminated solvents, and the like. Bigelow-Liptak Corp. **173**

**Bacterial treatment.** Case history tells how PHENOBAC® Mutant Bacterial Hydrocarbon Degrader handled chemical wastes in aerated lagoons. Polybac Corp. **174**

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***Companies interested in a listing** in this department should send their releases directly to Environmental Science & Technology, Attn: Literature, 1155 16th St., N.W., Washington, D.C. 20036*

**Chlorine dioxide.** Brochure discusses $ClO_2$ as an alternative to chlorine for controlling trihalomethanes, iron, manganese, and other impurities in drinking water. Technical guidance is given. Olin Corp. **175**

**Portable analyzer.** Bulletin describes Model 1075 pH/ORP analyzer/simulator to analyze for pH and provides laboratory simulations of field conditions. Uniloc **176**

**Chlorophenol detection.** Application Note tells how to use CMX-20 Electrochemical Detector to determine phenols and chlorophenols. Ask for LC News No. 101. CHROMATIX **177**

**Wastewater treatment.** Brochure details full systems and capabilities available for industrial-municipal wastewater treatment, including plants, filters, pumps, and many other items. Clow Corp. **178**

**Hydrogen generation.** Data sheet describes hydrogen generator which gives $H_2$ flow up to 225 $cm^3$/min and is designed especially for GC use. Varian Instrument Group **179**

**HCl monitoring.** Release announces CEA 555 portable analyzer for hydrogen chloride monitoring at low levels in workplaces and ambient air. Can detect down to 25 ppb using EPA method. CEA Instruments, Inc. **180**

**Filtration.** "1980 Filtration Catalog and System Design Guide" lists many items for filtration and microfiltration—over 540 products, systems, and services. Gelman Sciences, Inc. **181**

**Analysis.** Catalog offers large selection of analytical equipment, reagents, test kits, other items. Also, an announcement describes a hazardous materials detection kit, with easy-to-run tests. Hach Chemical Co. **182**

**GC columns.** Brochure lists columns and other items needed for GC systems, including ferrules and packings. Alltech Associates **183**

**Water services.** Brochure describes services in reverse osmosis, water purification, deionization, and waste treatment offered by new firm. $C_3$ International **184**

**Isotope-labeled compounds.** Catalog lists more than 600 carbon-14 and tritium labeled compounds for research and analysis, as well as scintillation and other items. Research Products International Corp. **185**

**Toxic/hazardous chemicals.** Wall chart gives information for handling/storage/disposal of over 300 toxic/hazardous chemicals, as well as health and first-aid data. Lab Safety Supply Company **186**

**Reverse osmosis.** Brochure describes standard line of RO systems in the 25–9000 gpd range. Continental Water Systems Corp. **187**

**Automated analysis.** Special issue of *Environmental Sciences Newsletter,* which deals with automated analysis, warns of EPA method changes for total phosphorus, TKN, sulfate, COD, cyanide, phenolics. Technicon Industrial Systems **188**

**Environmental control.** "Aluminum and the Environment" tells what that industry is doing in the way of environmental control. The Aluminum Association, Inc., 818 Connecticut Ave., NW, Washington, DC 20006 (write direct).

**LC detection.** Report EPA-600/4-80-015 describes new liquid chromatography (LC) detection system for pollutants. Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, GA 30605 (write direct).

**Heavy-metal pollution.** "MELIMEX, an Experimental Heavy Metal Pollution Study." Separatum No. 770. Mainly covers fate, loading, and transport in lakes. Swiss Journal of Hydrology, Birkhäuser Verlag, Basel, Switzerland. Inquire as to price, (write direct).

**Water resources.** "The State of the States: Water Resources Planning and Management." U.S. Water Resources Council, 2120 L St., NW, Washington, DC 20037 (write direct).

**Resource recovery.** Resource Conservation and Recovery, Current Reports. Publication SW-536. U.S. Environmental Protection Agency, Washington, DC 20460 (write direct).

**Microbial processes.** "Microbial Processes Report" tells how this resource can be used in developing nations. Limited amount of single copies. Commission on International Relations (JH-215), National Academy of Sciences, 2101 Constitution Ave., Washington, DC 20418 (write direct).

**Phosphorus reduction.** Study says that measures to control phosphorus in the Great Lakes are working. Great Lakes Basin Commission, Box 999, Ann Arbor, MI 48106 (write direct).

**The textile industry.** Can that industry achieve BATEA? Report EPA-600/2-80-041, single copies. Office of Research and Development Publications, U.S. EPA, Cincinnati, OH 45268 (write direct).

**Bioenergy in Sweden.** By Lars Rey. What that country is doing. Swedish Information Service, Swedish Consulate General, 825 Third Ave., New York, NY 10022 (write direct).

**Energy.** "Energy in the 80's." Considers oil, coal, alternatives. Dames & Moore, 445 S. Figueroa St., Ste. 3500, Los Angeles, CA 90071 (write direct).

**Fluoride removal.** From industrial wastewater, with activated alumina. Report EPA 600/2-80-058, single copies. Industrial Research Laboratory, U.S. EPA, Cincinnati, OH 45268 (write direct).

**Ion chromatography.** How well does it work for anionic species in water? Report EPA-600/4-80-020. ORD Publications, U.S. EPA, Cincinnati, OH 45268 (write direct).

**Formaldehyde.** Assessment of health effects prepared by Committee on Toxicology. The National Research Council, Washington, DC 20418 (write direct).

**Geothermal energy.** Brochure available in limited quantities. ENERGY, Box 62, Oak Ridge, TN 37830 (write direct).

**Low-waste technology.** UN projects in low- and no-waste technology. Marvin B. Rubin, Rm. 3425, Office of Environmental Affairs, U.S. Dept. of Commerce, Washington, DC 20230 (write direct).

**Fluorocarbons/ozone.** Latest fluorocarbon/ozone update, June 1980, explains how ozone depletion might be avoided. John Stowell, Public Affairs Dept., DuPont, Wilmington, DE 19898 (write direct).

**Passive solar energy.** Bulletin, "Passive Solar Heating and Cooling," explains how passive solar energy is used. Send stamped, self-addressed business envelope. Jerry Kingery, Centerline Co., Dept. 162, 401 S. 36th St., Phoenix, AZ 85034 (write direct).

# ES&T BOOKS

**Stack Sampling Nomographs for Field Estimations. Booklet with 14 nomographs.** Entropy Environmentalists, Inc., Box 12291, Research Triangle Park, NC 27709. Attn: Ann Daniel. 1980. $5.95.

This is a revised edition for stack emission evaluation on a quick field basis. It is directed to the professional source sampler whose activities involve sampling sources.

**Environmental Glossary.** William Frick, Ed. 200 + pages. Government Institutes, Inc., Box 5918, Washington, DC 20014. 1980. $19.50.

The editor is a former general counsel of EPA, now a Washington attorney. The more than 2000-term compilation, with abbreviations and acronyms, is derived straight from environmental statutes, the Code of Federal Regulations, or the EPA. They can be cited in a court of law or in administrative proceedings.

**Reclaiming the West.** Daniel P. Wiener, 450 pages. INFORM, 25 Broad St., New York, NY 10004. 1980. $75.

Can surface-mined land in the West be reclaimed? Perhaps with great difficulty, if at all, the author believes. In fact, for some desert regions, "it is doubtful that reclamation can ever be fully successful, even with the best practices," he points out. The author explains his thesis, tells why "regulation improves practices," and gives cost pictures.

**Dealing with Filter Media and Fabric Filter Aspects for Coal-Fired Boilers and $SO_2$ Dry Scrubbing Applications.** Filter Media Consulting, Inc., Box 2189, LaGrange, GA 30241. 1980. $45.

This work deals with all aspects of fabric filters, their performance and problems, as well as materials. Emphasis is on those for coal-fired power plants, especially those able to remove $SO_2$, which the publisher believes will have very large potential over the next 5–10 years.

**Hazardous Waste Management: An Overview of the Proposed EPA Regulations and Their Impact Upon Industry.** Thomas S. Valovic. 51 pages. CU Risk Management, Inc., 600 Atlantic Ave., Federal Reserve Plaza, Boston, MA 02210. 1980. $25, paper.

RCRA can stipulate $10 million in liability coverage for owners/operators of hazardous waste disposal sites, according to its provisions. "Cradle-to-grave" regulations under RCRA are very complex. This book gives an overview of these regulations which may affect many different industries, and urges risk managers to take immediate action to minimize their companies' hazardous waste exposures.

**Natural Resource Conservation.** 3rd ed. Oliver S. Owen. xi + 883 pages. Macmillan Publishing Co., Inc., 866 Third Ave., New York, NY 10022. 1980. $19.95, hard cover.

This textbook covers many fields of conservation, such as soil protection, and other environmental issues, including pollution and its control, pesticide problems, and toxic substances.

***Dangerous Properties of Industrial Materials.*** Periodical. Van Nostrand Reinhold, 135 W. 50th St., New York, NY 10020. 1980 start-up. $96/year, U.S.; $120/year, elsewhere.

This report gives in-depth looks at various substances, including all common synonyms, degree of hazard, federal registration number, and other characteristics. It discusses government rulings and findings, carcinogenic information, disposal, legislation, and other related matters.

**A Nuclear Waste Primer.** Publication No. 391. League of Women Voters Education Fund, 1730 M St., NW, Washington, DC 20036. 1980. $1.25, paper.

This booklet sets forth issues in the nuclear energy debate. It traces the nuclear fuel cycle, reviews radioactive wastes, discusses costs of treatment methods, outlines past and present government waste management programs, and looks at future policy options and opportunities.

**Water Pollution: A Guide to Information Sources.** Allen W. Knight, Mary Ann Simmons, Eds. xviii + 278 pages. Gale Research Co., Book Tower, Detroit, MI 48226. 1980. $28.

This guide provides annotated listings of a wide range of information sources and assists in locating the various aspects and items of water pollution literature.

**Proceedings of the Conference on Advances in Particle Sampling and Measurement.** W.B. Smith, Ed. 416 pages. National Technical Information Service, Springfield, VA 22161. 1980. $21 ($3.50, microfiche).

These proceedings consist of 20 reports presented last October in Daytona Beach, FL. They describe the newest trends in particulate sampling and, among other topics, feature droplet sizing, inhalable particle sampling, and numerous other subjects.

**The Global 2000 Report to the President: Entering the Twenty-First Century.** Council on Environmental Quality. 3 volumes. Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. Vol. 1, $3.50; Vol. 2, $13; Vol. 3, $8.

These volumes have gloomy forecasts concerning pollution, quality of life, and the like, for the beginning of the next century. However, these gloomy predictions will likely materialize if worldwide public policies do not change. Prompt attention to world environmental, energy, economic, and social problems might help to alleviate present trends toward degraded quality of life, especially in the developing nations.

***Chemical Substances Control.*** Periodical. The Bureau of National Affairs, Inc., 1231 25th St., NW, Washington, DC 20037. 1980 start-up.

The Resource Conservation and Recovery Act, and its regulations, give companies and agencies until Nov. 19 to come into compliance. This periodical will help those affected to find necessary answers to questions on toxics, hazardous wastes, and pesticides, and to learn what is needed, administratively, to comply with regulations.

**Essentials of Ground-Water Hydrology Pertinent to Water-Resources Planning.** Stock No. 052-045-00083-5. Superintendent of Documents, U.S.

Government Printing Office, Washington, DC 20402. 1980. $2.50.

This work updates the United States Water Resources Bulletin 16 of 1973. It presents the essential aspects of groundwater hydrology pertinent to water resources planning, and discusses advances in groundwater systems analysis, management, and administration.

**Decontamination and Decommissioning of Nuclear Facilities.** Marilyn M. Osterhout, Ed. xv + 803 pages. Plenum Press, 227 W. 17th St., New York, NY 10011. 1980. $75, hard cover.

Occasionally, nuclear reactors build up certain contaminants that must be removed. In other cases, a reactor may approach the end of its useful life and need to be decommissioned, which also requires certain decontamination procedures. This book contains papers on the subject by experts from the U.S., Canada, France, Germany, Sweden, and other countries. It covers actual experiences and offers a considerable amount of "how-to" information.

**Biodegradation Techniques for Industrial Organic Wastes.** D. J. DeRenzo, Ed. x + 358 pages. Noyes Data Corp., Mill Rd. at Grand Ave., Park Ridge, NJ 07656. 1980. $28, hard cover.

One possible means of breaking down industrial organic wastes, even highly hazardous ones, could be by using both natural and specially mutated bacteria. This book considers the latest technology in this field, and looks at what can and cannot be biodegraded, classes of wastes, innovative reactor designs, aerobic and anaerobic digestion, and many other closely related subjects.

**Biomass: Applications, Technology, and Production.** Nicholas P. Cheremisinoff et al. xii + 221 pages. Marcel Dekker Inc., 270 Madison Ave., New York, NY 10016. 1980. $29.50, hard cover.

This work presents an overview of biomass processes and an in-depth examination of the state of the art. It covers energy/fuel production from organic materials and wastes; methanol feedstocks, as well as those for ethanol, methane, and charcoal; impacts on energy supplies; other materials from biomass; and similar topics.

**Analytical Techniques in Environmental Chemistry.** J. Albaiges, Ed. xii + 646 pages. Pergamon Press Inc., Maxwell House, Fairview House, Fairview Park, Elmsford, NY 10523. 1980. $85, hard cover.

This book contains 59 papers covering recent advances in new methodologies, instrumentation, and monitoring strategies for determining inorganic and organic compounds in the environment. Detection and measurement of specific pollutants are given special emphasis. Both well-established and new techniques are discussed. The book's papers were presented at a congress in Barcelona, Spain.

**Radioelement Analysis Progress and Problems.** W. S. Lyon, Ed. xii + 424 pages. Ann Arbor Science Publishers Inc., Box 1425, Ann Harbor, MI 48106. 1980. $29.95, hard cover.

This book comprises proceedings of a conference on the subject, held in Gatlinburg, TN, last October. Papers presented cover neptunium, plutonium, polonium, chromatographic methods, on-line monitoring, mass "spec," quality assurance, and other related topics.

**Hazardous Wastes/RCRA Handbook.** Three-ring binder. Government Institutes, Inc., Box 5918, Washington, DC 20014. 1980. $65.

RCRA regulations are perhaps the most complex that EPA ever promulgated. This handbook describes these regulations and is aimed at helping industry avoid needless costs, penalties, and business disruptions. It was prepared by the Washington law firm of Crowell & Moring.

**Acid Rain: A Bibliography.** Library Bibliography Series No. 8, Univ. of Central Florida, Box 25000, Orlando, FL 32816. 1980. $2, paper.

This bibliography carries references concerning threats to fish, hydrobiological changes, sulfate washout, chemical composition, and many other aspects of this yet little-understood phenomenon.

**The Effects on Populations of Exposure to Low Levels of Ionizing Radiation: The BEIR III Report.** National Academy of Sciences, 2101 Constitution Ave., NW, Washington, DC 20418. 1980. $16.25 each.

This report updates the 1979 report, adding new material concerning cancer risk estimates in humans. A limited number is available to the general public.

# MEETINGS

**October 19–23** Richland, WA
**Coal Conversion and the Environment.** U.S. Doe and Battelle Memorial Institute, Pacific Northwest Laboratories

*Write:* Patricia Bresina, Symposium Secretary, Biology Dept., Battelle, Pacific Northwest Laboratories, Richland, WA 99352

**October 20–21** Chicago, IL
**The 7th Mineral Waste Utilization Symposium.** IIT Research and the U.S. Bureau of Mines

*Write:* Sy Bortz, IIT Research Institute, 10 W. 35th St., Chicago, IL 60616

**October 20–21** Orlando, FL
**ASTM Committee E-27 on Hazard Potential of Chemicals Meeting.** American Society for Testing and Materials

*Write:* ASTM, 1916 Race St., Philadelphia, PA 19103

**October 20–23** Washington, DC
**The 94th Annual Meeting of the Association of Official Analytical Chemists.** The Association of Official Analytical Chemists

*Write:* Kathleen Fominaya, AOAC, 1111 N. 19th St., Arlington, VA 22209

**October 20–23** San Diego, CA
**The 16th Department of Energy Nuclear Air Cleaning Conference.** U.S. DOE

*Write:* Dr. Melvin W. First, Harvard University, School of Public Health, Dept. of Environmental Health Sciences, 665 Huntington Ave., Boston, MA 02115

**October 22–25** Portsmouth, NH
**Northeast Conference on Hazardous Waste.** Industry Generators and Managers of Hazardous Waste

*Write:* Alan J. Borner, University of New Hampshire, Environmental Research Lab., Durham, NH 03824

**October 26–29** Boston, MA
**The 10th Annual North American Thermal Analysis Society Meeting.** North American Thermal Analysis Society

*Write:* Robert Johnson, DuPont Central R&D Dept., Exp. Sta., Bldg. 228, Wilmington, DE 19898

**October 27–28** Newport Beach, CA
**International Symposium on Industrial Process Combustion Technology.** The American Flame Research Committee

Environmental topics will be discussed. *Write:* S. C. Hunter, KVB, Inc., Box 19518, Irvine, CA 92714

**October 27–28** Pittsburgh, PA
**The Fundamentals of Ground Water Quality Protection.** Geraghty & Miller

*Write:* Richard Miller, President, American Ecology Services, Inc., 127 E. 59th St., New York, NY 10022

**October 27–29** Louisville, KY
**Coal Conference & Expo VI.** Coal Age

*Write:* McGraw-Hill Conference & Exposition Center, 1221 Avenue of the Americas, Ste. 3677, New York, NY 10020

**October 27–31** Chicago, IL
**A Multi-Discipline Symposium.** The Chicago Section of the Society for Applied Spectroscopy

*Write:* Donald Arendt, Wells Manufacturing Co., 7800 N. Austin Ave., Skokie, IL 60077

**October 27–31** Hollywood, FL
**The American Society of Civil Engineers Convention.** The American Society of Civil Engineers

*Write:* A. J. Favata, ASCE, 345 E. 47th St., New York, NY 10017

**October 28–30** Kansas City, MO
**Remote Sensing for Resource Management.** The Soil Conservation Society of America

*Write:* The Soil Conservation Society of America, 7515 Northeast Ankeny Rd., Ankeny, IA 50021

**October 28–31** Houston, TX
**Symposium on Flue Gas Desulfurization.** The U.S. EPA, Industrial Environmental Research Laboratory

*Write:* Franklin Ayer, Research Triangle Institute, Box 12194, Research Triangle Park, NC 27709

**October 29–31** Reston, VA
**The International European Waste-to-Energy Technology Conference.** U.S. DOE and U.S. EPA

*Write:* Miriam Holden, Director of Conference Planning and Management, Argonne National Lab., 9700 S. Cass Ave., Argonne, IL 60439

**October 30–31** Washington, DC
**Water Pollution Control Laws & Regulations Seminar.** Government Institutes

*Write:* Government Institutes, Box 5918, Washington, DC 20014

**November 10–11** Bal Harbor, FL
**Industrial Methods for Testing in High-Temperature Environment Symposium.** Committee G-1 on Corrosion of Metals of the American Society for Testing and Materials

*Write:* ASTM, 1916 Race St., Philadelphia, PA 19103

**November 10–12** Indianapolis, IN
**The Annual Meeting of the Indiana Water Pollution Control Association.** The Indiana Water Pollution Control Association

*Write:* Al Goodman, Education Committee, City of Jeffersonville, Wastewater Treatment Plant, 9th St. and Illinois Ave., Jeffersonville, IN 47130

**November 17–20** Hollywood, FL
**The 2nd Symposium on Management, Conservation, and Utilization of the Coastal Zone.** The American Society of Civil Engineers, Office of Coastal Zone Management

*Write:* Coastal Zone '80, Dept. of Civil Engineering, Clemson University, Clemson, SC 29631

**November 18–20** Houston, TX
**3rd International Coal Utilization Exhibition & Conference.** Coal Technology and The Edison Electric Institute

*Write:* Coal Technology '80, 6006 Bellaire Blvd., Ste. 100, Houston, TX 77081

**November 19–20** St. Louis, MO
**Hazardous Waste Regulations Update.** The Missouri Dept. of Natural Resources, the University of Missouri, and others

*Write:* Carol Leriche, University Extension Center, St. Charles, MO 63301

## Courses

**October 21–22** Newark, NJ
**Hazardous Wastes Regulations & Management.** New Jersey Institute of Technology
Fee: $425. *Write:* Div. of Continuing Education, NJ Institute of Technology, 323 High St., Newark, NJ 07102

**October 22–24** Pocono Mountains, PA
**Refining of Precious Metals.** The International Precious Metals Institute (IMPRI)
Fee: $250, members. *Write:* IMPRI Headquarters, Polytechnic Institute of New York, 333 Jay St., Brooklyn, NY 11201

**October 23** East Boston, MA
**Solar Export Management Seminar.** The Solar Energy Research Institute
Fee: $25. *Write:* The Conference Group, SERI, 1617 Cole Blvd., Golden, CO 80401

**October 27–29** E. Brunswick, NJ
**Industrial Toxicology.** The Center for Professional Advancement
Fee: $575. *Write:* General Information, Box H, E. Brunswick, NJ 08816

**October 28–30** Akron, OH
**Understanding Respiratory Protection.** The American Industrial Hygiene Association
Fee: $400. *Write:* J. R. Conti, AIHA, 475 Wolf Ledges Pkwy., Akron, OH 44311

**November 3–5** Phoenix, AZ
**Hazardous Waste Engineering.** Vanderbilt University, School of Engineering Continuing Education
Fee: $475. *Write:* Janet Vance, Vanderbilt University, Box 1525, Sta. B, Nashville, TN 37235

**November 3–7** Washington, DC
**Energy Efficient Design of Buildings.** The George Washington University
Fee: $635. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, DC 20052

**November 6–7** Washington, DC
**Synfuels Industry Opportunities.** Government Institutes, Inc.
Fee: $335. *Write:* Martin Heavner, Government Institutes, Box 5918, Washington, DC 20014

**November 10–13** Minneapolis, MN
**Sampling and Evaluating Airborne Asbestos Dust.** Midwest Center for Occupational Health and Safety
Fee: $320. *Write:* Ruth McIntyre, Midwest Center for Occupational Health and Safety, Dept. of Medicine, 640 Jackson St., St. Paul, MN 55101

**November 10–13** E. Brunswick, NJ
**Gas Fluidization.** The Center for Professional Advancement
Fee: $675. *Write:* General Information, Box H, The Center for Professional Advancement, E. Brunswick, NJ 08816

**November 11–14** Houston, TX
**Strategic Planning for Disposal of Solid Wastes.** The Center for Energy and Environmental Management
Fee: $330. *Write:* Center for Energy and Environmental Management, Box 536, Fairfax, VA 22030

**November 12–14** Kansas City, MO
**Industrial Hygiene Sampling Strategies.** Midwest Center for Occupational Health and Safety
Fee: $375. *Write:* Ruth McIntyre, Midwest Center for Occupational Health and Safety, Dept. of Medicine, 640 Jackson St., St. Paul, MN 55101

**November 12–14** Washington, DC
**Rights-of-Way and the Environment.** The George Washington University
Fee: $495. *Write:* Director, Continuing Engineering Education, George Washington University, Washington, DC 20052

**November 13–14** Washington, DC
**Transportation in the 1980s: A Concern for the Environment.** The George Washington University
Fee: $355. *Write:* G. Hiller, Continuing Engineering Education, George Washington University, Washington, DC 20052

**November 17–18** New York, NY
**Destruction Methods for Toxic Organic Chemicals.** Chemical Engineering
Fee: $445. *Write:* Barbara Bancroft, McGraw-Hill Seminar Center, Rm. 3112, 305 Madison Ave., New York, NY 10017

**November 17–21** Newark, NJ
**Hazardous Waste Management.** IMS America, Ltd., and Vanderbilt University, Toxic Substances Control Lab.
Fee: $595. *Write:* Dr. Thomas H. F. Smith, Environmental Resources Group, IMS America, Ltd., Ambler, PA 19002

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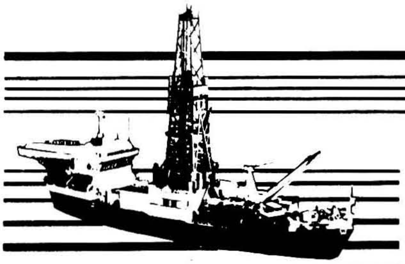

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RESEARCH

# Dilution Source Sampling System

**Robert J. Heinsohn* and John W. Davis**

Center for Air Environment Studies, 226 Fenske Laboratory, The Pennsylvania State University,
University Park, Pennsylvania 16802

**Kenneth T. Knapp**

Particulate Emissions Research Section, Environmental Sciences Research Laboratory, Environmental Protection Agency,
Research Triangle Park, North Carolina 27711

■ A source sampling system has been designed and tested that is lighter and easier to use than the conventional EPA Method 5 sampling systems. The heart of the system is an ejector pump that uses dry air to pump, cool, and dilute a sample of a process gas stream. The sample is treated as a miniscule plume, and the particles are removed from the sample after it has been cooled and diluted with dry air.

## *Introduction*

An inherent limitation in all contemporary source sampling systems is their inability to obtain particles in the state that they will have after the plume has mixed with the atmosphere. In-stack devices capture particles at stack gas temperature and gas composition, and the EPA Method 5 system captures particles on a filter at ~120 °C. In both cases condensation, adsorption, and agglomeration that occur in the diluted plume do not occur in a similar fashion in the sample gas stream. The need for a sampling system that will enable operators to capture particles that represent those that a plume transfers to the atmosphere has long been recognized and is the basis for a novel source sampling system reported in this paper. A source sampling system with dilution (hereafter abbreviated SSD) has been designed that treats the sampled gas as a miniscule plume and removes particles after the sample has been diluted with clean dry air. A discussion of earlier work can be found in ref *1–4*. The purpose of this paper is (a) to describe the design and operation of the SSD system and (b) to analyze simultaneous samples taken with the SSD system and a conventional EPA Method 5 system.

## *Design of SSD System*

The SSD system is shown schematically in Figure 1; it consists of six components:

(1) *Probe:* null reading isokinetic nozzle, impactor preseparator, heated probe.

(2) *Pump and Filter Assembly:* ball valve, sample orifice, heated enclosure, dilution ejector pump (DEP), filter holder.

(3) *Umbilical Cord:* dilution air line, 120 V ac power cable, pressure lines, thermocouple leads.

(4) *Control Unit:* pressure transducer, pressure regulator, pressure gauges, temperature controller, critical flow orifice, dilution air filter.

(5) *Flow Measurement Unit:* electronics for indicating elapsed time, volumetric flow rate, and sampled volume.

(6) *Dilution Air Cleaner and Dryer:* filters to remove oil and foreign matter, regenerative dryer to remove water vapor.

The SSD system is designed so that volumetric flow rates similar to those used in EPA Method 5 (0.0140–0.0425 $m^3$/min) can be maintained. This allows for the use of standard sampling nozzles so that isokinetic conditions can be achieved. In the SSD system the gas sample and the dilution air are completely mixed before the particles are removed by the filter, and the temperature of the diluted mixture is within 5 °C of atmospheric temperature. The entire apparatus is easily cleaned.

**Dilution Ejector Pump.** The dilution ejector pump (DEP) shown in Figure 2 is the heart of the system. Sample gas is pumped by a high-velocity stream of dry dilution air passing through the annular space around the sample tube and transfers momentum to the slower moving sample gas stream. From the results of other workers (*5–8*), it is believed that the two streams mix and achieve uniform conditions at the end of the mixing tube. The diluted sample then passes through a filter to remove particles. The DEP was designed to use a minimum amount of air to cool the sample yet keep it above the dew point. Figure 3 shows the sample temperature as a function of the dilution ratio (on the basis of volume), the inlet sample temperature, and the moisture content assuming a "well-mixed" adiabatic system. The SSD system was designed to accommodate dilution ratios of 10–20.

**Control of Sample Flow Rate.** Dilution air enters the control unit, is regulated to a set pressure, ($P_0$), and passes through a three-wave valve and an orifice and into the DEP. The dilution air is filtered twice. The pressure, $P_0$, controls the sample flow rate and is set by the pressure regulator. The supply pressure is $P_1$. A three-way valve is used to pass the dilution air to the DEP or to a separate calibration system. The sample mass flow rate ($m_s$) is controlled by the mass flow rate of the dilution air ($m_d$). Since the geometry of the DEP is constant, the mass flow rate of the dilution air is a function of the regulated pressure, $P_0$. the pressure of the mixed gas before the filter ($P_m$) affects the sample mass flow rate, but, as this pressure only changes slightly as particles are collected on the filter, the regulated pressure ($P_0$) is the principal factor controlling the sample flow rate.

The sample flow rate also depends on the size of the nozzle and the length of the probe. Figure 4 is a graph of sample volumetric flow rate ($Q_s$) and the dilution ratio ($Q_d/Q_s$) vs. the control pressure $P_0$. For the SSD system, accurate measure-

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ment of dilution volumetric flow rate is not needed since the operator adjusts it to achieve isokinetic sampling conditions and a diluted sample temperature within 5 °C of atmospheric temperature. It is essential that the sample volumetric flow rate be measured accurately.

**Measurement of Volumetric Flow Rate and Total Volume of Sample.** An electronics system was designed to measure the total volume of the sample, the sample volumetric flow rate, and the elapsed time and to display these values. An orifice (0.635 cm in diameter) mounted upstream of the DEP was used to measure the sample volumetric flow rate. The temperature of the orifice housing and the probe was held at 93 °C (200 °F).

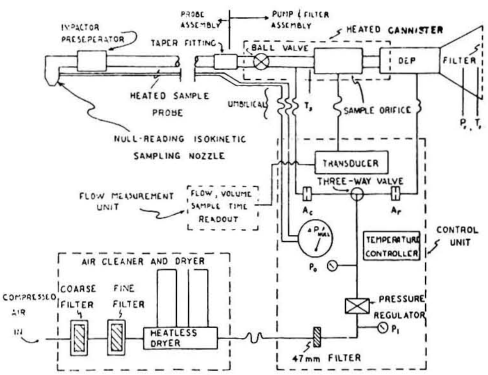

**Figure 1.** Schematic diagram of sampling system.

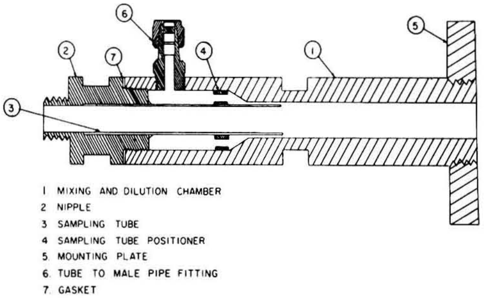

**Figure 2.** Scale drawing of the dilution ejector pump (DEP).

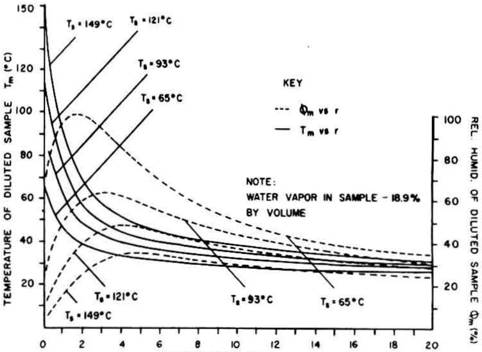

**Figure 3.** Temperature and relative humidity of diluted sample vs. dilution ratio for dilution air at 27 °C and relative humidity less than 10%.

**Calibration and Cleaning System.** By means of the ball valve and the three-way valve, the operator can either withdraw a gas sample from the stack or pass clean dry air through the system at a selected rate so as to remove particles from the orifice and DEP or to check the calibration of the orifice. The dislodged particles will pass through the system and collect on the filter. Thus no particles will be lost during the cleaning and calibration operation which can be performed without removing the probe from the stack. The numerical value of the sampled gas volume is electronically stored before cleaning and calibration and can be recalled after sampling has resumed. If particles collect around the orifice and change its discharge coefficient, it will be detected by the calibration procedure. To compensate for a change in calibration, a "calibration adjust" potentiometer mounted on the face of the flow measurement unit enables the operator to adjust the recorded flow rate and to set it equal to the calibration flow rate.

### *Simplified Stack Sampling System*

In addition to its capacity to withdraw and dilute simultaneously a sample as described previously, the DEP can be used simply as a pump to obtain samples following EPA Methods 5 or 17. In essence, the mechanical pump that is presently used is replaced by the DEP. Used in this fashion, the particles are removed by a filter before the gas enters the DEP and the DEP performs purely as an ejector pump. The dilution air is solely used as the pumping medium. Using a DEP reduces the mass and the complexity of the sampling train. Experiments reveal that the DEP shown in Figure 2 accomplishes this function providing the stack gas pressure is no less than a few inches of water below atmospheric pressure and the pressure drop across the filter is a few inches of water. There is no fundamental reason that an ejector pump cannot be used to sample under more severe pressure differences, but a pump with different operating characteristics would have to be designed.

### *Operation in the Field*

In the field the SSD system is operated as follows:

(1) A nozzle is selected such that the sample flow rate will be between 0.0140 and 0.0425 standard m$^3$/min (0.5–1.5

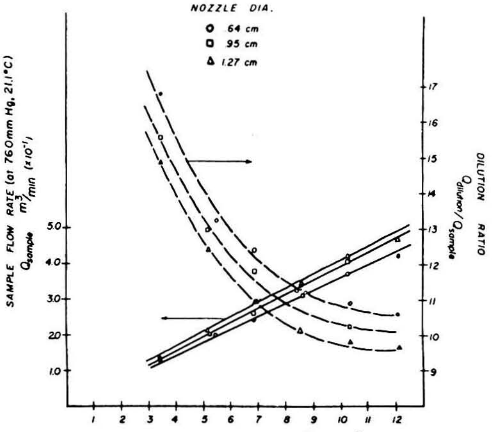

**Figure 4.** Operating characteristics of the DEP using a glass fiber filter and different inlet nozzles.

SCFM). (If a null-reading nozzle is not used, an independent S-type Pitot must be attached to the sampling probe.)

(2) With the ball valve closed, the probe is inserted in the stack and the stack gas velocity is determined. The three-way valve is set and the dilution pressure ($P_0$) adjusted to pass dilution air through the DEP at a rate calculated to withdraw the sample at the isokinetic sampling rate.

(3) The ball valve in the sampling train is opened, allowing the sampled gas to flow through the orifice. The dilution air flow rate is readjusted to maintain isokinetic sampling.

**Apparatus.** The DEP is considerably lighter and smaller than the mechanical pump used in commercially available EPA Method 5 systems. The SSD has no glassware, impingers, ice, or impinger box to be carried to the sampling site. The dilution air cleaner and dryer can be left unattended on the ground. The ball valve in the sampling train is a positive shut-off. When a large probe is used, the ball valve may be beyond the catwalk or roof and require the operator to reach over the railing. If the valve cannot be reached, the system can be shut off by bringing the dilution air pressure ($P_1$) to zero. This, however, is not a positive shut-off.

**Deposition of Particles in the Sampling System.** Deposition of particles in the sampling system (probe, orifice, and DEP) proved to be less than what occurs in an EPA Method 5 system. An Andersen-2000 preseparator was mounted between the sampling nozzle and the upstream end of the heated probe. In laboratory experiments a monodisperse aerosol of uranine dye was drawn through the sampling system at a volumetric flow rate of 28.3 standard L/min (1 SCFM). It was shown that (a) the preseparator has a cut size of ~5 $\mu$m and is capable of removing particles above 10 $\mu$m, (b) deposition in the sampling nozzle and the orifice meter is never more than 10% of the sampled aerosol, (c) deposition in the DEP is never more than 20% of the sampled aerosol, and (d) the final filter is the principal agent collecting particles that leave the preseparator.

**Water Content of Samples.** One important difference between the SSD system and an EPA Method 5 system is the procedure used to calculate the water content of the sample gas. EPA Method 5 trains condense the water vapor and measure the remaining volume of gas in a positive displacement meter. The water content of the sample gas is easily determined by measuring the water in the impingers. The SSD system measures the total volume of sampled stack gas including the water vapor. The SSD system, thus, requires a separate procedure (such as EPA Method 4) to determine the water content.

On the other hand isokineticity is easily achieved in the SSD system. An EPA Method 5 train uses a Pitot tube to measure the stack gas velocity, and the sample flow rate is adjusted to achieve isokinetic conditions. To calculate the sample volumetric flow rate needed to achieve isokinetic conditions, one must know the temperature and the water vapor of the gas entering the nozzle. Since the sample gas flow rate is measured after the water vapor has been condensed, the water content must be assumed to calculate the velocity. The SSD system measures the actual volumetric flow rate before condensation, and the above assumption does not have to be made.

### *Comparison Tests*

Several samples were taken simultaneously with the SSD and an EPA Method 5 sampling train from the following sources: (1) a coal-fired, traveling grate stoker boiler with cyclone collectors (test 1–5), (2) a glass melting tank with an electrostatic precipitator (tests 6–11), and (3) a lime kiln with a baghouse (tests 12–14).

In tests 1, 6, 7, and 12–14, simultaneous full-scale source certification tests were conducted. Tests 2–5 and 8–11 were conducted to determine the size distribution and the elemental analysis of the particles. Test 7 was made with the electrostatic precipitator turned off. In tests 2–5 simultaneous samples were obtained with the SSD system and an Andersen-2000, 8-stage in-stack impactor with preseparator. In tests 8–11 particles were deposited on glass fiber filter paper, and the size distribution was determined with a scanning electron microscope and a PDP-11 computer code that computed the size distribution and the elemental composition for each size range. Table I shows the mass concentrations that were obtained by gravimetric means. Table II shows the size distribution.

### *Analysis of Test Results*

**Mass Concentration.** Table I shows that the particle mass concentration measured with the SSD system is larger than that measured by the EPA Method 5 system when the soluble matter collected in the impingers is ignored and, with only one exception, is also larger even when the impinger soluble and insoluble matter is included. The results are consistent with the belief that the difference is due to the collection of "condensables" by the SSD system. Unfortunately, the difference is within the experimental error of the two separate concentration measurements. The difference in mass concentration is more reliable in tests 1 and 7 when the concentrations are the largest and near the maximum permissible levels for the processes involved. In the remaining tests the concentrations are smaller and the relative difference is inconsistent. In tests with the lime kiln and the glass melt tank, one would not expect a large amount of condensable material to be present, and it is not surprising to see no clear trend.

**Size Distribution.** Figure 5 typifies data from tests 2–5 on the coal-fired stoker boiler. The graph shows that there are small particles in the diluted (SSD) sample that do not exist when the gases were at the stack temperature. The mass mean diameters of the two samples are shown in Table II. Both the SSD system and the in-stack impactor used the same preseparator. While there is a small degree of gravitational settling in the SSD system that is not present in the in-stack measurements, the amount cannot explain the difference in the observed mass mean diameters. It is concluded that the SSD system makes it possible to measure "condensables" in a stack gas that become particulates when the plume mixes with the atmosphere.

**Elemental Analysis.** Particles were sorted into size ranges, and an analysis was conducted to determine the relative abundance of selected elements in each size range. The tests were inconclusive. The relative abundance of sulfur in the SSD sample was in general lower than that in the in-stack impactor for particles of less than approximately 5 $\mu$m but larger for

**Table I. Comparison of the Mass Concentration Determined by the SSD System with That Determined by Method 5 System**

| source | test | SSD | loading (EPA Method 5), mg/NCM[a] | |
|---|---|---|---|---|
| | | | with impingers | without impingers |
| coal-fired boiler | 1 | 495.6 | 462.1 | 407.6 |
| glass melt tank | 6 (ESP on) | 71.7 | 45.8 | 38.9 |
| | 7 (ESP off) | 351.7 | 331.8 | 323.6 |
| lime kiln | 12 | 116.2 | 126.6 | 111.0 |
| | 13 | 99.4 | 83.8 | 70.0 |
| | 14 | 139.0 | 140.3 | 123.6 |

[a] NCM = normal cubic meter.

particles above this size. Since the accuracy of these tests is not known, it is difficult to draw meaningful conclusions.

### *Discussion*

The SSD system attempts to replicate the processes of particle growth that occur when the plume enters the atmosphere. No attempt is made to replicate processes that occur several hours after discharge. If the diluted sample is to behave as a miniscule plume, then vapor-phase adsorption and the processes of nucleation, condensation, and coagulation ought to occur as they do in the full-scale plume. Furthermore, the sample ought to mix with dilution air the same way that the full-scale plume mixes with the atmosphere. In this research no attempt was made to model analytically these processes in the plume or in the diluted sample, but several general conclusions can be drawn on the basis of published literature (*8–12*).

Coagulation processes are slow and principally affect particles after several minutes. Since the diluted sample is within the SSD system for approximately 0.5 s, little coagulation is expected to occur. Nucleation and condensation processes are rapid, indeed so rapid that it is expected that particle growth will be governed more by the slower rate at which the sample and dilution gas mix than by the rate of nucleation and condensation. The time in which the diluted sample is within the SSD system is adequate to assure that it is "well mixed" and nucleation and condensation occur. Research concerning particle formation in the exhaust of internal combustion engines indicates (*13, 14*) that the dilution ratio significantly affects the condensation of heavy hydrocarbons emitted by these engines. Engine exhausts mix very rapidly with air in the wake region of a vehicle, and it has been suggested that dilution ratios of 100–1000 should be used. At dilution ratios of 10–20, there is the chance that inordinately large saturation ratios (partial pressure divided by the saturation vapor pressure) occur which exaggerate condensation and produce conditions that do not duplicate the behavior of actual engine exhausts.

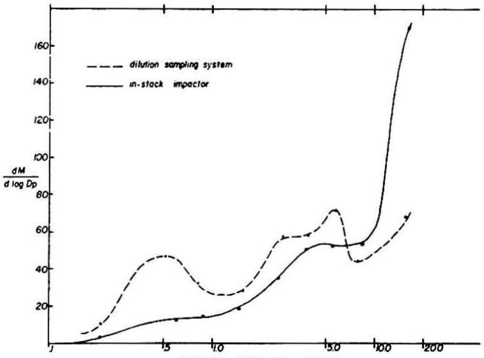

Figure 5. Particle size distribution.

The likelihood of condensation and the rate at which particles grow cannot be argued solely on the basis of the saturation ratio. Because of the Kelvin effect, the rate at which particles grow by heterogeneous condensation is influenced by the molecular weight of the condensing species, the particle diameter, and the saturation ratio in addition to the obvious dependence on temperature and initial concentration. Furthermore, heterogeneous condensation can occur for saturation ratios less than unity. Preliminary calculations show that the rate at which particles grow by heterogeneous condensation is very rapid for particles less than 5 μm and that there is sufficient time for growth to this size before the diluted sample gas passes through the filter of the SSD system.

**Inhalable Particles.** To comply with inhalable particulate standards being considered, it may be necessary to develop improved source sampling systems Not only may a preseparator be required to remove particles larger than 15 μm with a prescribed accuracy, but it may also be necessary to capture all particle-producing matter that a source emits to the atmosphere. It is suggested that the SSD system is eminently suited to accomplish this task.

### *Conclusions*

A new source sampling system has been designed that is easier to use than a conventional EPA Method 5 system. The heart of the system is a dilution ejector pump (DEP) that uses dry atmospheric air to withdraw a sample from a process gas stream and simultaneously dilute and cool it with atmospheric air. The particles in the sample are cooled to approximately ambient temperature and are deposited on a filter for analysis.

Tests have been conducted in which source samples were simultaneously withdrawn by the SSD system and an EPA Method 5 system; tests were also made with the SSD system and an in-stack inpactor. Comparison of the particles obtained by the three systems reveal the following:

(1) The SSD system records larger particle mass concentrations than an EPA Method 5 system.

(2) The size distribution of the particles obtained with the SSD system is different from that obtained with an in-stack impactor. Depending on the combustion process, the sample obtained with the dilution system indicates the presence of

**Table II. Mass Mean Diameters of Particles Obtained with the SSD System and an In-Stack Impactor**

| source | test | sampling train | dry gas vol, NCM[a] | mean diam, μm | method of particle sizing[b] |
|---|---|---|---|---|---|
| coal-fired boiler | 2 | in-stack | 0.335 | 7.2 | 1 |
| | | SSD | 1.902 | 0.4 | 2 |
| | 3 | in-stack | 0.262 | 10.2 | 1 |
| | | SSD | 1.376 | 3.0 | 2 |
| | 4 | in-stack | 0.295 | 9.6 | 1 |
| | | SSD | 1.351 | 0.3 | 2 |
| | 5 | in-stack | 0.312 | 4.1 | 1 |
| | | SSD | 1.389 | 0.4 | 2 |
| glass melt talk | 8 | in-stack | 0.192 | 0.4 | 1 |
| | | SSD | 1.000 | 0.4 | 3 |

[a] NCM = normal cubic meter. [b] (1) Andersen-2000, 8-stage impactor inside stack; (2) Andersen-2000, 8-stage impactor adapted to capture particles at filter downstream of DEP; (3) size distribution determined by SEM and PDP-11 computer program analyzing particles on filter downstream of DEP.

submicrometer particles emitted to the atmosphere that are not present at stack gas temperature.

*Nomenclature*

$D_p$ = particle diameter ($\mu$m)
$m_d$, $m_s$ = mass flow rate of dilution air, sample (g/s)
$M$ = cumulative mass distribution
$P_i$, $P_m$, $P_0$, $P_{sat}$ = pressure of supply air, pressure of diluted sample, control pressure, vapor saturation pressure (N/m$^2$)
$\Delta P_s$ = pressure difference across the sample orifice (N/m$^2$)
$Q_d$, $Q_s$ = volumetric flow rate of dilution air and gas sample (m$^3$/min)
$r$ = dilution ratio ($Q_d/Q_s$), each corrected to standard conditions
$T_d$, $T_m$, $T_s$ = temperature of dilution air, diluted sample, sample (K)
$t$ = time (s)
$\phi_m$ = relative humidity of diluted sample

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# Chlorinated Paraffins and the Environment. 1. Environmental Occurrence

**Ian Campbell* and George McConnell**

Imperial Chemical Industries Limited, Research and Development Department, Mond Division, The Heath, Runcorn, Cheshire, P.O. Box No. 8, WA7 4QD, United Kingdom

■ Studies have been in progress since 1974 to measure the distribution and persistence of chlorinated paraffins in the environment, to determine their pathways through the environment, and to measure their concentrations in animal and vegetable life, including human tissue and human foodstuffs. The studies have used a newly developed sensitive and selective method of analysis for chlorinated paraffins in water, sediment, organic material, etc. Results are presented showing actual chlorinated paraffin levels measured in river and sea water and their sediments, in marine and land birds and their eggs, in fresh and saltwater fish and other aquatic vertebrates and invertebrates, in domesticated animals and foodstuffs derived from them, in foodstuffs of vegetable origin, and on human hands and in human tissues and organs from 24 subjects including a neonate. The results form a basis, in conjunction with toxicology studies by other workers, for an evaluation of the consequences of the use of chlorinated paraffins.

## *1. Introduction*

**1.1. Current Position.** Chlorinated *n*-paraffins, widely used throughout the world, are relatively chemically stable, and this paper describes studies whose aim is to measure their distribution and persistence in the environment, to determine their pathways through the environment, and to measure their concentrations in animal and vegetable life.

Past studies of chlorinated hydrocarbon inputs to the environment (*1*) showed that they do not all have the same behavior patterns and characteristics and that not all chlorinated hydrocarbon classes exert harmful effects. Simple chlorinated olefins such as perchloroethylene and trichloroethylene appear at low levels in the biosphere but do not accumulate because they are rapidly degraded. Polychlorinated biphenyls however, and some pesticides such as DDT, are very stable and widely distributed in the biosphere, where they bioaccumulate and may show toxicity.

**1.2. Manufacture and Uses of Chlorinated Paraffins.** Chlorinated paraffins as defined here and abbreviated hereafter to CP are made by chlorinating a number of different straight-chain paraffins oils and waxes in the $C_{10}$–$C_{30}$ range. These feedstocks are typically chlorinated to varying degrees in the range 40–70% w/w to produce a range of products which are used as fire retardants and plasticizers in PVC, rubber, other plastics, varnishes, sealants, and adhesives and as extreme pressure additives in lubricants and metal cutting oils.

World CP consumption in 1977 is estimated at 230 kton/yr with a compound annual growth rate of 5% p.a. over the past 5 yr. The main uses are as indicated in Chart I. Where CP is used as a fire retardant or plasticizer in PVC, elastomers or other plastics, sealants, paints, adhesives, etc., it is effectively bound into a polymer system and will, therefore, find its way into the environment from such products only very slowly, if at all. The disposal of oils containing CP could present a more rapid route into the environment if these products are not properly disposed of or factory effluents are not correctly treated, and this may have been the major route for CP into the environment. Use of CP in oil probably represents about 20% of the total, viz., 45 000 ton world wide.

**1.3. Structure and Properties of CPs.** A CP contains a range of carbon chain lengths with varying numbers of chlorine atoms in positional isomeric distribution, mainly secondary and nonvicinal, e.g., $—CH_2CHClCH_2—$. CPs have very low vapor pressures, e.g., $(1–2) \times 10^{-6}$ mmHg at 20 °C for a $C_{14-17}$ paraffin with 52% chlorine. (Note: the percentage chlorine in a CP is 100× the fraction of chlorine in the product molecular weight.)

Water solubility is very low, and radioactive tracer measurements gave the values in Chart II. Except for the $C_{20-30}$ CP with high chlorine content, CPs are viscous, pale-colored dense oils, with the properties listed in Chart III. The $C_{20-30}$ CP with 70% chlorine is a solid with density 1.63 g/mL and softening point 90 °C. CPs are stable up to ca. 200 °C, and then they begin to dehydrochlorinate. CPs are completely destroyed by incineration and cannot volatilize in exhaust gases from an incinerator. Marketed CPs contain low levels of stabilizers (typically <0.05% w/w) against decomposition and acidity in storage and transport, but after environmental dispersal the stabilizers may become ineffective by evaporation, dissolution in water, adsorption, or dilution.

In reactivity toward ionic reagents, CPs are similar to chlorohydrocarbons such as 1,2-dichloroethane and hydrolyze or dehydrochlorinate easily when dissolved in nonaqueous media together with the reagents but are so insoluble in aqueous solutions of reagents that reaction is immeasurably slow.

**1.4. Aim of the Present Study.** The present study had three aims: (a) to determine actual CP levels in environmental and living organism samples and to compare these with one another, (b) to relate the levels to CP chemical and physical properties, and (c) to study CP pathways in the environment and to assess whether there is any environmental impact.

**Chart I. 1977 World Consumption of CP (Excluding Eastern Europe), kton/yr**

| paraffin | % chlorine | consumption | main use |
|---|---|---|---|
| $C_{10-13}$ | 50–70 | 60 | EP lubricants, FR additives, sealants, etc. |
| $C_{14-17}$ | 45–60 | 110 | secondary PVC plasticisers |
| $C_{20-30}$ | 40–70 | 60 | paints, EP lubricants, FR additives |

**Chart II.**

| carbon chain length of chlorinated paraffin | % chlorine | temp, °C | solubility, μg/L | |
|---|---|---|---|---|
| | | | freshwater | seawater |
| $C_{16}$ | 52 | 16–20 | 10 | 4 |
| $C_{25}$ | 42 | 16–20 | not measured | 3 |

**Chart III.**

| | $C_{10-13}$, 50% Cl | $C_{14-17}$, 52% Cl | $C_{20-30}$, 42% Cl |
|---|---|---|---|
| density, g/mL at 25 °C | 1.19 | 1.25 | 1.16 |
| viscosity, P, 25 °C | 0.8 | 16 | 22 |
| viscosity, P, 50 °C | 0.2 | 1.8 | 3.2 |

## 2. *Environmental CP Levels*

Bearing in mind the physicochemical properties and use patterns of CPs, we chose the following environmental regions as the sources of samples for analysis: three categories of water and their sediments and organisms (industrialized waterways, marine water remote from industry, fresh water remote from industry); human foodstuffs; wildlife samples selected from the species at the upper trophic levels where experience suggested that CP concentrations would be at their highest; and human tissues.

**2.1. CP Analysis Method.** A sensitive selective analysis method for CP in water, sediments, tissues, etc., has been developed by Shell (UK) and ICI Mond Division. The method, described elsewhere (2), combines solvent extraction/partition, column chromatography, and TLC with argentation. It is reliable, but lengthy (3 days elapsed time) and tedious. A minimum of 50 ng of CP is detectable, and detection limits, depending on enrichment factor, are 5 in $10^{10}$ w/v (water) or 5 in $10^8$ w/w (semisolids). The method differentiates between $C_{10-20}$ and $C_{20-30}$ CPs, but not between 45 and 52% chlorinates of one paraffin or between $C_{10-13}$ and $C_{14-17}$ types. Response intensity is chlorine-content dependent, so for safety, and to err on the high side, we used the lowest chlorine content CP in calibration. Accuracy is ca. ±10% for a 500 ng TLC spot, or ±50% at the 50-ng detection limit. There is no interference with CP measurement by any of the 23 non-CP halogenated compounds so far tested. A $^{14}C$-labeled CP radioassay comparison shows that the method is quantitative.

**2.2. CPs in Water and Sediments.** Table I gives CP levels in UK marine waters and sediments. (See paragraph at end of text regarding supplementary material.) Water and sediment were sampled at coincident locations.

Half the waters show $C_{10-20}$ CP, at 0.5–4.0 parts in $10^9$, and less than half show $C_{20-30}$ CP, at 0.5–2.0 parts in $10^9$. CPs are seen in only a few sediments, at up to 0.5 ppm. Thus mud and water levels are near or below detection limits. Attempts have been made to compare CP levels in deep and surface sediments but were unsuccessful because all marine corings taken so far were free of CPs at all levels.

Table II (extended version in supplementary material) gives CP levels in nonmarine and fresh waters and sediments in industry-free areas. They range from 0–1 ppb of either CP type. The sample percentage with no CP (65%) is almost twice that of seawaters, but CP levels where seen are close to marine water levels. Sediment levels are comparable with marine sediments.

Table III shows analyses of UK waters and sediments receiving industrial/domestic effluent. CP levels in water are 1–6 ppb, in sediments 1–10 ppm, $C_{10-20}$ CP predominating (ppm = parts in $10^6$ w/w, ppb = parts in $10^9$ w/w).

**2.3. Aquatic Organisms and Aquatic-Habitat Birds.** Table IV (extended version in supplementary material) gives CP levels in seal, marine shellfish, and salt- and freshwater fish, the latter a predator. $C_{20-30}$ CP is hardly seen (max 0.2 ppm), and the $C_{10-20}$ type is seen at only 0.4 ppm in organisms from waters not receiving effluent from CP manufacture. Mussels from the Wyre, which receives CP plant effluent, have up to 1.0 ppm of $C_{10-20}$ CP in general, and 6–12 ppm close to the effluent discharge. CP levels in organisms, even predators at the top of the food chain, are close to those in sediments below the water in or from which they live.

Table V (extended version in supplementary material) gives seabird egg CP analyses from nine UK coastline species. $C_{20-30}$ CP is rarely seen, and $C_{10-20}$ CP exceeds 0.6 ppm only once but occurs at a lower level in more than half the eggs. CP levels do not correlate with species or location. CP levels in eggs, compared with levels in potential food sources (Table IV), show little biomagnification.

**2.4 Occurrence in Human Tissues and on Hands, and in Human Foodstuffs.** Figures 1, 2, and 3 show the results of analyses by ICI and Shell of certain post-mortem human tissues, expressed as histograms (see also Table VII, supplementary material). In the main $C_{10-20}$ CP was seen, predominantly in the fat. Eight volunteers' hands were swabbed with toluene, and all had 0.8–4.0 μg of $C_{10-20}$ CP (per two hands). Only one showed $C_{20-30}$ CP (2 μg). A worker in a CP laboratory had 800 μg of $C_{10-20}$ CPand 400 μg of $C_{20-30}$ CP.

Table VI (extended version in supplementary material) shows CP analyses in human foods. $C_{20-30}$ CP is rarely seen, and $C_{10-20}$ CP is seen up to 0.5 ppm in ca. 70% of samples. The sheep tissues were from animals grazing remote from or near a CP plant. Those near the plant showed traces of $C_{10-20}$ CP, the others none.

**2.5. Release of CP from Plasticized PVC Sheet.** Air passing over plasticized PVC sheet in a closed box was afterwards solvent-scrubbed, and the trapped CP analyzed, the conditions and the results being the following.

Plasticized PVC sheet with 8% of a $C_{14-17}$ CP containing 52% Cl: sheet area, 1.05 $m^2$; box volume, 0.125 $m^3$; air volume, 12.75 $m^3$ during 21 days; analysis, ca. 1 mg of CP in solvent used to scrub effluent air. At a CP molecular weight of 443, this represents ca. $3 \times 10^{-9}$ mmHg vapor pressure.

### 3. *Discussion of Environmental Levels of CP*

Because chlorinated paraffins are involatile and therefore cannot be transported and dispersed by atmospheric air movements, their transport by moving water is probably the only large-scale dispersion mechanism available to the product. Comparing Tables I–III, one finds that CP levels are low (0–1 ppb) in rivers and reservoirs not receiving industrial/domestic effluent, although CP occurs occasionally and inexplicably even here (e.g., 1 ppb at Bala Lake head or 0.5 ppb in the River Banwy). Tables I–III show an increase in CP occurrence and quantity as river water passes from the uplands into industrialized areas, and a decrease when the river joins the sea. Effluent and shipping contributions to river

**Table I. $C_{10-20}$ and $C_{20-30}$ CP in Marine Waters and Sediments**[a]

| | waters, ppb (w/w) | | sediments, ppm (w/w) | |
|---|---|---|---|---|
| | $C_{10-20}$ | $C_{20-30}$ | $C_{10-20}$ | $C_{20-30}$ |
| Irish Sea | 1.0 | ND | 0.1 | ND |
| | 0.5 | ND | ND | ND |
| | 0.5 | ND | NM | NM |
| | 0.5 | ND | 0.1 | ND |
| | ND | ND | ND | ND |
| | ND | ND | ND | 0.6 |
| | NM | NM | ND | ND |
| Barmouth Harbour | 0.5 | ND | 0.5 | ND |
| Menai Straights (Caernarfon) | 0.5 | 0.5 | ND | ND |
| Tremadoc Bay (Llandanwg) | ND | ND | ND | ND |
| North Minch: Ardmair | 0.5 | 1.0 | ND | ND |
| Port Bùn a' Ghlinne | ND | ND | ND | ND |
| Port of Ness | 0.5 | ND | ND | ND |
| Goile Chròic (Lewis) | 0.5 | 0.5 | ND | ND |
| Sound of Taransay (Traigh Seilebost, Harris) | 4.0 | 2.0 | ND | ND |
| Sound of Arisaig | 1.0 | 2.0 | ND | ND |
| North Sea: | | | | |
| (N 55° 5.7′ W 1° 9.3′) | ND | ND | ND | ND |
| (N 57° 26.2′ W 1° 17.0′) | ND | ND | ND | 0.1 |
| (N 57° 56.5′ W 1° 22.0′) | ND | ND | 0.05 | 0.3 |

[a] NM = not measured; ND = not detectable, therefore less than the limit of detection, 0.5 ppb.

**Table II. Chlorinated Paraffins in Fresh and Other Nonmarine Waters and Sediments Remote from Industry**[a]

| | waters, ppb (w/w) | | sediments, ppm (w/w) | |
|---|---|---|---|---|
| | $C_{10-20}$ | $C_{20-30}$ | $C_{10-20}$ | $C_{20-30}$ |
| River Banwy (Llangadfan) | 0.5 | ND <0.5 | ND <0.05 | ND <0.05 |
| River Lea (Welwyn) | ND <1.0 | NM | NM | NM |
| River Lea (Batford) | ND <1.0 | NM | 1.0 | NM |
| River Clwyd (Ruthin) | ND <0.5 | ND <0.5 | ND <0.05 | ND <0.05 |
| Bala lake | 1.0 | 0.5 | NM | NM |
| River Dee (Corwen) | ND <0.5 | ND <0.5 | 0.3 | 0.05 |
| River Wnion (Merioneth) | 0.5 | 0.5 | ND <0.05 | ND <0.05 |
| Firth of Lorne (Ganevan) | 0.5 | ND <0.5 | NM | NM |
| Loch Linnhe (Corran Narrows) | ND <0.5 | ND <0.5 | NM | NM |
| Firth of Clyde (Ashcraig) | ND <0.5 | ND <0.5 | NM | NM |
| Firth of Clyde (Girvan) | 0.5 | 2.0 | NM | NM |
| An Garbh Allt | 0.5 | 0.5 | NM | NM |
| five drinking water reservoirs (Manchester area) | ND <0.5 | ND <0.5 | ND <0.25 | ND <0.25 |
| sewage sludge (Liverpool) | NM | NM | 4–10 | ND <0.05 |
| sewage sludge (Manchester) | NM | NM | ND <0.05 | ND <0.05 |

[a] NM = not measured; ND < = Not detectable, therefore less than the stated limit of detection.

**Table III. Chlorinated Paraffins in Fresh Waters and Sediments Close to Industry**[a]

| | waters, ppb (w/w) | | sediments, ppm (w/w) | |
|---|---|---|---|---|
| | $C_{10-20}$ | $C_{20-30}$ | $C_{10-20}$ | $C_{20-30}$ |
| River Aire: | | | | |
| Leeds | 2.0 | NM | 10.0 | NM |
| Woodlesford | 2.0 | NM | NM | NM |
| River Ouse: | | | | |
| Boothberry Edge | 1–2 | NM | NM | NM |
| Goole | NM | NM | 2.0 | NM |
| River Trent: | | | | |
| West Bromwich | 1–2 | NM | 6.0 | NM |
| Walton-upon-Trent | 2–3 | NM | 1.0 | NM |
| Swarkestone | 1–2 | NM | 14.0 | NM |
| Newark | 4.0 | NM | 8.0 | NM |
| Gainsborough | 2.0 | NM | 3.0 | NM |
| confluence with Humber | 6.0 | NM | NM | NM |
| Humber estuary: | | | | |
| Hull | 1–2 | NM | 2.0 | NM |
| Grimsby | 3.0 | NM | NM | NM |
| Stone Creek | NM | NM | 2.0 | NM |
| Mersey Estuary: | | | | |
| New Brighton | 3.0 | NM | 3.0 | NM |
| Liverpool | | | | |
| Pier Head | 4.0 | NM | 8.0 | NM |
| River Thames: | | | | |
| Oxford | 2.0 | NM | NM | NM |
| Sanford | 1–2 | NM | 1.0 | NM |
| Wyre Estuary: | | | | |
| site of old jetty | NM | NM | 1.6 | 3.2 |
| East bank (Brookvale) | NM | NM | 1.2 | ND <0.05 |
| Station 1 | 0.5 | 0.5 | NM | NM |
| Station 2 | <0.5 | <0.5 | NM | NM |
| Station 3 | ND <0.5 | ND <0.5 | NM | NM |
| Station 4 | ND <0.5 | ND <0.5 | NM | NM |
| Station 5 | <0.5 | ND <0.5 | NM | NM |
| Station 6 | 1.5 | ND <0.5 | NM | NM |
| Station 7 | 0.5 | ND <0.5 | NM | NM |
| Burn Hall No. 1 | NM | NM | 1.0 | 0.2 |
| Burn Hall No. 4 | NM | NM | 0.1 | 0.05 |
| Burn Hall No. 6 | NM | NM | ND <0.5 | ND <0.5 |
| Mersey Estuary: | | | | |
| all 14 sediments sampled | NM | NM | ND <0.05 | ND <0.05 |
| River Tees: | | | | |
| Low Dinsdale | ND <0.5 | ND <0.5 | 0.3 | 0.1 |
| Middlesborough | ND <0.5 | ND <0.5 | 15.0 | 3.0 |
| North Gare breakwater | 0.5 | ND <0.5 | 0.05 | 0.05 |

[a] NM = not measured; < = small trace seen, but less than nominal detection limit stated; ND < = not detectable, therefore less than the stated limit of detection.

water CP levels are clearly seen in comparing 0–1 ppb levels in unpolluted rivers with 1–6 ppb levels in industrialized waterways. In all cases there is a 1000-fold ratio between sediment and water CP levels. CP occurrence in rivers is understandable, since limited measurements on effluents from factories known to be using CP-based cutting oils suggest that they may contain 10–100 ppb of CP, and sewage sludge from Liverpool and Manchester treatment plants contained 0–10 ppm of $C_{10-20}$ CP.

Comparison of sediment CP levels with aquatic organism tissue levels shows little or no bioaccumulation, the tissue levels being close to the levels in the sediment near which the organisms live. There is no indication of biomagnification in any food chain, aquatic or on land, including the human food chain.

CP in water at a level above solubility (see Section 1.3) is as a suspension or adsorbed on suspended solids, and both ultimately settle out. Thus Tables I–III show sediment levels 1000 times the supernatant water.

CP traces occasionally found in unpolluted upland waters are difficult to explain. CP transport on airborne dust is a possibility, or traces may volatilize (see Section 2.8). The feed and the water for sheep grazing near a CP plant (Table VI) were free of CP, but their fleeces contained 0.35 ppm of $C_{10-20}$ CP, suggesting aerial transport. Seabirds' egg CP levels do not evidence high biomagnification as seen with chlorinated hydrocarbon pesticides or PCBs and are uniformly low across all species and locations. As for all analyses, $C_{10-20}$ CP levels were slightly higher than $C_{20-30}$ CP levels.

The occurrence of predominantly $C_{10-20}$ CP in human tissues (2.6) and foodstuffs (2.7) and on human hands (2.6) suggests that the diet is the main source of human intake,

### Table IV. Chlorinated Paraffins in Aquatic Organisms Taken from Rivers and the Sea in the UK area

| species | No. of specimens analyzed | chlorinated paraffin type and concn in tissues (means and ranges) | | | |
|---|---|---|---|---|---|
| | | $C_{10-20}$, ppm (w/w) | | $C_{20-30}$, ppm (w/w) | |
| | | mean | range | mean | range |
| *Pleuronectes platessa* (plaice) | 6 | 0.03 | ND <0.05 −0.2 | 0.03 | ND <0.05 −0.2 |
| *Trisopterus luscus* (pouting) | 4 | 0.1 | ND <0.05 −0.2 | ND <0.05 | ND <0.05 |
| *Mytilus edulis* (mussel) | 9 | 3.25 | 0.1–12.0 | 0.01 | ND <0.1 −0.1 |
| *Esox lucius* (pike) | 2 | 0.025 | ND <0.05 −0.05 | 0.025 | ND <0.05 −0.05 |
| *Halichoerus grypus* (grey seal) liver and blubber | 4 | 0.075 | 0.04–0.1 | ND <0.05 | ND <0.05 |

### Table V. CPs in Seabirds/ Eggs

species studied: *Phalocrocoracidae carbo* (cormorant); *Morus bassanus* (gannet); *Catharacta skua* (great skua); *Uria aalge* (guillemot); *Rissa tridactyla* (kittiwake); *Frateruela arctica* (puffin); *Puffinus puffinus* (manx shearwater); *Alca torda* (razorbill); *Phalacrocorax aristotelis* (shag)

no of eggs analyzed:[a] 23

| CP type | ND (<0.05 ppm) | 0.05 ppm | 0.1 ppm | 0.2 ppm | 0.3 ppm | 0.4 ppm | 0.6 ppm | >0.6 ppm |
|---|---|---|---|---|---|---|---|---|
| $C_{10-20}$ | 7 | 3 | 3 | 5 | 1 | 2 | 1 | 1 (=2 ppm) |
| $C_{20-30}$ | 17 | 3 | 3 | | | | | |

chlorinated paraffins in seabirds:

| species | organ | $C_{10-20}$ CP, ppm (w/w)[b] | $C_{20-30}$ CP, ppm (w/w)[b] |
|---|---|---|---|
| heron (*Ardea cinerea*) | liver | 0.5–1.2 | ND <0.1 |
| | liver | 0.1–1.0 | 0.1–1.5 |
| guillemot (*Uria aalge*) | liver | 0.1–1.1 | ND <0.1 |
| herring gull (*Larus argentatus*) | liver | 0.2–0.9 | 0.1–0.5 |

[a] We gratefully acknowledge the provision of these egg samples by the Institute of Terrestrial Ecology, Monks Wood Research Station, Abbotts Ripton, Hunts, UK. [b] On wet weight of tissue.

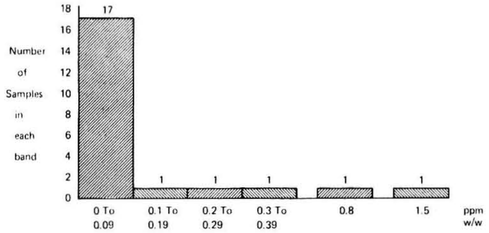

**Figure 1.** Histogram of $C_{10-20}$ chlorinated paraffin levels in human liver tissues (ppm w/w on wet tissue basis).

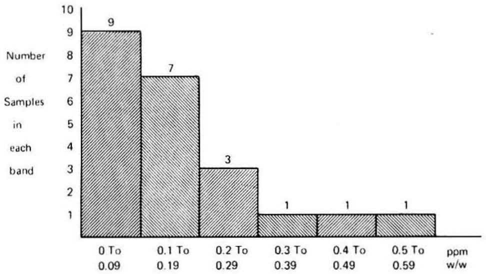

**Figure 2.** Histogram of $C_{10-20}$ chlorinated paraffin levels in human adipose tissues (ppm w/w on wet tissue basis).

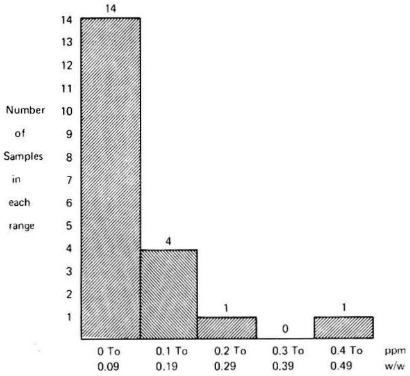

**Figure 3.** Histogram of $C_{10-20}$ chlorinated paraffin levels in human kidney tissues (ppm w/w on wet tissue basis).

$C_{10-20}$ Chlorinated Paraffin levels in human brain tissue were all < 0.09 ppm

$C_{20-30}$ Chlorinated Paraffin levels were ND on all 24 subjects, except:

| | | |
|---|---|---|
| 3 SUBJECTS | : | FAT 0.1 ppm |
| 1 " | : | LIVER 0.08 ppm |
| 1 " | : | FAT 3.5 ppm; LIVER 0.2 ppm |

(NOTE: ND means not seen, so < 0.05 ppm)

directly and possibly by manual contamination. In both human and other animal tissues, the adipose tissue generally contained greater concentrations reflecting the high lipid solubility of CP; occurrence in the liver may also be due to retention in the hepatic lipids or to binding by other components of this organ. The general predominance of $C_{10-20}$ over $C_{20-30}$ CP in all analyses may reflect the production ratios.

## 4. *Conclusions*

The water and sediment analyses show that CPs are absent, or are present at barely detectable levels. $C_{20-30}$ CPs occur less

**Table VI. Chlorinated Paraffins in Human Foodstuffs**

| foodstuff class[d] | $C_{10-20}$ CP,[c] av ppm (w/w) | no. of foodstuff samples tested |
|---|---|---|
| dairy products | 0.3 | 13 |
| vegetable oils and derivatives | 0.15 | 6 |
| fruit and vegetables | 0.025 | 16 |
| beverages | ND | 6 |
| | $C_{20-30}$ [c] | $C_{10-20}$ [c] |
| sheep (Welsh):[a] liver, brain, kidney, mesenteric fat | ND | ND |
| sheep (Weston Point):[b] | | |
| heart | ND | ND |
| liver | ND | 0.2 |
| lung | ND | ND |
| mesenteric fat | ND | 0.05 |
| kidney | ND | 0.05 |
| perinephritic fat | ND | ND |

[a] The welsh sheep were grazed remote from production of chlorinated paraffins. [b] The Weston Point sheep were grazed near a plant producing chlorinated paraffins. [c] ND implies not detectable, i.e., less than the detection limit of 0.05 ppm (w/w). [d] $C_{20-30}$ was found in only one sample of cheese (0.19 ppm), one of potato crisps (0.025 ppm), and one of peach fruit (0.025 ppm).

often and at lower levels than $C_{10-20}$ CPs. A comparison of nonindustrialized with industrialized waters and the sea shows a slightly increasing occurrence near industry and towns with almost complete disappearance as the river enters the sea. The ratio of 1:1000 between levels in water and sediment, with the low solubility of CP in water, suggests that CP is transported on suspended solids in the water. The relative absence of CP from seawater may be due to sedimentation of colloidal silt in the more saline seawater.

$C_{20-30}$ CP is almost absent from aquatic organisms, and even the $C_{10-20}$ CP is present only occasionally at low levels. The median concentration distribution in seabirds' eggs is 0.2 ppm of $C_{10-20}$ CP, the $C_{20-30}$ CP being almost absent.

Mean levels in dairy/oil foods are higher (0.15–0.3 ppm) than in fruit/vegetables and beverages (0–0.025 ppm), in line with the oil solubility of CPs.

Some CP was detected, at low levels, in at least one human tissue from every subject analyzed. The higher CP concentrations were found in the fat, and, on this basis, the total body burden of CP for a 60-kg human is estimated to be in the range 0–7 mg with an average of 2.3 mg; in view of the currently known mammalian toxicology of CP (*4*), this quantity will not pose any health hazard to man.

The pathway by which CP is dispersed into the aquatic environment from effluent and sewage, and thence into the organisms of the aquatic-based food chain, is clear from a study of the available analytical results. The findings from organisms taken from nature agree well with CP levels achieved in laboratory organisms fed CP artificially (*3*). The route by which CP enters land animals and humans is less clear. In the case of humans, the small content in foodstuffs may contribute, as may direct transfer from manufactured articles via the hands.

The low aqueous solubility, low vapor pressure, and inability of CP to come into reactive contact with reagents by which it would otherwise be degraded cause CPs to be relatively chemically stable in the environment. At the same time, their rapid adsorption onto solids and consequent sedimentation tends to remove them from contact with organisms and helps to avoid entry into food chains.

## *Acknowledgment*

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***Supplementary Material Available:*** *Extended versions of Tables I, II, and IV–VI, Table VII describing analysis of human postmortem organ and tissue samples for CP; Figures 4–6 showing locations of sampling points, and an appendix of substances not interfering with the analytical method (13 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Business Operations, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Full bibliographic citation (journal, title of article, author) and prepayment check or money order for $6.50 for photocopy ($8.00 foreign) or $3.00 for microfiche ($4.00 foreign) are required.*

# Chlorinated Paraffins and the Environment. 2. Aquatic and Avian Toxicology

**John R. Madeley* and Robin D. N. Birtley**

Imperial Chemical Industries Limited, Research and Development Department, Mond Division, The Heath, Runcorn, Cheshire, P.O. Box No. 8, WA7 4QD, United Kingdom

■ The toxicity of certain chlorinated paraffins (CPs) to fish and birds is presented. No toxic response could be demonstrated. A high molecular weight CP (42% Cl w/w) containing a $^{14}C$ radiolabel was taken up into the tissues of rainbow trout and mussels. Comparison of CP concentration in tissues, as measured by a thin-layer chromatographic technique and $^{14}C$, indicated that mussels expelled the CP as the parent compound. Trout, however, appeared to metabolize the material. The ability of aerobic microorganisms to oxidize a range of CPs depends upon their previous acclimatization, the hydrocarbon chain length, and its degree of chlorination. Short-chain compounds are the most readily oxidized at chlorine levels below 60% (w/w). Complete breakdown has been demonstrated for a long-chain CP over a period of 8 weeks. Anaerobic microorganisms, under the experimental conditions examined, did not degrade a specific CP in 30 days.

## 1. *Introduction*

A sensitive analytical method has been developed for the measurement of chlorinated paraffins (CP) in a range of environmental samples (*1*). Use of this method (2) has enabled some knowledge to be gained of the distribution of these compounds in the aquatic and terrestrial environments, birds, and man.

It appears that CPs are widely distributed, albeit at low concentrations; therefore, it becomes important to know of their toxicity, behavior, persistence, and fate in relation to these levels.

The aim of this particular paper in the three-part series is to present results of laboratory studies on toxicity, bioaccumulation, and biodegradation in the aquatic environment, with some information on avian toxicity. Mammalian toxicology, although summarized here, is presented in detail elsewhere (*3*).

## 2. *Effects on Aquatic Organisms*

**2.1. Introduction.** Laboratory studies to determine the toxicity, bioaccumulation, and possible biomagnification of CPs have, in the past, been hampered by the lack of a sensitive analytical method. With the benefit of such a method, our own investigations have been designed to highlight areas where environmental problems could possibly arise and indicate where further assessments may be required for a more complete understanding of CP behavior.

**2.2. Acute Toxicity and Sublethal Observations.** Acute toxicity studies have been carried out to ascertain the 96-h $LC_{50}$ value—the concentration required to kill 50% of fish in 96 h—for Cereclor 42 ($C_{20-30}$ 42% Cl w/w) by using rainbow trout (*Salmo gairdneri*) as test species. Cereclor is a trade mark of Imperial Chemical Industries Limited for chlorinated paraffins. Concentrated emulsions of the CP were prepared and subsequently diluted for exposure of 10 fish per concentration. Static bioassays were carried out at 15 ± 1 °C, emulsions being changed every 24 h. Emulsion concentration was determined by infrared spectrophotometry after extraction of CP in carbon tetrachloride.

Some loss of CP from emulsion occurred, particularly from the higher concentrations; quoted values are means from several sets of analytical figures.

Over 96 h CP emulsions were nontoxic to rainbow trout at a mean concentration of 770 ppm (range 520–1630 ppm). No sublethal effects were observed owing to the opacity of emulsions. No unusual fish behavior was noted. The CP can therefore be considered as nontoxic over a short exposure period. By comparison, a PCB, Aroclor 1242, was found to be toxic to rainbow trout; the 96-h $LC_{50}$ value was between 49 and 77 ppm.

Similar results for a series of CPs were obtained by Johnson (*4*) who demonstrated 96-h $LC_{50}$ values in excess of 300 ppm to rainbow trout and bluegills (*Lepomis macrochirus*). However, at concentrations of 40 ppb, for an unidentified CP, he demonstrated certain neurotoxic effects in flowthrough experiments. Loss of motor function and immobilization were described. These observations have been confirmed by Svanberg et al. (*5*) over exposure periods in excess of 14 days. Bleaks (*Albernus albernus*), exposed to 1.0 and 0.1 ppm of Hüls chlorparaffin 70C ($C_{10-13}$ 70% Cl w/w) added to the test water from acetone solution, showed signs of disorientation and tetanic spasm which led to the death of three individuals.

Short-term toxicity tests (96 h) demonstrate the very low acute toxicity of CPs to the test species examined. Neurotoxic symptoms, observed during more prolonged exposure, appear to be restricted to the lower molecular weight compounds. The effects could be related to their higher water solubility, possibly enhanced by method of addition, as well as the higher "biological activity" of these CP grades.

**2.3. Bioaccumulation in the Laboratory.** It has been suggested (*6*) that the high molecular weight of CPs would appear to limit their potential for bioaccumulation in the aquatic environment. In addition, their very strong tendency to adsorb on suspended particles would reduce the availability of CPs to food-chain organisms. This suggestion was based in part on the work of Zitko (*7*) and Lombardo et al. (*8*); test fish fed on CP-dosed food showed that the compounds were detected but were not accumulated to any significant extent in tissues.

Since then, however, Svanberg et al. (*5*) have detected an accumulation of organic chlorine in fish exposed to low concentrations of a low molecular weight CP in water.

In the studies described here, CP was uniformly mixed with food to examine specifically this route of administration to the common mussel (*Mytilus edulis*) and rainbow trout (*Salmo gairdneri*). Experiments were carried out by using a CP based on a wax feedstock ($C_{20-30}$) chlorinated to 42% by weight (Cereclor 42). The availability of $^{14}C$ centrally labeled pentacosane ($C_{25}$), subsequently chlorinated to 42% by weight, allowed concentrations of CP to be followed in food and animal tissues by radiocarbon analysis. For experimental purposes the chlorinated pentacosane was mixed with Cereclor 42 before use.

In the case of mussels, suspended yeast cells were finally chosen as the CP-dosed food source; attempts to contaminate marine unicellular algae uniformly had previously proved unsuccessful. Commercial trout diets (Cooper Nutrition No. 4 pellets) were similarly dosed with CP as the sole food for rainbow trout.

All test organisms were maintained in glass-reinforced plastic tanks; dosing lines were constructed from glass. Test solutions were maintained at 16 ± 2 °C for mussels and 12 ± 3 °C for rainbow trout.

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The test and control populations were sampled regularly during the feeding of dosed food, and also after clean diet substitution. Six mussels and three fish were sacrificed on each sampling occasion and dissected into appropriate tissue and organs for $^{14}C$ examination. Analysis was carried out by combustion in a Packard sample oxidizer (Model 306) where appropriate, followed by counting in a Packard Tricarb scintillation spectrophotometer (Model 3320).

**2.3.1. Rainbow Trout Study.** Separate rainbow trout populations each of 40 individuals were fed diets containing average concentrations of 47 ppm (w/w dry) and 385 ppm (w/w dry) CP for a period of 35 days; a similar control group was fed the same but uncontaminated diet. Subsequently all fish were fed control diets for a further 49 days.

Table I compares the $^{14}C$ concentration in tissues of fish on the final days of feeding both the dosed and clean diets. Quantities found in tissues after 35 days were closely related to food dose levels, and, further, the $^{14}C$ remaining after depuration was related to the amount originally accumulated in the tissues.

The uptake and loss of $^{14}C$ in the tissues of fish fed on diets containing 47 ppm CP are illustrated in Figure 1. During accumulation a wide variation of $^{14}C$ in gut tissue was determined; this however, could be expected owing to difficulties in dissection and bearing in mind the administration route. By comparison the uptake of $^{14}C$ in liver was much more uniform. The concentration in both liver and gut approached that administered in the food. Other tissues showed less uptake, so that the calculated total body level was well below the concentration administered and reached a plateau by day 35.

Liver and gut samples lost $^{14}C$ rapidly and markedly within 49 days, at a rate much greater than other tissues. The form of all depuration curves indicated that $^{14}C$ in all tissues would reach low residual levels within a period in excess of 50 days.

Fish populations were carefully scrutinized for any unusual symptoms throughout the test. One death occurred in the control tank. The condition of individuals was estimated by measurement of the "condition factor" (*9*); these were always >1, indicating their prime condition throughout the test.

**2.3.2. Mussel Study.** Dry baker's yeast was dosed with CP at a mean concentration of 524 ppm (w/w dry) before suspension in freshwater for addition to the test tanks. These treated yeast cells were fed to mussels for 47 days; controls received untreated yeast. After this time all mussels received untreated yeast for a further 56 days.

The uptake of $^{14}C$ by mussels continued up to the end of the 47-day accumulation period (Table II). Compared to the concentration in food this uptake was small. Within the

**Table I. $^{14}C$ Concentration in Fish Tissues Measured on the Final Days of Feeding CP-Containing Diets and Clean Diets**

| treatment | exposure period, days | mean concn $^{14}C$ in tissues (ppm dry wt) liver | gut | flesh | remains | total[a] |
|---|---|---|---|---|---|---|
| diet containing 47 ppm (dry wt) | 35 | 29.5 | 36.4 | 2.5 | 6.8 | 10.3 |
| subsequently fed clean diet | 49 | 2.8 | 4.8 | 1.4 | 3.1 | 3.3 |
| diet containing 385 ppm (dry wt) | 35 | 263 | 353 | 23.1 | 66.3 | 100.6 |
| subsequently fed clean diet | 49 | 21.8 | 47.3 | 17.2 | 29.8 | 31.6 |

[a] Total derived from measurements of tissue weights and $^{14}C$ concentration for individual fish.

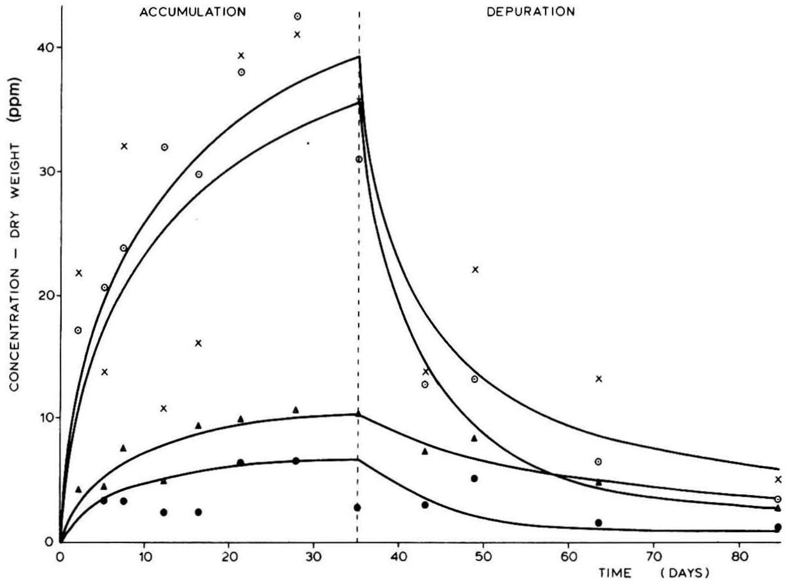

**Figure 1.** Uptake and loss of $^{14}C$ by rainbow trout (diet containing 47 mg of Cereclor 42/kg): (⊙) liver; (×) gut; (●) flesh; (▲) total body (calculated). Regression curves derived from equations: (i) accumulation phase, $c = k_1 \log e(t + 1)$; (ii) depuration phase, $c = 1/[k_2 + k_3(t - t_D)]$; where $c$ = concentration at time $t$ from start of test, $t_D$ = start time for depuration phase, $k_1$, $k_2$, and $k_3$ = constants derived by regression analysis.

mussels the $^{14}C$ was concentrated in the digestive gland. In all other tissues examined the levels remained below 10 ppm (w/w dry).

Mortality was assessed by observation of excessive shell opening; any "gaping" individuals were considered "dead" if, upon removal from the tank, they were incapable of fully closing within 1 min. On this basis deaths recorded were 10 individuals in the test tank and 7 in the control.

**2.3.3. Analysis of CP in Fish and Mussels.** The experiments undertaken were primarily designed to assess the extent of accumulation, distribution, and loss of CPs from organisms by radiolabel techniques. However, measurement of the parent compound concentration in the same tissues for comparison is capable of providing evidence on the occurrence of CP breakdown. During the course of the $^{14}C$ studies, certain individuals were retained for analysis by the TLC procedure (*1*).

Three individual fish were retained at the end of the study for this comparative analysis. Table III shows the mean $^{14}C$ values for the tissues examined by direct combustion. Also shown are the mean $^{14}C$ values on the extracts after cleanup in the CP analytical procedure, together with the mean CP figures obtained on the same extracts after TLC separation and quantification.

The concentrations of $^{14}C$ and CP in the extracts were generally similar but very much lower than the $^{14}C$ level obtained after tissue combustion. If one takes into account any losses of CP during preparative stages, these differences would appear significant, leading to the conclusion that not all $^{14}C$ in fish tissue was present as parent CP. This suggests that some CP was dehydrochlorinated or metabolized to smaller molecules (below $C_{10}$) and incorporated into other degradative or synthetic pathways within the animal.

The behavior of $^{14}C$ originally entering the animal from food dosed with CP has been followed through the major steps of extraction and cleanup before TLC separation. Recoveries of $^{14}C$ have been compared with those for the same CP dissolved in hexane. Results are presented for two individual fish in Table IV.

Recovery of CP from spiked fish tissue was ~90% (*1*). It has also been shown that the recovery of $^{14}C$-labeled CP present in hexane was similar, whereas final extracts from experimentally dosed fish contained only 27–33% of $^{14}C$ originally present. Failure to recover major quantities of $^{14}C$ occurred

**Table II. Concentration of $^{14}C$ in Tissues/Organs of Mussels Examined during Accumulation/Depuration (days)**

| tissue/organ examined[a] | | accumulation period (concn of $^{14}C$ in tissue/organ, ppm dry weight) | | | | | | | | depuration period (concn of $^{14}C$ in tissue/organ, ppm dry weight) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | day | 5 | 9 | 12 | 19 | 26 | 33 | 42 | 47 | 7 | 21 | 28 | 39 | 49 | 56 |
| digestive gland | | | | | | 155.2 | 36.6 | 100.7 | 80.5 | 35.1 | 37.0 | 42.2 | 15.8 | 11.3 | 7.0 |
| foot | | | | | | 2.6 | 1.3 | 2.2 | 5.4 | 1.8 | 3.3 | 3.1 | 2.9 | 1.7 | 0.9 |
| gonad | | | | | | 2.8 | 1.9 | 3.5 | 1.9 | 1.4 | 2.0 | 1.0 | 2.0 | 1.5 | 0.9 |
| gill | | | | | | 3.5 | 5.3 | 4.4 | 7.0 | 3.3 | 3.1 | 1.9 | 3.6 | 2.5 | 1.5 |
| remaining tissue | | | | | | 1.8[c] | 2.9 | 4.6 | 6.8 | 1.7 | 1.7 | 1.5 | 1.7 | 1.3 | 0.6 |
| total body[b] | | 1.8 | 2.4 | 4.2 | 5.1 | 4.3 | 5.9 | 6.6 | 11.2 | 5.5 | 2.9 | 2.0 | 2.2 | 3.1 | 1.2 |

[a] Mean for three individuals. [b] Mean for three *separate* individuals. [c] One high value (36.0) omitted.

**Table III. Concentration of Cereclor 42 in Fish Tissues (Means from Three Individuals) Measured by TLC and $^{14}C$ Scintillation Counting**

| | | ppm (dry weight) of $^{14}C$ and Cereclor 42 in tissues | | |
|---|---|---|---|---|
| | | | chemical extraction and cleanup, followed by | |
| previous feeding regime and sampling date | tissues/organs examined | $^{14}C$ concn by combusting and scintillation counting | $^{14}C$ count of extract | CP concentration spot intensity measurement |
| food containing 385 ppm (w/w dry) Cereclor 42, sampled day 49 of depuration period | liver | 21.8 | 1.5 | 6.5 |
| | gut | 47.3 | 8.7 | 5.4 |
| | flesh | 17.2 | 4.8 | 3.7 |
| | remains | 29.8 | 5.9 | 5.7 |

**Table IV. Distribution of $^{14}C$ in Extracts Obtained during Preparative Stages of the TLC Procedure for Quantification of CP in Tissues[b]**

| major preparative stages in TLC procedure for CP measurement | fish A | | fish B | | $^{14}C$-labeled CP in hexane | |
|---|---|---|---|---|---|---|
| | $^{14}C$, μg | % total | $^{14}C$, μg | % total | $^{14}C$, μg | % total |
| 1. total $^{14}C$ in sample | 62.7[a] | 100[a] | 32.2[a] | 100[a] | 50.3 | 100.6 |
| 2. extraction | | | | | | |
| (i) 1st Soxhlet extraction, 3 h hexane | 43.4 | 69.2 | 24.4 | 75.5 | | |
| (ii) 2nd Soxhlet extraction, 3 h hexane | <0.9 | <1.4 | <0.9 | <2.7 | | |
| (iii) residue plus $Na_2SO_4$ after extractions | 19.3 | 30.8 | 7.8 | 24.2 | | |
| 3. Cleanup: hexane/dimethylformamide (DMF) partitions | | | | | | |
| (i) hexane after DMF extraction | 3.4 | 5.4 | 2.9 | 9.0 | 2.1 | 4.2 |
| (ii) hexane wash | 1.6 | 2.5 | <1.0 | <3.0 | 1.6 | 3.2 |
| (iii) bulked DMF plus 2% $Na_2SO_4$ after back extraction | 6.5 | 10.3 | 3.7 | 11.4 | 1.7 | 3.4 |
| 4. TLC plate | | | | | | |
| (i) final hexane extract "spotted" on plate | 17.2 | 27.4 | 10.5 | 32.6 | 44.9 | 89.8 |

[a] Owing to small size of fish, this figure is the sum of 2.i, ii, and iii. [b] Two fish previously fed $^{14}C$ CP in food for 13 days. Comparison of distribution of $^{14}C$-labeled CP dissolved in hexane.

during Soxhlet extraction and the back extraction step into hexane, where >90% recovery could be expected. These data demonstrate that the bulk of the $^{14}C$ was not present as the parent CP.

Further evidence for the breakdown of CPs has been gained during the development of TLC plates for their quantification. Certain developed spots occurred with lower $R_f$ values than those for Cereclor 42. Portions of the aluminium oxide coating incorporating these spots were scraped off the plates and subjected to $^{14}C$ scintillation counting. Although counts were too low to quantify, evidence for $^{14}C$ presence above background levels was established. For development, these spots must contain chlorine; their presence indicates splitting of the paraffin chain before removal of all chlorine atoms from the molecule.

A similar detailed comparative study was not possible for mussels retained from the laboratory study owing to their small size. Instead, individuals taken at the same time during the experiment were examined for CP by either TLC analysis or $^{14}C$ counting. The comparison figures are shown in Table V.

The concentrations of CP in mussels were similar as measured by the two techniques for animals sacrificed at the same time, bearing in mind both small sample size and variation between individuals. Metabolism, on this evidence, cannot be considered a major route for CP removal from mussels; rather, loss would appear to be in the form of the parent compound.

**2.4. Biodegradation.** Literature references to biodegradation of CPs are sparse and somewhat inadequate. Hildebrecht (*10*) has measured oxygen consumed by microorganisms in the presence of Chlorowax preparations in a Warburg respirometer and BOD tests. The presence of both a surfactant and unspecified nutrients makes interpretation difficult, but the Chlorowax 500C ($C_{10-13}$ 60% Cl w/w) was apparently partially degraded. Chlorowax 40 ($C_{20-30}$ 40% w/w) also exerted a BOD.

By specific analysis Zitko and Arsenault (*11*) have shown a loss of Cereclor 42 and Chlorez 700 from spiked sediments. They concluded that the compounds were biodegraded, particularly by anaerobes.

We have examined the microbial degradation of several CPs in extended biochemical oxygen demand (BOD) tests. Concentrated emulsions of a range of Cereclor formulations were prepared in distilled water. After standing for 24 h, a portion of the bulk emulsion was decanted, and the quantity of CP determined by infrared spectrophotometry after extraction in carbon tetrachloride. All test emulsions were added to BOD dilution water at approximate concentrations of 2, 10, and 20 ppm, determined by analysis, with the appropriate microbial seed.

Microorganisms, cultured from soil obtained close to a CP production plant, were acclimatized in shake flasks over an 8-week period to a range of CP emulsions. A basal medium was used containing 20–50 ppm (w/v) of each CP to be examined. Nonacclimatized microbial populations were obtained from the effluent of laboratory activated sludge units treating domestic sewage.

Replicate BOD bottles were set up for each CP concentration; the concentration of dissolved oxygen remaining in each bottle was measured after incubation for 5, 10, 15, 20, and 25 days. Results, expressed as BOD (g/g) for each CP tested, are shown in Table VI.

From the results obtained for the CPs examined, certain conclusions can be reached:

(a) Microorganisms previously acclimatized to specific CPs showed a greater ability to degrade the compounds than organisms normally treating domestic sewage.

(b) Degradation of the paraffin chain as measured by BOD would appear to be related to carbon chain length and percentage chlorination.

(c) Increasing chlorination percentage inhibited biodegradation.

(d) The short-chain CP ($C_{10-13}$) would appear to be degraded most rapidly and completely by acclimatized microorganisms at 50% chlorine by weight. Sewage treatment organisms also brought about significant breakdown.

(e) For longer-chain paraffins chlorinated up to 45%, the BOD expression, although slower and reduced, indicated substantial breakdown by acclimatized organisms.

(f) Similarly, the only wax-grade CP examined ($C_{20-30}$ 42% Cl w/w) was degraded when organisms were previously acclimatized.

To examine the extent of breakdown of long-chain CPs, we emulsified $^{14}C$ centrally labeled chlorinated pentacosane, mixed with "Cereclor" 42, and added it to a series of Hach respirometers (*12*) with nonacclimatized microorganisms. Carbon dioxide was collected in potassium hydroxide solution. After incubation for 8 weeks, any $^{14}CO_2$ evolved was measured by scintillation counting. Of the $^{14}C$ originally present 11.0% (mean) was collected as $^{14}CO_2$, indicating that, where it occurred, breakdown of the chlorinated pentacosane had taken place sufficiently to release the central carbon atom of the CP.

From this, and the BOD tests, virtually complete breakdown of certain $C_{10-13}$ CPs can be considered possible. Partial breakdown of longer-chain compounds has been demonstrated. Provided the percentage of chlorine on the degraded paraffin chains remains below 50%, their more complete degradation could be envisaged.

A preliminary assessment of the effect of a CP on anaerobic microorganisms has been undertaken. A convenient source of active mixed populations can be obtained from anaerobic sewage sludge digesters, containing both robust facultative genera and more fastidious strict anaerobes.

Gas production (methane and $CO_2$) in the presence of increasing quantities of emulsified Cereclor 42, compared to controls, was taken as a sensitive measure of effect in small laboratory digesters (*13*).

Over 30 days, at CP concentrations up to 10% (w/w) on dry sludge solids, no significant increase or reduction of bacterial activity was noted. Thus, this specific CP was not toxic or

**Table V. Comparison of the Concentration of Cereclor 42 in Whole Mussels Measured by $^{14}C$ Scintillation Counting and by TLC**

| | ppm (dry weight) of Cereclor 42 in whole mussels as measured by | |
|---|---|---|
| mode of exposure and sampling time | $^{14}C$ direct combustion and scintillation counting | chemical extraction and cleanup followed by TLC [a] |
| accumulation from food, day 47 accumulation phase | 11.07, 9.12, –, 8.31, 9.52, – | 4, 16, 3 |
| accumulation from food, day 56 depuration phase | 2.59, 1.05, 0.72, 0.57, 1.13, 1.49 | 7, 2, 3, <1 |
| control mussels | | <1, 2, <1, <1 |

[a] All values rounded to the nearest whole number owing to small sample size.

inhibitory to the microflora at the concentrations examined, but, where readily biodegradable alternative carbon sources were available, the compound was not actively broken down.

### 3. *Avian Toxicity*

**3.1. Introduction.** There has been no previously published work on the toxicity of chlorinated paraffins to avian species. This section describes the determination of the acute and subacute toxicity and tissue concentrations in two avian species of one grade of chlorinated paraffin.

**3.2. Experimental Section. Test Species.** Ring-necked pheasants (*Phasianus colchicus*) and mallard ducks (*Anas platyrynchos*) were supplied from Lincolnshire Pheasantries, England.

**Test Substance.** Cereclor S52 is derived from *n*-paraffins containing between 14 and 17 carbon atoms which are then chlorinated to 52% by weight. Technical dieldrin was obtained from Shell Research Limited.

**Procedure. Toxicity Studies.** The acute oral LD$_{50}$ and subacute dietary LC$_{50}$ study designs were as described by the U.S. Environmental Protection Agency (*14*). All birds were allowed at least 7 days to acclimatize to their environment prior to treatment. Food and water were available ad libitum.

**3.2.1. Acute Oral LD$_{50}$ Studies.** Groups of one male and one female bird were used in an initial dose range-finding study in which Cereclor S52 was given by oral gavage either as the undiluted liquid or as a 25% v/v mixture with liquid paraffin. Each bird received a volume up to 15 mL (pheasant) or 10 mL (duck) and was observed for abnormal clinical signs or mortality for 14 days after dosing.

In the main acute toxicity study, groups of five male and five female birds received either the maximum practicable dose of undiluted Cereclor S52, i.e., 10 mL per bird (duck) or 15 mL per bird (pheasant), or, in the case of control groups, equivalent volumes of water. During the 14 days after dosing, each bird was examined once daily for mortality or any abnormal clinical signs; body weight was recorded on the day of dosing and 3, 7, and 14 days afterwards. Weekly food intake per group of pheasants was measured; the untidy feeding habits of young adult mallard ducks precluded any meaningful food consumption measurements being made in this species. At the end of the observation period, each bird was subjected to a gross post-mortem examination, and any abnormalities were noted.

**3.2.2. Subacute Dietary LC$_{50}$ Studies.** One-day-old male and female birds were allowed 11 days of acclimatization prior to treatment. Dieldrin or Cereclor S52 was incorporated into the diet at various concentrations by admixture with the appropriate weight of test material dissolved in a fixed volume of corn oil. Corn oil alone was mixed with diet for the control groups; corn oil was added to diet for all birds for 3 days prior to and after the commencement of treatment.

Groups of five male and five female birds were used in a preliminary dose-range study to assess the subacute toxicity of Cereclor S52 administered continuously in the diet for 5 days. Each bird was observed for any abnormal clinical signs or mortality during this period. In the main study, three groups of birds acted as negative controls, two groups received Cereclor S52 at 1000 or 24 063 ppm in diet, and six groups received dietary concentrations of dieldrin (positive control) of 8, 20, 38, 65, 106, and 156 (pheasant) or 50, 62, 80, 107, 148, and 208 ppm (duck). During the 5-day treatment period and the subsequent 3 days, each bird was observed daily for abnormal clinical signs or mortality. Each bird was weighed 3 days before and on the day that treatment commenced and then on the fifth and eighth days after treatment started. Food intake for each group was recorded during the treatment period and during the 3 days before and after this period. At the end of the observation period, up to five birds per group were subjected to a gross post-mortem examination and any abnormalities were noted. LC$_{50}$ values were calculated by a method similar to that described by Finney (*15*).

**3.2.3. Analysis of Chlorinated Paraffin Content of Tissues.** Two adult mallard ducks were given a single oral dose of 10 g of Cereclor S52/kg. In addition, two groups each of 10 pheasant chicks received 1000 ppm of Cereclor S52 in the diet for 5 days. Three days after the last treatment, all birds were killed, and the following tissues were removed from each bird, identical tissues being pooled (pheasants only) and analyzed for chlorinated paraffin content after appropriate extraction procedures and thin-layer chromatography: liver, gut, heart, muscle (both species); subcutaneous fat and feathers (mallard duck only). Simultaneous analysis for short and long carbon-chain-containing chlorinated paraffins was undertaken (*1*).

**Table VI. Biochemical Oxygen Demand (BOD) of a Series of Chlorinated Paraffins Using Acclimatized and Sewage Treatment Microorganisms**

| | | BOD gr/gr at day | | | | |
|---|---|---|---|---|---|---|
| chlorinated paraffin | microorganism inoculum [a] | 5 | 10 | 15 | 20 | 25 |
| $C_{10-13}$ 49% Cl | NA | 0.02 | 0.08 | 0.12 | 0.20 | 0.29 |
| | A | 0.25 | 0.46 | 0.55 | 0.65 | 1.02 |
| $C_{10-13}$ 60% Cl | NA | | no significant oxygen uptake | | | |
| | A | | | | | |
| $C_{10-13}$ 70% Cl | NA | | no significant oxygen uptake | | | |
| | A | | | | | |
| $C_{14-17}$ 40% Cl | NA | 0.02 | 0.32 | 0.41 | 0.37 | 0.29 |
| | A | 0.10 | 0.30 | 0.49 | 0.54 | 0.42 |
| $C_{14-17}$ 45% Cl | NA | | 0.05 | 0.14 | 0.19 | 0.18 |
| | A | | 0.20 | 0.37 | 0.49 | 0.57 |
| $C_{14-17}$ 52% Cl | NA | | 0.02 | 0.06 | 0.04 | 0.07 |
| | A | 0.02 | 0.03 | 0.07 | 0.09 | 0.10 |
| $C_{14-17}$ 58% Cl | NA | | no significant oxygen uptake | | | |
| | A | | | | | |
| $C_{20-30}$ 42% Cl | NA | | 0.16 | 0.18 | 0.31 | 0.14 |
| | A | | 0.01 | 0.14 | 0.37 | 0.43 |

[a] NA = Nonacclimatized microorganisms. A = Acclimatized seed, shake flask culture (see text).

**3.3. Results and Discussion. 3.3.1. Acute Oral $LD_{50}$ Studies.** Doses up to 10 280 mg/kg (duck) and 24 606 mg/kg (pheasant) failed to produce any abnormal clinical signs or mortality in any bird. Thus, the $LD_{50}$ is in excess of these values for Cereclor S52. Body weight gain, food intake, and the observations made at autopsy were considered to be within the normal range. Cereclor S52 therefore has a low acute oral toxicity to ring-necked pheasants and mallard ducks.

**3.3.2. Subacute Dietary $LC_{50}$ Studies.** All of the birds which received control and Cereclor S52-containing diets remained in good health throughout the experiment, while those treated with dieldrin showed lethargy and loss of muscle function. The $LC_{50}$ values and 95% confidence limits for dieldrin were calculated to be 65 ppm (51–82 ppm) in ducks and 43 ppm (29–64 ppm) in pheasants. From this study, the $LC_{50}$ value for Cereclor S52 in both species of birds is in excess of 24 063 ppm in diet.

In ducks, inferior food intake was noted in groups receiving Cereclor S52 at 24 063 ppm and dieldrin at most concentrations compared with control groups. This was evident before as well as during treatment but the weight gains of these groups were generally comparable with control groups. In pheasants, dieldrin caused a dose-related reduction of weight gain and food intake compared with controls; no such effects were attributable to Cereclor S52 treatment. No abnormalities were noted at autopsy in either species of bird.

Cereclor S52 is therefore of low subacute toxicity when fed to ring-necked pheasants and mallard ducks, whereas dieldrin produced the expected type and intensity of toxic response.

**3.3.3. Analysis of Chlorinated Paraffin Content of Tissues.** The results are summarized in Table VII. A significant accumulation of short-carbon-chain *n*-paraffin derivative occurs in the fat, both intestinal and subcutaneous; that and the residual level in the gut suggest that appreciable absorption took place, even from the single gavage dose. Levels in other tissues, especially liver, are very much lower.

The high level on the feathers may be an artifact, due to contamination from gloves, etc.; no particular effort had been made to avoid it, but if genuine it could be accounted for by transfer from preen gland.

Because of the immaturity of the pheasant chicks, no visible fat was available for analysis; but the levels of short-carbon-chain *n*-paraffin derivatives in the other organs were surprisingly low, indicating a low rate of absorption and translocation.

Levels of long-carbon-chain *n*-paraffin derivative in all tissues were below the limit of detection.

### 4. *Mammalian Toxicology*

The results obtained by ICI to date on the mammalian toxicology of CPs are published elsewhere (*3*). These show that CPs are of very low acute oral toxicity and that the low molecular weight grades cause slight skin irritation on repeated application. Feeding a $C_{14-17}$ 52% chlorinated CP in the diet for 3 months at levels of 500 ppm (rats) or 30 mg $kg^{-1}$ $day^{-1}$ (dogs) or more caused hepatocellular changes. After continuous feeding to rats, CP was detected in adipose tissue at concentrations which did not exceed those in the diet; after treatment was stopped, CP was removed from adipose tissue with a half-life of a few weeks. Three grades of CP, representative of the grades produced commercially, showed no indication of mutagenic potential in two predictive in vitro tests.

### 5. *General Conclusions*

The low water solubility of CPs has complicated all studies to determine the effect of these compounds on aquatic organisms. When the various artificial means available for exposing test animals to a range of these compounds in water have been used, it has been shown that, apart from the $C_{10-13}$ grades of commercial products (*4, 5*), CPs are not acutely toxic, even at very elevated concentrations which are not practically possible in the environment. The acute toxicity of CPs to birds and mammals has also been demonstrated to be exceedingly low (*3*).

One of the major routes for CP dispersal in the environment could well be via water, through sewage and industrial waste disposal and eventually into the aquatic food chain (*2*). There would, however, be a considerable removal from the aqueous phase by adsorption onto solid surfaces. If the behavior of Cereclor 42 is typical of CPs, then these compounds could become distributed within the bodies of invertebrates which filter particulate matter from water. In the case of mussels used in our study, the level of CP in the body tissues was always less than that adsorbed on food particles filtered from the water. This uptake was reversed on subsitution of "clean" diets, and the CP appeared to be expelled from the animal in its original form.

By contrast rainbow trout appeared to metabolize CP as measured by the difference between $^{14}C$ and TLC analysis on the same tissues at the same time. Up to 80% of assimilated $^{14}C$ in tissues was not recognizable as CP after a period of 13 days.

Mammals (*3*) and fish, therefore, apparently metabolize CPs without any development of toxic symptoms. However, a major portion of the environmental input of CPs is likely to remain in the aquatic environment adsorbed on surfaces, so that microbial degradation of these compounds is important in the determination of their persistence and fate. From limited investigations it appears that aerobic conditions facilitate biodegradation. Acclimatized mixed bacterial cultures can break down CPs provided the chlorination percentage remains below 52% w/w. Shorter paraffin chains are more rapidly biodegraded. Extensive if not complete oxidation of the CP chain has been demonstrated for that portion of the total CP degraded by microorganisms.

This paper describes the results obtained to date in an ongoing program designed to evaluate the toxicological aspects of CPs. Longer-term studies of the effects of CPs on aquatic and mammalian species are still in progress.

From present information it can be stated that there is no reason to believe that CPs pose any significant environmental problem. The acute toxic effects observed for the $C_{10-13}$ group of CPs have to be weighed against their more rapid biodeg-

**Table VII. Mean Concentration (ppm Wet Weight) of Chlorinated Paraffin Containing Short (14–17) and Long (22–26) Chain Carbon Atom *n*-Paraffins in Various Tissues after Administration of Cereclor S52 to Mallard Ducks as a Single Oral Dose of 10 g/kg or to Pheasant Chicks in Diet (1000 ppm) for 5 Days**

| species of bird | type of chlorinated paraffin | tissue | | | | | |
|---|---|---|---|---|---|---|---|
| | | liver | gut | heart | muscle | fat | feathers |
| mallard duck | short | 2.4 | 15 | 7.0 | 2.2 | 67 | 115 |
| | long | <0.05 | <0.05 | <0.1 | <0.1 | <0.1 | <0.1 |
| pheasant | short | 0.6 | 1.4 | 3.1 | 0.3 | | |
| | long | <0.05 | <0.05 | <0.1 | <0.1 | | |

radiation, low water solubility, and adsorption characteristics, and the small fraction of this group present in the total CP in the environment at large.

*Acknowledgment*

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# Optical Absorption Constant of Suspended Particulate Matter. An Air Pollution Index

**I. Allegrini**

C.N.R., Istituto sull'Inquinamento Atmosferico, Area della Ricerca di Roma, C.P.10-00016 Monterotondo Stazione, Italy

■ A method for measuring the optical absorption constant based on diffuse reflectance has been applied to ambient particulate matter collected on membrane filters. Results obtained with artificially generated aerosols of known characteristics demonstrate the validity of this procedure. Measurements carried out on ambient aerosols indicate that the imaginary part of their refractive index ranges between $3 \times 10^{-3}$ and $80 \times 10^{-3}$. Experimental values obtained during the day as well as their correlation with particulate lead indicate that the observed increases in the optical constant can be ascribed to the increase of vehicular traffic density. These results also indicate that particulate measurements carried out by using the staining filter method are related to the optical constant rather than the surface mass density. The spectral dispersion of the imaginary part of the refractive index gives good evidence that the measured values of the optical constant are due to the presence of free carbon particles whose concentration can be estimated, providing a simple, reliable, and direct method for the evaluation of the "graphitic" fraction in urban particulate matter. The evaluation of both the free carbon concentration as well as the absorption coefficient of the atmosphere (as defined by Beer's law) obtained by means of optical constant data are in agreement with values found in other locations.

## *Introduction*

The nature of suspended particulate matter is very complex, being the result of a mixture of naturally emitted and anthropogenic particles. Classical analytical methods have severe limitations since they are unable to differentiate between different particulate sources.

Within the framework of an extensive research project on the optical properties of particulate matter, we found that the measurement of the optical constant is a very useful tool for determining the impact of primary emitted aerosols in the atmospheric environment.

As is well-known, the interaction between photons and a particle can be described by the Mie equation which can be easily solved for spherical and isotropic particles, providing that size and refractive index are known (*1*). The latter can be expressed as $m = n_1 - in_2$ where the imaginary part takes into account the light absorbed and is related to the optical constant $K$ (cm$^{-1}$), as defined by Beer's law, as $n_2 = K\lambda/4\pi$ with $\lambda$ the wavelength of the radiation.

On the basis of simple models, the quantity $n_2$ is the dominant factor affecting the radiative balance between the earth and the atmosphere; $n_2 = 0.01$ is the value for which no thermal effects are calculated. Higher values are likely to increase the surface temperature and vice-versa (*2, 3*).

The optical absorption constant could be used to differentiate sources of particulate matter which consist, as is well-known, of sea spray, volcanic dust, particles originating from gas conversion, and particles emitted by anthropogenic activities. These are mainly due to combustion processes which emit a large amount of "graphitic particles", i.e., particles containing carbon in elemental form and which are black in appearance. The optical constant is an additive parameter: $K = \sum_i k_i x_i$ where $k_i$ is the optical constant of the $i$th component present at concentration $x_i$. For airborne particulate matter, neglecting the contribution of transparent particles, one gets $K = k_n x_n + k_c x_c$ where the indices n and c refer to natural and carbonaceous particles, respectively. For natural aerosols and for red radiations, $k_n$ is about 300 (cm$^{-1}$), thus, for $K > 500$ the term $k_n x_n$ can be neglected and $K = k_c x_c$. By knowing the value of $k_c$ and measuring $K$, it is then possible to estimate $x_c$, i.e., the amount of graphitic particles, and ultimately to estimate the contribution of combustion processes to the concentration of suspended particulate matter.

The aim of this work is the evaluation of $K$ or the related value of the imaginary part of the refractive index ($n_2$) for ambient particulate matter by means of a simple and reliable method in order to meet several requirements such as the following: (A) to contribute to a better understanding of at-

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mospheric optics, including the climatic effect due to an increase in particle loading; (B) to correlate the response of optically based instruments, such as lidars and nephelometers, to other pollution indexes if quantitative data have to be extracted from optical signals (*4*); (C) to differentiate between primary and secondary and/or natural and anthropogenic aerosols by taking advantage of the additive properties of the optical constant, assuming—and usually it is so—graphitic particles to be the largest contributors.

In addition, recent investigations have proved soot (graphitic particles) to be an extremely effective catalyst for $SO_2$–sulfate conversion, thus increasing the need to understand carbonaceous particle emission into the atmosphere (*5*).

The method which has been used throughout the work is based on diffuse reflectance. A detailed discussion of the procedure has been reported previously (*6*). For convenience, the entire set of equations, including nomenclature, for extracting the value of the optical constant or the imaginary part of the refractive index is given in Table I. Reduction of reflectance data to optical constants has been done by a proper application of the Kubelka–Munk theory of diffuse reflectance.

The application of this method to dust collected on filters is not, however, so straightforward. First, in order to compute the Kubelka–Munk scattering coefficient, one must determine the thickness of the dust layer, and, in addition, the very small thickness usually obtained on loaded filters does not ensure that light entering the sample is completely diffused as required by the mathematical development of the theory (*7*).

This paper reports an investigation on the feasibility of the Kubelka–Munk method for the measurement of the optical constant of particulate matter collected on membrane filters. Laboratory tests were carried out on artificially generated aerosols of known composition, while field measurements were carried out on ambient particulate matter collected during winter months at the laboratory location.

### *Experimental Section*

**(a) Sampling Site.** Ambient aerosols were collected on the roof of the laboratory building which is located on the outskirts of Rome, approximately 13 km east from the center and 4 km from the nearest urban area. A motorway and a road near the building provide the only significant source of pollution in the area. Traffic on the motorway is very intense and includes a large number of trucks and buses powered by diesel engines which are, in some instances, not well tuned. Unpaved roads very near the building might provide a source of "natural" particulate matter.

**(b) Instrumentation.** Both ambient and laboratory aerosols were collected on Millipore filters of 0.8-$\mu$m pore diameter. The sampling train consists of a pump operating at 15 L $min^{-1}$ on a sequential sampler equipped with 4.7-cm filter holders; 2.5-cm diameter filters were used for collecting laboratory aerosols, prepared by spraying dilute solutions containing NaCl and nigrosine, a dye with a high absorption constant.

The solute concentrations were such that submicrometer-sized particles were obtained. A laser-light scattering method provided a measurement of the mean particle size with a response which is largely independent of the real and complex part of the refractive index (*8*). The mean particle size for the aerosols of NaCl–nigrosine was found to be ~0.7 $\mu$m in diameter.

Particulate thickness was measured by means of a $\beta$ gauge developed in our laboratory. This consists of a $^{14}C$ radioactive source of 100 $\mu$Ci $cm^{-2}$ activity and a Geiger–Müller detector with a very low dead time. An electronic circuit processes the input pulses which are read on 7-segment display. The counting frequency with unloaded filters is ~3 kHz; thus a counting time of $10^2$–$10^3$ s provides a statistical accuracy which is better than 10% (1 $\sigma$) in most cases. Performances of the instrument are discussed elsewhere (*9*).

Reflectance measurements between 400 and 800 nm were made on a Beckmann DK-2A spectrophotometer equipped with a 25-cm diameter integrating sphere, coated with freshly sublimated MgO. Highly refined $BaSO_4$ (white standard DIN 5033, Merck, Darmstadt) was used as a reference white, while optical black paper of negligible reflectance serve as black background.

Lead analysis was performed by means of atomic absorption spectrometry.

### *Results for Laboratory Aerosols*

The feasibility of the technique was first tested with NaCl–nigrosine aerosols. By varying the fraction $X_N$ of nigrosine, we generated aerosols of different optical absorption constants, the ratio $K/X_N$ providing an estimate of the constant of pure nigrosine. For $X_N$ ranging from 0.16 to 1.96 × $10^{-2}$, the ratio $K/X_N$ was found constant within 10% standard deviation. The measured value of $K$ was 1.09 × $10^5$ $cm^{-1}$ at 600 nm, and an imaginary part of the refractive index of 0.59 can be inferred. Such a value is typical of highly absorbing compounds, including graphitic particles.

Table II shows results for the mixtures. The reproducibility test was run for $X_N = 7.41 \times 10^{-2}$. The resulting standard deviation for ten different runs was ~10%.

**Table I. Kubelka–Munk Equations and Nomenclature**

$$R_0 = \frac{R_3/R_1 - R_4/R_2}{R_3 - R_4 + {R_2}^{-1} - {R_2}^{-1}} \qquad (1)$$

$$T = \left[(R_4 - R_0)({R_2}^{-1} - R_0)\right]^{1/2} \qquad (2)$$

$$a = (1 + {R_0}^2 - T^2)/2R_0 \qquad (3)$$

$$b = (a^2 - 1)^{1/2} \qquad (4)$$

$$S = \tanh^{-1}\left[bR_0/(1 - aR_0)\right]/2b \qquad (5)$$

$$s = S/d \qquad (6)$$

$$K = (a - 1)s \qquad (7)$$

$$n_2 = (K\lambda)/(4\pi) \qquad (8)$$

$R_1$ = diffuse reflectance of filter on black background
$R_2$ = same as above on white background
$R_3$ = same as $R_1$ with loaded filter
$R_4$ = same as $R_3$ on white background
$T$ = diffuse transmittance
$R_0$ = diffuse reflectance of the dust alone on a black background
$S$ = Kubelka–Munk scattering power
$s$ = Kubelka–Munk scattering coefficient ($cm^{-1}$)
$K$ = optical absorption constant ($cm^{-1}$)
$n_2$ = refractive index, imaginary part
$d$ = dust thickness (cm)
$\lambda$ = wavelength (cm)

**Table II. NaCl–Nigrosine Aerosols. Optical Constants for Different Nigrosine Fractions**

| $10^{-2}$ $X_N$ | $K$, $cm^{-1}$, at 600 nm | $(K/X_N)10^3$ |
|---|---|---|
| 1.96 | 2 100 | 107 |
| 3.85 | 3 780 | 100 |
| 5.66 | 4 910 | 88 |
| 7.41 | 7 870 | 106 |
| 9.1 | 11 746 | 129 |
| 16.6 | 18 980 | 114 |

A question of major interest concerns the effect of dust thickness on the measured value of $K$. The main assumption of the Kubelka-Munk theory of diffuse reflectance is that light entering the sample must be diffuse. Practically the assumption becomes reasonably true for fairly large thicknesses because the first layer of particles acts very much like an efficient Lambertian radiator so that inner layers receive diffused light even though irradiation is provided with nearly parallel light. In the case of filters loaded with particulate matter, the dust layer is very thin; thus deviations from the theory might occur, and experimental measurements were devised to check this possible source of error.

A preliminary test was performed with nigrosine–NaCl aerosols of $X_N = 5.66 \times 10^{-2}$ for loads ranging from 0.26 to 0.8 mg, which are typical of atmospheric particulate matter samples. Changing the amount of aerosols collected on the filters and measuring the corresponding optical constant, we obtained a standard deviation of 8.7%.

Another test was carried out with cement dust and for loads ranging from 2 to 22 mg. Results are given in Table III which show a standard deviation of 9% for $K = 410\ \text{cm}^{-1}$ at 800 nm. This value is close to that measured for natural aerosols.

After having tested the linearity of the method and its reproducibility, which can be estimated to be ~10%, we compared results obtained on filters with values given by the dilution method (*10*) to test the accuracy. As is well-known, the dilution method meets the Kubelka-Munk requirements, thereby providing very accurate results, although it is impractical for short-term sampling.

The value obtained for cement dust is only 8% smaller than that given by the direct application of the Kubelka-Munk theory on filters, whereas the optical constant of pure nigrosine was found to be $5 \times 10^4\ \text{cm}^{-1}$, which is about 50% less than the value obtained from the ratio $K/X_N$. This discrepancy may be attributed to the large particle size of nigrosine, as obtained by mechanical grinding and mixing with $BaSO_4$.

A test on NaCl–nigrosine mixture ($X_N = 7.41 \times 10^{-2}$) aerosols deposited on filters and then scraped off gave a $K$ value which is only 20% less than that observed directly on filters. This confirms the effect of the particle size on the dilution method. It is worth stressing that the dilution method, in this case, gives a reproducibility of ~25%.

These preliminary results indicate that, despite the fact that the Kubelka-Munk assumptions are not fulfilled for aerosols deposited on filters, the technique is quite effective for the quantitative measurements of the optical absorption constant of aerosols.

### *Results for Ambient Aerosols*

Typical reflectance spectra for ambient particulate matter are shown in Figure 1. The scanned region ranges between 350 and 800 nm. As a general rule, the reflectance decreases with the frequency, while $R_3$ and $R_4$ tend to approach the same value at 350 nm, as a result of extremely high absorption in the near-UV region.

From eq 1 of Table I, it appears that the measurement errors can be very large for small values of the difference R4 − R3 so that we have restricted our measurements to the spectral region 400–800 nm, i.e., in the visible region.

An example of results for the optical constants of a series of particulate-loaded filters is shown in Figure 2A. The values were computed at 800 nm, where the measurements are not affected by large errors because of the large values of the difference $R_4 - R_3$; and, in addition, at 800 nm the contribution of iron oxides, which have a high absorption constant in the blue–green region, is negligible. The optical constant has been expressed in terms of the imaginary part of the refractive index which ranges from $5 \times 10^{-3}$ to $8 \times 10^{-2}$. This is consistant with the values reported by other investigators who measured $n_2 = 2 \times 10^{-3}$ for natural aerosols and larger values for urban particulate matter (*10–12*).

Temporal variations of $n_2$ show large values in the late afternoons (17:00–21:00 sampling period) with minima in late mornings–early afternoons (9:00–13:00 sampling period) and overnight with a few unresolved maxima in the morning. This is consistent with the source of pollution in the laboratory area which mostly comes from vehicular traffic. This is very heavy in the morning and the late afternoon. In the latter instance inversion and atmospheric stability, experienced in the sam-

**Table III. Cement Dust. Optical Constant for Different Loadings**

| loading, mg | $K$ at 800 nm |
|---|---|
| 5.53 | 390 |
| 8.33 | 440 |
| 9.04 | 440 |
| 12.0 | 368 |
| 17.5 | 380 |
| 22.93 | 410 |

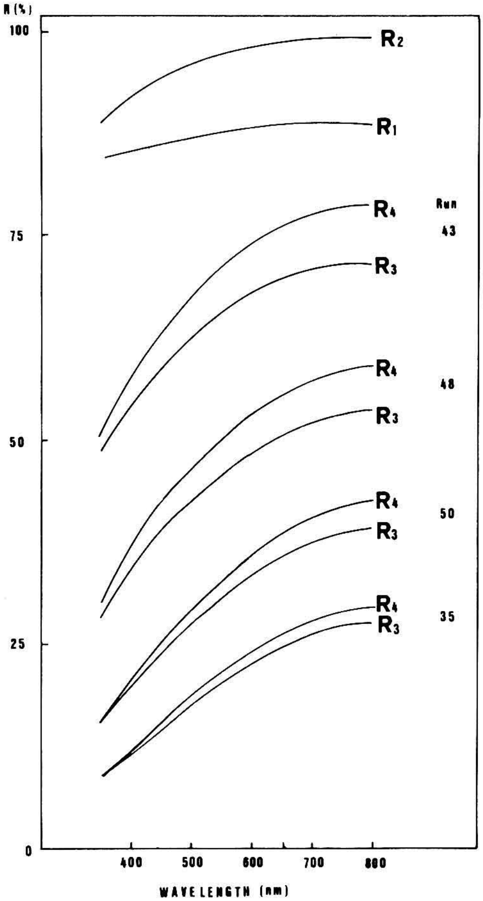

**Figure 1.** Reflectance spectra of filters loaded with particulate matter against a black ($R_3$) and a white ($R_4$) background. $R_1$ and $R_2$ are diffuse reflectance spectra of blank filters against black and white background, respectively.

pling location, prevent pollutant dispersion, thereby increasing particulate stagnation. This is also confirmed by the profile of particulate matter shown in Figure 2B.

Although an increase in mass concentration corresponds to a maximum in the optical constant, the linear correlation between their values yields an insignificant regression coefficient, suggesting that some aerosols might also come from other sources such as unpaved roads, open-air incineration, and so on.

It is worth noting that over weekends, when automotive traffic is reduced, small values of optical constants are observed, with minimum values comparable to those found for natural aerosols.

By assuming, as discussed previously, that the optical constant is entirely due to free carbon, it is possible to estimate the amount of carbonaceous materials by simply rationing $n_2$ for particulate matter to $n_2$ for carbon which is ~0.35. The carbon concentration estimated in this way ranges from a few percent to 20%. No direct measurement of free-carbon concentration was carried out; thus we cannot claim that the reliability of the method, if used for free-carbon-particle quantitation, is proven. However, the values seems to be reasonably correct and consistent with other observations (*13–14*).

The lack of data concerning the true concentration of free carbon particles is due to the difficulty of developing a reasonably correct procedure for such a measurement. Carbon is present, on particulate matter, in several forms: elemental carbon, i.e., graphitic particles, solid and liquid hydrocarbons, different organic compounds such as acids, phenols, etc., either as such or adsorbed on particles, and finally carbonates. Techniques such as solvent extraction can be used for organics only, whereas CHN combustion is sensitive to carbon in any form. In conclusion, it seems that no reference method can be used to measure graphitic material directly. Although a few tests were run to tentatively separate different contributions (*15*), we have found unsatisfactory results. The method based on diffuse reflectance can, at least, provide a simple, rapid, and nondestructive estimate.

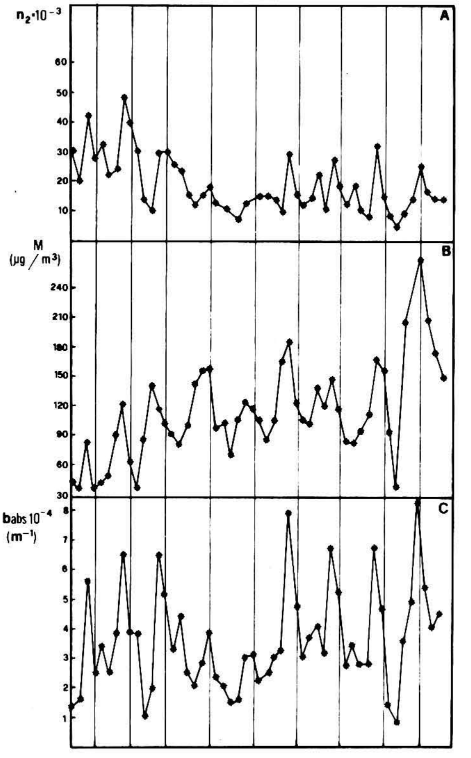

**Figure 2.** Monitoring of optical absorption constant during Nov 1978 at Rome: (A) imaginary part of the refractive index ($n_2$) for particulate matter computed at 800 nm; (B) mass concentration in $\mu g\ m^{-3}$ ($M$); (C) Kubelka-Munk absorption coefficient ($b_{abs}$, $m^{-1}$). Sampling frequency is 4–6 samples per day. Vertical lines identify midnights.

The assumption that most of the graphitic material directly comes from automobile sources was also confirmed by profiling the particulate lead concentration.

Table IV shows an example of monitoring lead and the optical absorption constant, including the calculated concentration of graphitic material, given as carbon concentration. Table IV also shows the corresponding values of the Kubelka–Munk absorption coefficients (see below).

Linear-regression analysis between lead concentration and the optical constant yields a correlation coefficient of 0.67 (32 data points). The ratio $C_{carb}/C_{lead}$, where $C_{carb}$ and $C_{lead}$ are concentrations in $\mu g\ m^{-3}$ of graphitic materials and lead, determined by means of the optical constant and atomic absorption spectrometry, respectively, has a mean value of 10.3 with ~25% standard deviation. The same value was also observed in other ambient samples with alternative techniques (*16*).

From eq 5 of Table I, it is possible to calculate the Kubelka–Munk scattering power and, by using eq 7, the related value of absorption. The absorbing power determined in such a way is that associated with the particles collected on membranes which can be considered, before sampling, to be dispersed in a tube of air of length $l$ and having volume $V$ equal to that of sampled air and whose diameter is equal to that of the filter. Thus the ratio $K/l = 4KV/\pi d^2$ can be regarded as the absorption coefficient of the sampled air. This parameter is very similar to the absorption coefficient as defined by Beer's law, and the two parameters coincide if the properties of suspended particulate matter are not altered during the sampling stage.

Unfortunately that is not true because particles might clump together, evaporate if liquid, or react, so that the approximation can introduce, at least in principle, serious errors. If one keeps in mind such limitations, the Kubelka–Munk absorption coefficient is an extra parameter which can be derived by diffuse reflectance measurements and can be used for evaluating pollution.

Results for $b_{abs}$ ($m^{-1}$) determined by diffuse reflectance are given in Figure 2C. It ranges approximately from $1 \times 10^{-4}$ to $8 \times 10^{-4}\ m^{-1}$, which is in agreement with the results found in New York, measured in a more direct way (*12*). Figure 3 shows the correlation between $b_{abs}$ and the mass concentration ($\mu g\ m^{-3}$). The values are in reasonable agreement although the mean ratio $M/b$ found for the sampling location is lower than that found for New York aerosols by a factor of 1.5. The wide scattering of data points is due to the daily trend of pollution episodes. Indeed a good correlation between absorption coefficient and mass concentration would only indicate that the properties of particulate matter do not change with time. Changes in such properties are evident by observing that weekend data are statistically well below points taken during weekdays.

Long-term fluctuation in the optical constant is shown in Figure 4. Particulates were sampled in 24-h intervals with the exception of weekends when sampling extended from Friday to Monday morning. Even in this case a statistically low value of $n_2$ for weekends is observed, while the poor correlation with gravimetric data is confirmed.

From the results previously discussed, it is clear that the optical absorption constant of particulate matter is due mainly to the presence of graphitic particles. This suggestion is confirmed by the spectral dispersion of the imaginary part of the refractive index. Typical examples are shown in Figure 5. Apart from small deviations, due to experimental errors, all curves are flat as a result of the $\lambda^{-1}$ variation for the optical absorption constant over the visible spectrum region. It is well-known that only graphitic materials behave in a similar way (*17*).

### *Correlation with Smokeshade or Soiling Index Measurements*

From a practical point of view, the measurements of optical constants can be traceable to those usually indicated as "smokeshade" or "soiling index", which measure the amount of light absorbed or reflected by a filter loaded with particulate matter in order to estimate the surface mass concentration and, ultimately, the gravimetric concentration (*18*).

Although these methods do not provide a physical characterization of particulate matter, they have been extensively used over the past few years as an air pollution index because of their simplicity. Suitable standard curves provide reduction of reflectance readings to gravimetric content.

Previous investigations show that correlations between gravimetric content as measured by standard methods and that extracted from standard curves are in very poor agreement.

Lee et al. (*19*) show that smokeshade determinations are lower than gravimetric ones in case of low pollution, whereas the reverse is true for high-pollution episodes. This agrees with our findings. According to Ball (*20*) an increase in smokeshade index may be attributed to vehicular traffic because of the good correlation with lead concentration.

Discrepancies between soiling indexes and gravimetric values can be expected when a change in the physical parameters of aerosols occurs. It is also clear that soiling indexes are very sensitive to variations in the imaginary part of the refractive index, i.e., to the free-carbon content of particles. Thus it was thought that the optical constant might play an important role in defining the index.

In order to study this relationship, we made reflectance measurements on filters loaded with particles. Although standard procedures require filter paper such as Whatman

**Table IV. Comparison of Gravimetric Concentration, Parameters Extracted from Diffuse Reflectance Measurements, and Particulate Lead Concentration**

| Run Id. | mass concn, $\mu g\ m^{-3}$ | $n_2$ | $10^{-4}\ b_{abs}$, $m^{-1}$ | graphitic part., $\mu g\ m^{-3}$ | lead, $\mu g\ m^{-3}$ | ratio C/Pb |
|---|---|---|---|---|---|---|
| 54 | 125 | 0.039 | 3.01 | 4.64 | 0.4 | 11.60 |
| 56 | 118 | 0.048 | 2.2 | 4.84 | 0.6 | 8.07 |
| 57 | 88 | 0.046 | 2.5 | 3.85 | 0.3 | 12.83 |
| 58 | 105 | 0.043 | 3.0 | 4.3 | 0.3 | 14.33 |
| 59 | 176 | 0.032 | 3.2 | 5.02 | 0.7 | 7.17 |
| 60 | 188 | 0.09 | 7.8 | 16.11 | 2.1 | 7.67 |
| 61 | 125 | 0.05 | 5.2 | 5.95 | 0.85 | 7.0 |
| 62 | 105 | 0.037 | 2.9 | 3.7 | 0.47 | 7.87 |
| 66 | 148 | 0.086 | 6.58 | 12.12 | 1.2 | 10.10 |
| 67 | 115 | 0.054 | 5.0 | 5.9 | 0.6 | 9.83 |
| 68 | 85 | 0.037 | 2.7 | 3 | 0.3 | 10.0 |
| 71 | 110 | 0.026 | 2.7 | 2.7 | 0.2 | 13.5 |
| 72 | 170 | 0.100 | 6.7 | 16.2 | 1.3 | 12.46 |
| 73 | 156 | 0.05 | 4.7 | 7.28 | 0.6 | 12.13 |
| 80 | 100 | 0.044 | 3.6 | 4.23 | 0.37 | 11.43 |

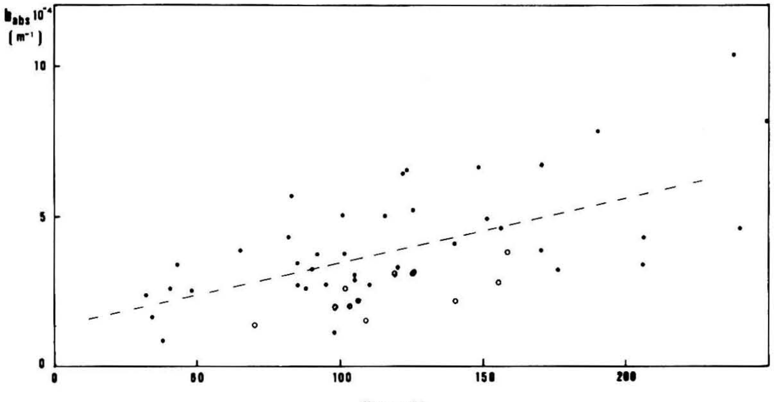

**Figure 3.** Scatter diagram of Kubelka-Munk absorption coefficient ($b_{abs}$) against mass concentration. Open circles are weekend data points. Regression line for weekdays: $b(10^{-4}\ m^{-1}) = 0.021M(\mu g\ m^{-3}) + 1.3$ ($r = 0.65$).

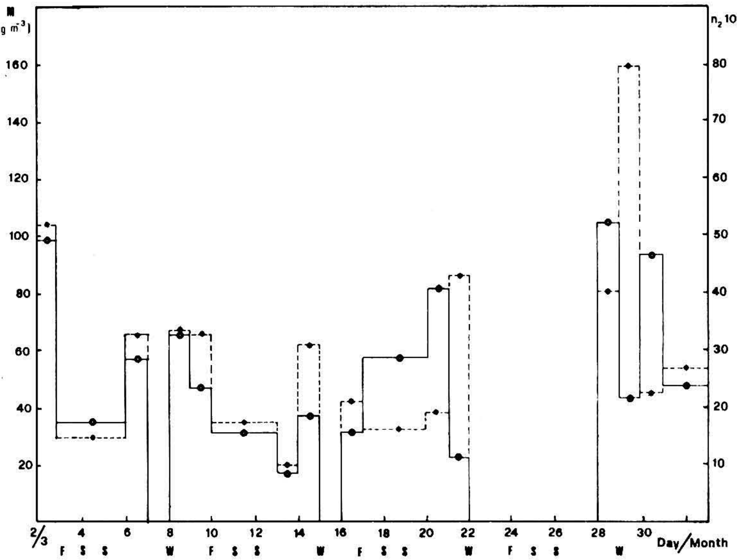

**Figure 4.** Average imaginary refractive index (dashed line) and mass concentration (full line). Some data are lost because of rainy weather conditions. Sampling period, March 1978.

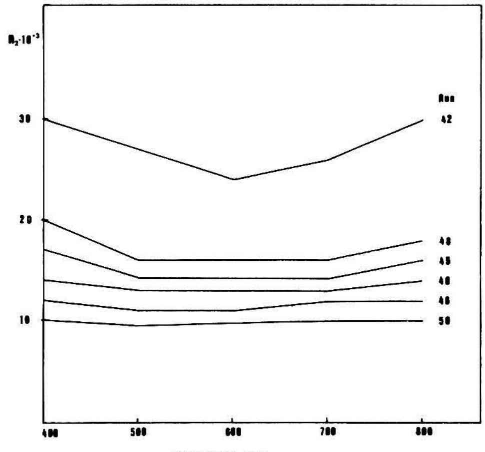

**Figure 5.** Spectral dispersion of the imaginary part of the refractive index for ambient particulate matter.

no. 1, a different filter medium gives a similar exponential relationship between mass loading and optical indexes as measured by means of an approved reflectometer.

A standard reflectance curve (*21*) was fitted by means of an exponential equation, $S = 0.12N^{1.62}$ where $N$ is the soiling index defined by (100 − reflectance) and $S$ the surface mass density expressed in $\mu$g cm$^{-2}$. A multiple linear regression between $S$, $N$, and $K$, with $K$ the optical absorption constant, was performed on the equation

$$\log N = aK^{b_1}S^{b_2}$$

The coefficient $a$ and the exponents $b_1$ and $b_2$ were found to be 0.0097, 0.1273, and 0.0735, respectively. The partial correlation coefficients were found to be $r_{N,K} = 0.61$ and $r_{N,S} = 0.27$ while $r_{S,K} = 0.077$, indicating that the soiling index is better correlated with the optical constant rather than with the surface mass density.

The low value of $r_{S,K}$ indicates a poor correlation between gravimetric data and the optical constant. The total correlation coefficient is $R = 0.67$.

It is worth stressing that assuming a fixed value for $S$ and changing the optical constant from $10^3$ to $10^4$ cm$^{-1}$, values typical of our findings, the multiple regression equation gives value of $N$ such that, when scaled on the standard curve, errors larger than a factor of 5 on $S$ are possible. This is in agreement with results obtained by Ball (*20*), who measured ratios of smokeshades to gravimetric measurements ranging from $^1/_1$ to $^1/_6$.

### *Conclusions*

The results obtained lead to the conclusion that, besides being a very important physical parameter, the optical constant of particles is a very useful air pollution index related to primary emitted aerosol from combustion sources.

It is worth stressing that, from an experimental point of view, the measurements require just two reflectance readings and a thickness measurement easily done with $\beta$-ray gauges which are widely used for mass concentration measurements directly on loaded filters.

Although the method requires additional investigation in order to explore the effect of aerosol parameters on the optical constant, the amount of useful information provided by the Kubelka–Munk reduction of reflectance data are well worth future investigations. These should include comparison with results obtained from other instruments directly measuring physical parameters such as size distribution, scattering, and extinction coefficients and measurements on size-classified particles such as those from loaded filters from dichotomous samplers.

### *Acknowledgment*

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# Water Solubility and Octanol/Water Partition Coefficients of Organics. Limitations of the Solubility–Partition Coefficient Correlation

**Sujit Banerjee***

Life Sciences Division, Syracuse Research Corporation, Merrill Lane, Syracuse, New York 13210

**Samuel H. Yalkowsky and Shri C. Valvani**

Pharmacy Research Unit, The Upjohn Company, Kalamazoo, Michigan 49001

■ The water solubilities ($S$) and octanol/water partition coefficients ($K$) of a wide variety of organic compounds have been measured. It is shown that a previously described correlation between these two parameters may be invalid for high-melting solids. Alternative methods for constructing $K$–$S$ correlations are discussed.

The 1-octanol/water partition coefficient is of importance in environmental fate studies through its use in predicting physical and biological phenomena such as soil adsorption (*1*) and bioaccumulation (*2, 3*). Several years ago Hansch and co-workers demonstrated the existence of a relationship between partition coefficients and aqueous solubilities of low-molecular-weight organic liquids (*4*), and Chiou et al. have recently extended the correlation to include solids (*5*). These latter authors have also advocated the use of the correlation for assessing the reliability of partition-coefficient measurements and for directly correlating aqueous solubility with bioaccumulation data. The basis of the correlation has been discussed by Mackay (*6*), who expresses the partition coefficient ($K$) and the aqueous solubility ($S$) as follows:

$$K = 0.115\gamma_w/\gamma_0 \qquad (1)$$

$$S = 55.5 \times 10^6 (f/f_R)/\gamma_w \qquad (2)$$

where $\gamma_w$ and $\gamma_0$ refer to the activity coefficients in water and octanol, respectively, and $f/f_R$ is the ratio of the fugacity to the reference fugacity (for liquids $f/f_R = 1$). Thus, if $\gamma_0$ and $f/f_R$ remain constant, then a log $K$ vs. log $S$ correlation would be linear with a slope of $-1$. The experimentally determined slope is nearer $-0.7$, and Chiou and Freed have attributed the discrepancy to differences in the behavior of a compound in pure water vs. octanol-saturated water and in pure octanol vs. water-saturated octanol (*7*). On the other hand, Mackay has pointed out that, for solids, $f/f_R$ decreases with increasing melting point (mp) and molecular weight, and a precise relationship between $K$ and $S$ must, therefore, take into account factors such as the melting point, entropy of fusion, and the difference between solid and liquid heat capacities. A step toward this direction has been made by Yalkowsky and Valvani (*8, 9*), who propose an equation of the type

$$\log K = a(\log S) + b(\text{mp}) + c \qquad (3)$$

where $a$, $b$, and $c$ are constants. We have measured the aqueous solubilities and octanol/water partition coefficients of a number of organic compounds which are members of the group of 65 Consent Decree Chemicals for which the U.S. EPA is currently recommending water-quality criteria. In this paper we apply the above correlations to our data and define the limitations of the Chiou (*5, 7*) approach.

## *Experimental Section*

Most of the determinations were made by using $^{14}$C-labeled compounds, which were available, since bioaccumulation studies were conducted concurrently on the same materials (*10*). Consequently, the bulk of our analyses relied on the measurement of radioactivity through liquid scintillation counting. Radioactive materials were obtained from New England Nuclear, and the corresponding nonlabeled compounds were provided by the Aldrich Chemical Co.

### *Solubility*

Many of the compounds studied were volatile to some degree, and, to minimize evaporation losses, we conducted the

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experiments in sealed stainless steel centrifuge tubes. In a typical experiment, an excess of the compound was added to a tube containing distilled water, and the tube was sealed and allowed to equilibriate at 25 ± 0.2 °C with constant or intermittent shaking. Equilibration was generally complete within 1 week. The mixture was then centrifuged at 10 000 rpm for 60 min in a head preequilibriated to 25 ± 0.3 °C, following which aliquots of the solution were removed for analysis either with a pipet or, for the more volatile compounds such as chloroform, with a syringe. The entire procedure was carried out at least twice for each compound, and each analysis was also conducted in duplicate.

The nonradioactive compounds were analyzed by GC, high-performance LC, or UV spectrophotometry. Compounds **1**, **5**, **8**, **9**, **13**, and **15** in Table I were analyzed by high-performance LC using a Waters M6000A instrument fitted with a $\mu C_{18}$ Bondapak column. The mobile phase was a mixture of methanol/water or acetonitrile/water. Compound **14** was analyzed by GC after exhaustive extraction with hexane. A HP 5370A (fid) instrument and a 3% OV-1 on Chromosorb W column was utilized. RDX (**1**) and dichlorobenzidine (**2**) were analyzed (*11*) by UV spectrophotometry using a Cary 14 instrument.

### *Octanol/Water Partition Coefficients*

Partition-coefficient measurements were made by using the following procedure at 23 ± 1.5 °C. Octanol was purified by extraction with water and with aqueous NaOH, followed by distillation. A mixture of octanol and water was shaken for 30 min and separated by centrifugation (10 000 rpm, 30 min), and the test compound was dissolved in the water-saturated octanol. The octanol-saturated water was then added to the stainless steel tube which was sealed, and the mixture was equilibriated during several 4–5-min shaking periods spaced 10 min apart. The tubes were centrifuged for 30 min at 10 000 rpm, and both the octanol and water layers were sampled and analyzed. The concentration of the substrate in water was far below the solubility limit. The octanol fraction was diluted with methanol before analysis. The partition coefficient of dichlorobenzidine (**2**) was determined in an octanol/buffer (pH 8.7) system. As before, the results reported in Table I are averages of duplicate analyses from experiments conducted at least twice.

### *Discussion*

The solubility and partition-coefficient measurements are summarized in Table I and follow eq 4.

$$\log K = 5.2\text{–}0.68 \log S \qquad (\text{corr coeff} = 0.94) \qquad (4)$$

The relationship is illustrated in Figure 1. Compound **1** was not included for the derivation of the equation since it deviates considerably from the line. This is due to its high melting point as described below. The equation is very similar to that obtained by Chiou et al. (*5*), namely, eq 5.

$$\log K = 5.00\text{–}0.67 \log S \qquad (5)$$

It is unlikely that the deviation of RDX (the highest-melting compound considered) from the line reflects experimental error, since the partition coefficient for this material was obtained from two different experiments, the first utilizing $^{14}$C-RDX and radioscintillation counting, and the second utilizing cold RDX and spectrophotometric analysis. Both experiments led to results which were identical within ex-

**Table I. Water Solubility and Octanol/Water Partition Coefficients of Some Organic Compounds**

| no. | compd | mp, °C | $S^a$ (± % dev)$^b$ | $K$ (± % dev) | log $KS$ | analytical method$^d$ |
|---|---|---|---|---|---|---|
| **1** | 1,3,5-triaza-1,3,5-trinitrocyclohexane (RDX) | 205 | 2.69E2(2.0) | 7.41E0(6.2) | 3.30 | HPLC, UV, LSC |
| **2** | 3,3′-dichlorobenzidine | 132 | 1.23E1(4.0) | 3.24E3(4.2) | 4.60 | UV, LSC |
| **3** | diphenylnitrosamine | 67 | 1.77E2(3.5) | 1.35E3(3.1) | 5.38 | LSC |
| **4** | acenaphthene | 96 | 4.78E1(4.1)$^c$ | 8.32E3(1.5) | 5.60 | LSC |
| **5** | biphenyl | 71 | 3.91E1(6.0)$^c$ | 1.10E4(4.0)$^c$ | 5.63 | HPLC |
| **6** | pentachlorobenzene | 86 | 5.32E0(4.9)$^c$ | 8.71E4(1.3) | 5.67 | LSC |
| **7** | 1,2,3,5-tetrachlorobenzene | 55 | 1.86E1(4.0)$^c$ | 2.88E4(4.5) | 5.73 | LSC |
| **8** | dibenzofuran | 82 | 5.96E1(4.3) | 1.48E4(9.3)$^c$ | 5.84 | HPLC |
| **9** | hexachlorobutadiene |  | 1.24E1(2.5) | 6.09E4(8.5) | 5.88 | HPLC |
| **10** | tetrachloroethylene |  | 2.92E3(1.0) | 3.38E2(9.7)$^c$ | 6.00 | LSC |
| **11** | nitrobenzene |  | 1.70E4(0.6) | 6.76E1(1.6)$^c$ | 6.06 | LSC |
| **12** | *p*-dichlorobenzene | 54 | 5.02E2(6.0)$^c$ | 2.34E3(2.5)$^c$ | 6.07 | LSC |
| **13** | diphenyl ether | 28 | 1.06E2(2.5) | 1.20E4(7.4)$^c$ | 6.11 | HPLC |
| **14** | *p*-cymene |  | 1.74E2(3.1) | 1.26E4(6.0) | 6.34 | GC |
| **15** | styrene |  | 1.54E3(5.7) | 1.46E3(3.6) | 6.35 | HPLC |
| **16** | 1,2-dichloroethane |  | 8.07E4(3.5) | 2.82E1(1.9) | 6.36 | LSC |
| **17** | *m*-dichlorobenzene |  | 9.08E2(1.1)$^c$ | 2.75E3(3.9)$^c$ | 6.40 | LSC |
| **18** | *o*-dichlorobenzene |  | 1.06E3(0.9)$^c$ | 2.51E3(0.9)$^c$ | 6.42 | LSC |
| **19** | carbon tetrachloride |  | 4.92E3(2.5)$^c$ | 5.37E2(5.2)$^c$ | 6.42 | LSC |
| **20** | toluene |  | 1.68E4(2.3)$^c$ | 1.62E2(9.4)$^c$ | 6.44 | LSC |
| **21** | 1,1,1-trichloroethane |  | 1.00E4(2.1) | 2.95E2(1.0)$^c$ | 6.47 | LSC |
| **22** | trichloroethylene |  | 1.12E4(3.5) | 2.63E2(4.1)$^c$ | 6.47 | LSC |
| **23** | benzene |  | 2.24E4(0.7)$^c$ | 1.32E2(1.2)$^c$ | 6.47 | LSC |
| **24** | 1,1,2,2-tetrachloroethane |  | 1.77E4(0.6) | 2.45E2(2.3) | 6.64 | LSC |
| **25** | chloroform |  | 6.05E4(4.3)$^c$ | 7.94E1(0.9)$^c$ | 6.68 | LSC |
| **26** | *o*-chlorophenol |  | 8.83E4(0.5)$^c$ | 1.45E2(2.2)$^c$ | 7.11 | LSC |
| **27** | 2,4-dimethylphenol |  | 6.44E4(0.5) | 2.63E2(1.2)$^c$ | 7.23 | LSC |

[a] $S$ is given in $\mu$M. [b] Standard deviation. [c] Literature measurements for these compounds are available. Where comparison can be made with our values, the results are similar. [d] LSC = liquid scintillation counting; HPLC = high-performance liquid chromatography.

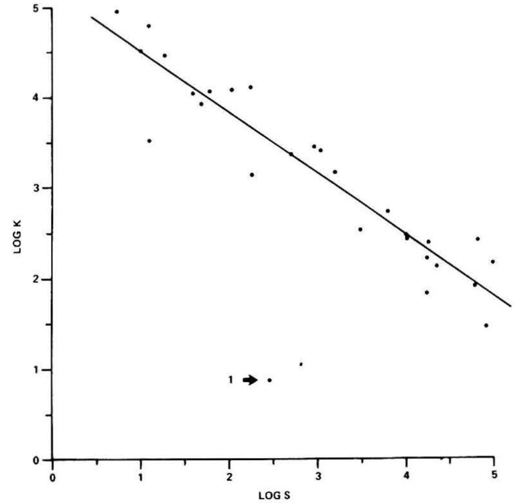

**Figure 1.** Relationship between partition coefficient and aqueous solubility according to eq 4.

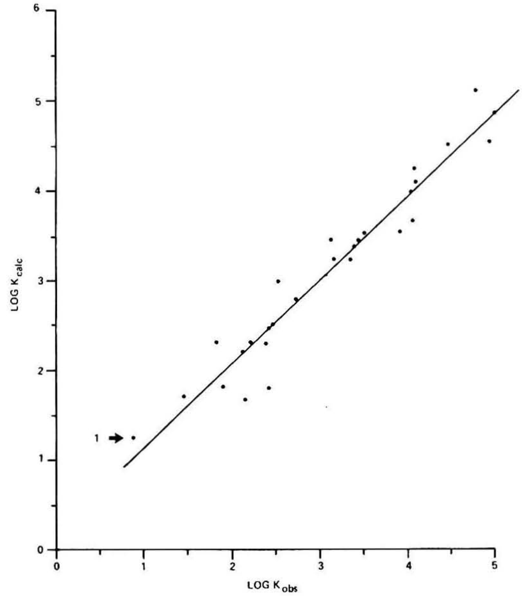

**Figure 2.** Comparison of observed and calculated partition coefficients according to eq 6.

perimental error. Thus, it is clear that while the correlation obviously applies to the majority of the compounds studied, it is *not* universal, and caution is required for the interpretation of results obtained from it.

In order to test Chiou et al's hypothesis that the solubility in water differs from that in octanol-saturated water and that this difference may influence the value of the slope in Figure 1, we measured the solubilities of compounds **1**, **7**, and **18** in pure water and in octanol-saturated water. The solubility in water was identical within experimental error with that measured in octanol-saturated water.

It appears, therefore, that the discrepancy of the slope (−0.7) from the theoretical value of −1 originates from variations in $\gamma_0$ and $f/f_R$. Inevitably, slopes of −1 are obtained if compounds with similar $\gamma_0$ and $f/f_R$ (or $KS$) values are grouped together as illustrated below. Similar treatment of Chiou's data (*5*) leads to the same conclusion. These results lead to an alternative to

| log *KS* | *n* | slope | intercept | corr coeff |
|---|---|---|---|---|
| 5.4–5.8 | 5 | −1.06 | 5.74 | 0.995 |
| 5.8–6.2 | 6 | −0.95 | 5.85 | 0.997 |
| 6.2–6.6 | 10 | −0.97 | 6.31 | 0.998 |

using the Chiou correlation for estimating $K$ from a knowledge of $S$ or vice versa. Compounds with similar structure and melting point will tend to have similar $KS$ values, and if an estimate of $K$ is required from a knowledge of $S$ for a compound in the same general series, this series alone should be used for the estimation. For example, if one requires $K$ for bromoethane and all one has is its solubility, the Chiou correlation should be utilized. However, if $K$ and $S$ for bromopropane, bromobutane, etc., are available, it is better to assume that they have a common value of $KS$ and estimate $K$ for bromoethane accordingly.

Treatment of the data by Yalkowsky and Valvani's procedure greatly improves the generality of the correlation. The equation appropriate to our data is

$$\log K = 6.5 - 0.89(\log S) - 0.015(\text{mp}) \qquad (r = 0.96) \quad (6)$$

and the correlation is shown in Figure 2. For liquid solutes, 25 °C was used instead of the melting point (*8*). It is highly significant that the coefficient of log $S$ (−0.89) in eq 6 is close to the theoretical value of −1.0 and that the high-melting compound RDX (**1**) now fits the correlation illustrated in Figure 2.

In summary, estimation of $K$ or $S$ for liquids should be made through the Hansch (*4*) correlation. For solids with known melting points, an equation such as eq 6 should be utilized. In the event that the melting point is unavailable, the estimate should be made from an average value of $KS$ obtained from compounds of similar structure and melting point. Use of the Chiou (*5*) correlation, which does not differentiate between liquids and solids, may result in serious error as exemplified by our experience with RDX.

### *Acknowledgment*

We thank Messrs. Gary Dec and Edward J. Pack, Jr., for performing the bulk of the analyses.

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# Improved Identification of Spilled Oils by Infrared Spectroscopy

**Carol P. Anderson**
University of Connecticut, Groton, Connecticut 06340
**Timothy J. Killeen**
University of Connecticut, Storrs, Connecticut 06268
**John B. Taft and Alan P. Bentz***
U.S. Coast Guard Research and Development Center, Groton, Connecticut 06340

■ Light oils are notoriously difficult to match to their sources after environmental weathering. A new accelerated laboratory-weathering procedure, combined with either log-ratio or vector pattern recognition, gives markedly improved identification of spilled light fuel oils by infrared spectroscopy.

## *Introduction*

In 1955, Rosen and Middleton (*1*) suggested that infrared spectra might be sufficiently characteristic to identify oils. Reviews by Brown (*2*) and Bentz (*3,4*) traced the evolution of the use of infrared techniques to identify oils that have been weathered by comparing them with likely sources. Numerous weathering studies, including major efforts by Frankenfeld (*5*) and Brown (*6*), served to provide detailed information as to the effects of weathering on infrared spectra. This information, coupled with an interlaboratory study, led to the development of a standard ASTM method for the infrared analysis of waterborne oils (*7*), as well as a standard field and laboratory procedure for use by the Coast Guard (*8*).

These techniques were, for the most part, qualitative—depending on visual inspection of overlayed spectra. The original ASTM procedure did give an option for using peak ratios according to a procedure recommended by Kawahara (*9*). Others began to look at pattern-recognition techniques which could be employed to give more objective interpretations and take into account the weathering effects. Mattson (*10*) and Brown (*6*) looked at various statistical pattern-recognition schemes. Brown's log-ratio technique was applied to digitized data from over 1200 infrared spectra, some 900 of which were from weathered oils. Of the 13–21 peaks he used for comparison, Brown found that if all of the log-ratio values lay within 10% of the average, the oils were from a common source; i.e., he allowed a 10% "weathering window" (*6*).

In our experience, the log-ratio technique (using 18 peaks) worked well with all but the very light oils, because of the fact that the magnitude of weathering changes was greater than differences between similar light oils. In an effort to improve the results, we applied weighting factors to the 18 peaks, such that the peaks which changed least with weathering were given the highest factor. A marked improvement was noted, but there were still problems with the light oils (*11*).

A new vector pattern recognition technique was developed by Killeen et al. (*11,12*) for the purpose of identifying weathered oils from both their fluorescence and their infrared spectra. To compare a weathered spill to its source by this method required a third sample, namely, a weathered-source sample. The spectral data from the latter were used with the data from the source to generate a weathering-response surface to obtain the closest match to a weathered oil.

The need for a weathered-source sample gave impetus to an already expressed need for a standardized weathering method (*13*) to enhance matching capabilities of all analytical methods. Thus, a good laboratory-weathering technique would fulfill both the requirement for a weathered suspect to facilitate matching a spill visually and also the requirement for the vector pattern recognition technique.

The development of such a laboratory-weathering procedure was the subject of this investigation. Secondly, we wanted to develop a method using 1 mL, or less, since real-world samples of spills are generally of limited quantity. A third, equally important objective was to see whether comparisons could be improved for the fast-weathering light oils. The vector technique also lent itself to quantitative analysis of mixtures; this application was evaluated during this study to see whether it would be possible to compensate for the presence of a second oil or perhaps an oil dispersant.

## *Pattern-Recognition Techniques Used in this Study*

In order to conduct more objective comparisons of oils, we employed computerized quantitative techniques by using 18 carefully selected data points (*11*). Table I lists the data points used, as well as some weighting factors which will be discussed later.

Two techniques have been used for our purposes. The first is the log-ratio method of Brown (*6*); the second is the vector method of Killeen et al (*12*).

**Log-Ratio Method.** The values of the percent difference in the peaks are sorted into ranges of 0–5, 5–10, 10–15, 15–20, 20–50, 50–100, and >100. Replicates of the same oil (a definite match) will have all peaks lie within the 0–5 range. To allow for weathering, a wider variation is permitted. Brown et al. (*6*) found that the weathered oils generally match with all peaks in the 0–10 range.

**Vector Method.** Briefly, the vector method considers the digitized spectra as 18-dimensional vectors ($n$-dimensional if $n$ digitized data points are used). The data are normalized to compensate for differences in sample thickness, etc. The vectors of the suspect and one, or more, weathered samples of that suspect span a hyperplane in 18-space. That is, the weathered vector(s) and the unweathered vector generate a "weathering surface" for the suspect. The spill sample may not lie on this surface; the orthogonal projection of the spill vector on the "weathering surface" gives the closest vector on the surface which is designated the "computer-simulated weathering" vector. The angle between the spill vector and its projection on the surface represents the "closeness" of the spill to the suspect. The position of the projection will indicate whether the spill is more, or less, weathered than the suspect. This method is an extension of a comparison technique used in fluorescence spectroscopy (*12*). The effectiveness of this technique is highly dependent on a reasonable simulation of real-world weathering.

## *Weighting-Factor Approach*

Peak-by-peak examination of the log-ratio data for many oils identifies peaks with greatest variability. Changes in the No. 6 oil were virtually nil in the 700–900 $cm^{-1}$ region but were very pronounced in the 900–1300 $cm^{-1}$ region. (This latter difference disappeared from the infrared spectrum with deasphalting.) Peak variability depends to some extent on the oil type due to compositional differences, such as higher aliphatic/aromatic ratios. According to our initial premise, the peaks that were relatively stable were assigned weighting factors of 0.9 or 1.0. Smaller weighting factors down to 0.3 were given to the peaks that varied the most. See Table I for the weighting factors used for each wavenumber.

Table II shows the improvement in the degree of match when using the weighting factor, as a function of oil type. The No. 6 oil has all peaks within the 0–5% range (originally two outliers); the No. 4 oil improves from 15 to 17 in the 0–5% range; the No. 2 goes from 9 to 12 in the 0–10% range; and the crude improves from 9 to 15 within the 0–10% range. Although the weighting factor gives noticeable improvement in comparing all oils with their weathered counterparts, it is unsatisfactory for light oils.

*Laboratory Weathering*

Many investigators have artifically weathered oils. The weathering systems have varied from a sophisticated indoor apparatus with recycling sea water, simulated wind, and sunlight (*5*) to simple wading pools (*14*) as well as a system which confined an oil in the actual marine environment (*6*). The sample size varied from 1 L (at The Research Institute of the Gulf of Maine in 2000-L outdoor tanks) to microliter quantities (*15*). Brown et al. (*6*) conducted a 2-year study comparing outdoor weathering with laboratory weathering. One of the most successful, rapid laboratory-weathering procedures was developed in his laboratory (*16*) in which 2 mL of unweathered oil is shaken with sea water in a test tube for 1 h at 35 °C, the water is removed, and the sample is placed under vacuum (0.05 torr) for 1 h. It was our intent to see whether this technique might be improved upon by modifications which would simulate oxidative weathering as well as loss of the lighter components.

The visual effects on the infrared spectrum of exposing an oil to the aquatic environment are clearly seen if spectra of unweathered and weathered oils are examined. Figure 1 shows the formation of carbonyl at 1710 $cm^{-1}$, the downward displacement of the base line in the 1300–900-$cm^{-1}$ region, and the numerous changes within the 900–700 $cm^{-1}$ region. It should be noted here that the changes in a light oil due to weathering are comparable in magnitude to the differences between individual light oils. The heavier oils do not show such distinctive differences upon weathering. However, *any* weathering changes can increase the difficulty of making identification of a spill source unless compensation is made for the weathering. In visual interpretation, the analyst must mentally compensate for known weathering effects. In the log-ratio method, the 10% allowance can be made for weathering, or weighting factors can be used in which those data points are weighted the least which change the most with weathering. Alternatively, a good simulated weathering will permit identification with *all* 18 peaks within 5% as seen later in Table III. With the vector technique, a laboratory-weathered sample is a necessary part of the comparison. For convenience in interpretation, the results are graphically displayed as shown in Figure 2.

The problem is not simple, since the natural "weathering" of an oil involves complex processes which cause chemical and physical changes in the hydrocarbon mixture. Evaporation, dissolution, oxidation, polymerization, and biodegradation are some of the processes whose combined effects are termed "weathering." The laboratory-weathering studies were set up to evaluate the following variables: oil type, time, light, temperature, solubility, and air flow as well as film thickness.

Polymerization and oxidation are temperature-dependent, light-induced processes. We studied infrared, short-, and long-wave ultraviolet light sources and found that the best simulation was effected with a long-wave ultraviolet source (about 360 nm, such as is used for TLC illumination).

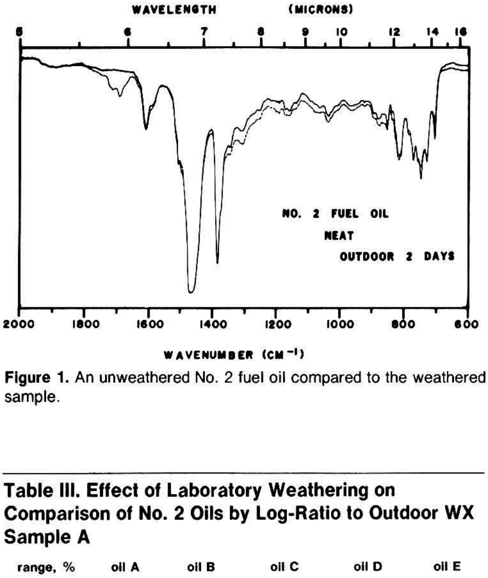

**Figure 1.** An unweathered No. 2 fuel oil compared to the weathered sample.

**Table I. Weighting Factors for the 18 Peaks Used for Comparison**

| wave-number, $cm^{-1}$ | wf | wave-number, $cm^{-1}$ | wf | wave-number, $cm^{-1}$ | wf |
|---|---|---|---|---|---|
| 1304 | 0.8 | 918 | 0.7 | 790 | 0.5 |
| 1165 | 0.5 | 890 | 1.0 | 782 | 0.4 |
| 1145 | 0.3 | 871 | 0.9 | 766 | 0.5 |
| 1070 | 0.3 | 849 | 1.0 | 744 | 0.7 |
| 1032 | 0.5 | 832 | 1.0 | 722 | 0.6 |
| 955 | 0.6 | 810 | 0.4 | 700 | 0.4 |

**Table III. Effect of Laboratory Weathering on Comparison of No. 2 Oils by Log-Ratio to Outdoor WX Sample A**

| range, % | oil A | oil B | oil C | oil D | oil E |
|---|---|---|---|---|---|
| 0–5 | 18 | 1 | 8 | 4 | 5 |
| 5–10 | 0 | 13 | 2 | 3 | 5 |
| >10 | 0 | 14 | 8 | 11 | 8 |
| av | 2.04 | 23.01 | 12.24 | 17.02 | 13.65 |

**Table II. Log-Ratio Comparisons of Different Oils Weathered vs. Unweathered with and without Weighting Factors**

| | No. 6 | | No. 4 | | No. 2 | | crude | |
|---|---|---|---|---|---|---|---|---|
| range, % | w/o | with | w/o | with | w/o | with | w/o | with |
| 0–5 | 16 | 18 | 15 | 17 | 4 | 8 | 8 | 6 |
| 5–10 | 2 | 0 | 3 | 1 | 5 | 4 | 1 | 9 |
| >10 | 0 | 0 | 0 | 0 | 9 | 6 | 9 | 3 |
| av | 3.24 | 1.60 | 2.94 | 2.07 | 12.75 | 7.07 | 8.23 | 7.09 |

Lighter components of oil are lost in the weathering process by dissolution in water and by evaporation. The effects of dissolution were studied by equilibrating the oils with aqueous media which included water taken from Long Island Sound, synthetic sea water, and distilled water. The effects of evaporation were studied by using air flow over an oil film and by vacuum treatment. We found that the best simulation of losses caused by evaporation *and* dissolution could be achieved by passing an air current of 2.6 m/s (equivalent to a 5-knot wind) over an oil film.

During the development of the laboratory-weathering procedure, the changes produced in the weathering experiments were monitored by computer plots of the 18 absorbances, normalized to the highest value which was given an arbitrary value of 1.0. This provided a ready, visual presentation for comparison to help us optimize the weathering parameters by minimizing the differential between the two curves, as shown in Figure 2. In this figure, the upper set of curves (prepared by connecting the 18 absorbances) shows that the nonoptimum laboratory-weathered oil was considerably more weathered than the outdoor-weathered oil. The lower set shows the close match between an oil weathered under recommended laboratory conditions and the outdoor-weathered oil.

The evolution of the weathering apparatus began with an empirical approach to the application of heat, light, water, and air to the oil. The final configuration of the apparatus, shown in Figure 3, uses neat samples of unweathered oils, without water, applied as a thin film, and irradiated with long-wavelength ultraviolet light. Air circulation is provided by a fan. With the lamp set at a distance of 10 cm, the effective energy intensity was ca. 15.6 mW/cm$^2$. An electric cooling block was found to be necessary to regulate the temperature of the sample at 20–25 °C. This technique can weather samples of approximately 1 mL in a 7.5-cm diameter petri dish down to as little as 30 mg on an infrared salt plate.

In this apparatus, 4–5 h of exposure to UV at room temperature was necessary to obtain weathering changes comparable to 1 or 2 days in the natural environment. The No. 2 fuel oil depicted in Figure 1 was weathered outdoors; differences from the unweathered oil are immediately apparent and would render identification difficult. Figure 4 shows a comparison of the same outdoor-weathered oil with the oil weathered in the laboratory; the vastly improved coincidence of the curves is readily seen—particularly over the standard 18 points selected. In this case, 4.5 h at 22 °C in our apparatus achieved the equivalent of 2 days of outdoor weathering. Achievement of this close a match for the No. 2 fuel oil is particularly gratifying, since light oils are notoriously difficult to identify after weathering. We reported this specific problem of identifying light oils using log-ratio or vector pattern recognition techniques at the 1978 Pittsburgh Conference (*11*). One of the most significant achievements reported in the present paper is the fact that laboratory weathering gave a marked improvement in matching light oils.

### *Results with Laboratory Weathering*

Since the magnitude of change with light oils is so profound on weathering, the question arises as to whether *all* light oils might not approach the composition of any one weathered oil. To see whether this is true, five laboratory-weathered fuel oils (A–E) were compared to one weathered outdoors for 1 day (oil A). The results shown in Table III clearly show that only the true source approached the outdoor-weathered sample when it was weathered in the laboratory.

Table IV shows log-ratio results of comparisons between a spilled No. 2 oil and two suspected sources. Before our artificial weathering technique was employed, the true source,

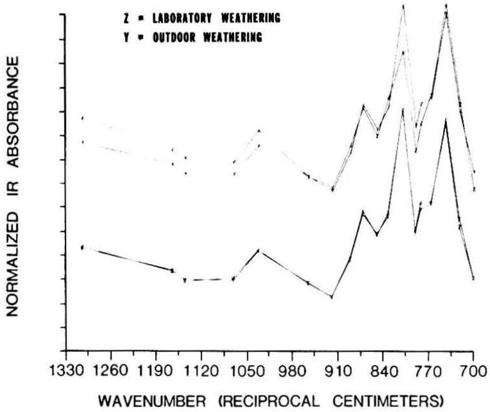

**Figure 2.** Comparison of outdoor-weathered and laboratory-weathered infrared spectral data: (upper set) poor simulation; (lower set) suggested laboratory-weathering conditions.

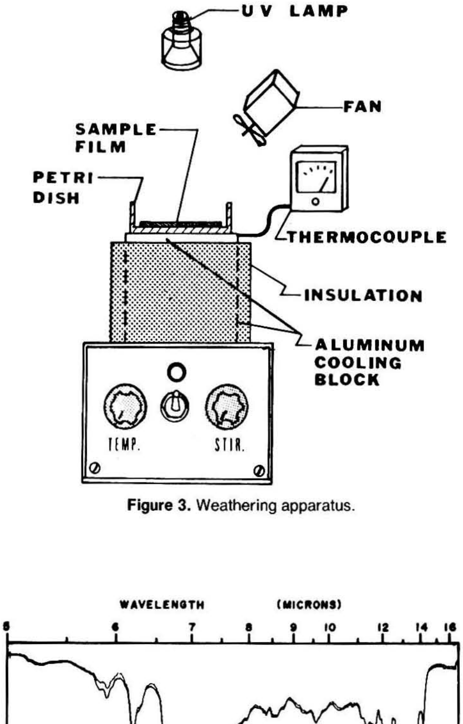

**Figure 3.** Weathering apparatus.

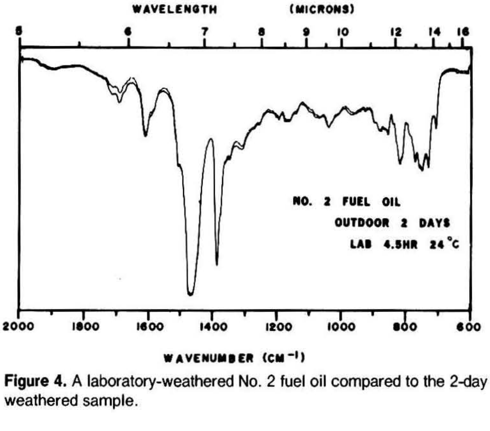

**Figure 4.** A laboratory-weathered No. 2 fuel oil compared to the 2-day weathered sample.

A, did not match the spill as well as did suspect B. After artificial weathering, suspect A is correctly identified as the spill source, while B is no longer as close a match.

There remained the question as to whether there were any significant improvements in matching by using our proposed weathering technique over that of Brown et al. (*16*). Brown and his group volunteered to use their technique to weather the same samples that we were testing. We then analyzed their laboratory-weathered samples, on our infrared spectrophotometer, by using the same digitizing hardware and comparison software. The results are shown in Table V, where the number of peaks lying within Brown's 10% "weathering window" are tabulated for comparisons made with oil which had been weathered outdoors for 1 and 2 days. The table clearly shows that laboratory weathering improves the degree of match for the light oils. Our present results show a slight edge over Brown's, particularly with the No. 2 fuel oils.

The true merit of our method becomes clear when we consider the 5% window as shown in Table VI. The trend is that Brown's method of laboratory weathering shows also general improvement over unweathered samples, and our proposed method again generally gave better results than Brown's. It must be emphasized that this generalization is made for the proposed method for the light oils *only*, since this was the thrust of this investigation, and our heavy-oil data base is limited.

*Vector Method*

The laboratory-weathering technique provides the required sample of weathered oil for the vector method. Figure 5 shows the simulated weathering vector (curve S) superimposed over a sample of the same No. 2 fuel oil weathered in the natural environment (curve Y). Both are significantly different from the unweathered oil (curve X). These data show that vector simulation is a valid method of identification of sources of light-oil spills using computerized infrared data. Similar vector comparisons for other oil types (No. 4, No. 6 fuel oils and crudes) show that the vector method can compensate successfully for weathering effects.

**Table IV. Spill Compared to Its Source and a Similar Oil**

| spill (oil A) vs. | range, % | peaks in range | |
|---|---|---|---|
| | | oil A | oil B |
| suspected source | 0–5 | 9 | 8 |
| | 5–10 | 3 | 8 |
| | >10 | 6 | 2 |
| | av | 8.6 | 6.5 |
| artificial weathered | 0–5 | 18 | 8 |
| | 5–10 | 0 | 6 |
| | >10 | 0 | 4 |
| | av | 1.17 | 7.4 |

*Analysis of Mixtures*

The vector method can be adapted to analyze mixtures, for example, in those cases where an oil spill is on water already contaminated by another oil, or when an oil is mixed with a dispersant used in cleanup, etc. In cases such as these, instead of weathered and unweathered spectra, the spectra selected are those of the components expected to be in the unknown mixture. The spectra of the individual components are used to generate a hyperplane. The distance from this plane to the spill vector is an indication of the closeness of the spill to any possible mixture of the components, while the position of the projection in the plane indicates the proportion of each suspect involved in the spill. Of course, if one component of the mixture is totally unknown, i.e., a reference spectrum is unavailable, then this analysis will be useless. The method *has* been applied to several known mixtures with promising results.

**Oil Mixtures.** The vector method, applied to a mixture of a No. 2 fuel oil and a No. 6 fuel oil, not only identified these two oils from several possible sources but also approximated the ratio of the two oils in the mixture. This is shown in Figure 6. The accuracy of this identification was particularly striking since one of the possible sources was a No. 4 fuel oil comprising a similar mixture of No. 6 and No. 2 fuel oils. The predicted concentration of component Z was 83.4%, whereas the actual concentration was 82.4% (wt %). This is typical of the several experiments which were run on oil mixtures.

**Oil/Dispersant Mixtures.** The vector method can approximate the composition of an oil/dispersant mixture down to the levels of visual detectability of the dispersant in the spectrum. Oil/dispersant mixtures which have been in contact with water give erroneous results because varying amounts of the dispersant components are removed by the water.

*Conclusions*

This study has demonstrated a useful laboratory-weathering technique and an improvement in oil matching by pattern-recognition techniques using either weighting factors or the laboratory weathering. The most dramatic improvement was in the identification of weathered light oils, which have been perennial problems.

The technique for accelerated laboratory weathering can be used with small samples of light oils using thin films, dry under a UV light. It has the following attributes:

(a) It improves comparisons by the log-ratio method to give excellent results even with light oils.

(b) It provides a weathered sample for the vector method.

(c) It promises to be versatile enough to serve as a basis for a standard weathering method for other analytical techniques besides infrared. Preliminary results of the comparison of laboratory-weathered light oils to outdoor-weathered oils by the other standard oil identification techniques, thin-layer chromatography, gas chromatography, and fluorescence, indicate that in all cases the laboratory-weathering technique

**Table V. Number of Peaks, Out of 18 Measured, Which Lie within 10% after 1 or 2 Days of Weathering for Various WX Methods**

| oil | Anderson | | Brown | | none | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 1 | 2 | 1 | 2 |
| A No. 2 FO | 18 | 14 | 15 | 7 | 9 | 4 |
| B No. 2 FO | 18 | 18 | 18 | 16 | 17 | 16 |
| C No. 4 FO | 18 | 16 | 18 | 13 | 15 | 8 |
| D No. 4 FO | 18 | 18 | 18 | 17 | 16 | 16 |
| E No. 5 FO | 18 | 18 | 18 | 16 | 18 | 12 |

**Table VI. Number of Peaks, Out of 18 Measured, Which Lie within 5% after 1 or 2 Days of Weathering for Various WX Methods**

| oil | Anderson | | Brown | | none | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 1 | 2 | 1 | 2 |
| A No. 2 FO | 18 | 7 | 6 | 2 | 4 | 1 |
| B No. 2 FO | 12 | 18 | 15 | 11 | 13 | 9 |
| C No. 4 FO | 18 | 13 | 14 | 8 | 5 | 4 |
| D No. 4 FO | 18 | 17 | 15 | 15 | 8 | 6 |
| E No. 5 FO | 18 | 10 | 18 | 10 | 14 | 8 |

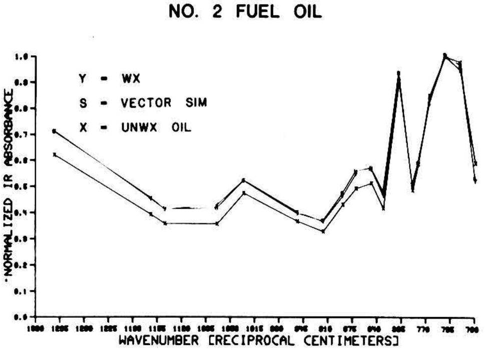

**Figure 5.** Vector simulation of No. 2 fuel oil.

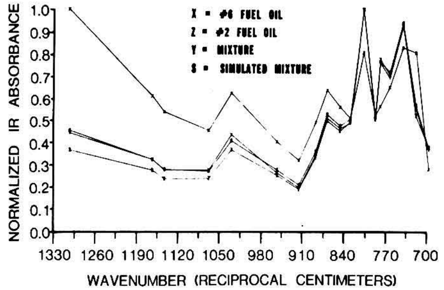

**Figure 6.** Analysis of an oil mixture by the vector method.

facilitates the identification of the unweathered oil.

The vector analysis provides a means of identifying oils and determining composition of mixtures of known components. The combination of the vector method and the laboratory-weathering technique is an especially powerful tool in the analysis of spilled oil.

*Acknowledgment*

We are indebted to Dr. Chris W. Brown and his group at the University of Rhode Island for laboratory weathering samples that we were investigating to permit a direct comparison of their accelerated weathering test (*16*) with that reported here.

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# Long-Term Stability of Urea–Formaldehyde Foam Insulation

**G. Graham Allan,* Jacek Dutkiewicz,[1] and Earl J. Gilmartin**

Department of Chemical Engineering and College of Forest Resources, University of Washington, Seattle, Washington 98195

■ The long-term breakdown of urea–formaldehyde (UF) foam was investigated by monitoring the changes in the content of hot-water-soluble, low-molecular-weight components. At 90% relative humidity and 40–90 °C, diffusion-controlled "postcuring" processes (activation energy, 20 kJ/mol) in the UF foam initially led to the formation of high-molecular-weight insoluble products. On further aging, degradation of the UF polymer (activation energy, 50 kJ/mol) is manifested by a decrease in the magnitude of the insoluble fraction. By comparison of acidic and "acid-free" foams, the inherent residual acidity is shown to be a critical factor affecting the hydrolytic breakdown of UF foams. In acid-free, in contrast to acidic, foams no formation of low-molecular-weight material was observed when foam was heated (40–100 °C) at 0% relative humidity. Formaldehyde emission, which accompanies the degradation of acidic UF foam, is characterized by an initial burst of release followed by a slow continuous evolution. The total amount of formaldehyde emitted from acidic UF foam (30 days, 55 °C, 90% relative humidity) was reduced by a factor of 6 when the acidic components were removed from the foam before testing.

Foams made from urea–formaldehyde (UF) resin have been known and used commercially since before World War II (*1*). More recently, because of their low heat conductivity (*2*), these foams have found broad acceptance in Europe and the United States as excellent insulation in both home and industrial situations. The resins used to produce UF foams are basically the conventional UF resins commonly encountered in such glued wood products as particleboard (*3*). Each manufacturing concern has its own proprietary formulation designed to produce a rapidly setting (10–120 s), low-density (0.75 lb/ft$^3$) material having a low degree of shrinkage (1–3%). However, in general, UF foam is obtained by aeration and admixture of two main components: an aqueous solution of UF resin and an aqueous solution of a surfactant containing a strong acid as a curing catalyst (*4*). The foams typically are agglomerations of microscopic-sized cells with up to 40% forming capillaries to the exterior surface. The void volume can be as much as 99%. Although UF resin foams have many positive features, occasionally these materials have been shown to be responsible for the emission of formaldehyde gas into dwellings at levels which have been irritating to the occupants (*5*). Moreover, under certain circumstances, the foamed insulation has been known to shrink and to become brittle and friable (*6*). Although the occurrence of these negative effects is often a consequence of improper foaming, it is obvious that the intrinsic chemical structure of the UF polymer is degradable under sufficiently severe conditions. This paper presents the findings of an investigation into the longer-term stability of UF foam.

## *Experimental Section*

**Materials.** The components used to prepare foam were a commercial grade UF resin (pH 7.2, solids 65%) and a phosphoric acid-based foaming agent–hardener (FAH), both donated by Rapco Inc., Costa Mesa, CA.

**Preparation of Foam Samples.** Small amounts (100 g) of foam were conveniently prepared at 20 °C in a Waring blender by rapid agitation of a mixture of the UF resin (55 mL), water (47.5 mL), and diluted FAH (2.5 mL) for 60 s. Larger samples (1000 g) of foam were obtained by using commercial foaming equipment (Isochaum Model 125, Rapperswill Corp., New York, NY) and standard techniques of operation (*1*). Before the tests, all foams were equilibrated under the same conditions (24 °C, 90% relative humidity, 24 h) and then ground to a fine powder in a Waring blender under reproducible conditions. The consistency of particle size achieved by this procedure was verified by extraction of quadruplicate samples of the same UF foam after equilibration (6 days, 40 °C, 90% relative humidity). The amounts of soluble fraction found were 59, 56, 58, and 56% of the dry weight of the foam. Where appropriate, "postcuring" was carried out in a closed vessel at a particular temperature in the presence of a salt solution selected to ensure attainment of a particular humidity.

**Determination of the Fraction of Foam Extractable with Hot Water.** A suspension of ground foam (500 mg, dry weight) in water (50 mL) was stirred at 80 °C for 30 min and then filtered. A series of preliminary tests demonstrated that this duration of extraction was an optimum. The filtrate was analyzed for its total carbon content by using an Environtech Model DC-50 TOC analyzer (Dohrman Environmental Corp., Mountain View, CA), and the ratio of this value to the total carbon content of the dry unextracted foam defines the fraction of hot-water-soluble material in the foam.

**Formaldehyde Analysis of the UF Resin.** The content of free formaldehyde and formaldehyde in the form of *N*-methylol groups was determined by the modified bisulfite method (*7*).

**Analysis of Gaseous Emissions from Foams.** Formaldehyde: A stream of air (500 mL/min) at a prescribed temperature and relative humidity was passed upward through a glass column containing a sample (10–20 g) of ground foam. The exiting gas, conducted through poly(fluoroolefin) tubing, was bubbled into water (80 mL), maintained at 15 °C, which was subsequently analyzed for dissolved formaldehyde by using the chromotropic acid procedure (*8*). Other gases: The air was replaced with a stream of nitrogen, and the aqueous solution of the absorbates was injected into a GLC apparatus (Model 3920, Perkin-Elmer Corp., Norwalk, CT) equipped with a flame ionization detector and containing Texan GC (Enka N.V., Holland) at 150 °C as the liquid phase. Helium at a flow rate of 30 mL/min was the carrier gas.

**Infrared Spectral Analysis.** Aliquots (1.5 mg) of UF foams or fractions thereof were examined in admixture with KBr (200 mg) by using standard pellets and a Model IR-10 spectrophotometer (Beckman Instruments, Inc., Fullerton, CA).

## *Results and Discussion*

In contact with the acidic hardening agent, UF resin rapidly gels, producing a highly cross-linked insoluble polymer of unidentified molecular weight. The formation of this polymer network is a consequence of the polyfunctionality of urea whose four amide hydrogen atoms are capable of reacting with the geminal hydroxyl groups of methylene glycol, the hydrate of formaldehyde existing in aqueous solution. For example, when a resin with the typical urea–formaldehyde molar ratio of 1:1.6 is hardened, if the difference between the reactivities

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[1] Present address: Institute of Man-made Fibers, Technical University of Lodz, Lodz, Poland.

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of primary and secondary amino groups are neglected, it can be calculated (*9*) that an infinite network will be created when 51% of the amide hydrogen atoms of the urea have reacted with 64% of the hydroxyl functions in the methylene glycol. Theoretically, this means not only that the resultant gelled UF resin should be composed of a mixture of highly cross-linked species, but also that there should be present certain amounts of low-molecular-weight material including some unreacted monomers. Since only somewhat more than half of the total hydroxyl functionality of the methylene glycol need react to assure gelation, the remaining unused 36% must be present as free formaldehyde hydrate and/or as *N*-methylol moieties at polymer chain ends. This calculation does not take into account the possible formation of dimethyleneoxy bridge units because of the relative infrequency of their occurrence.

Once the resin becomes a gel, further condensation reactions between the methylol and amido groups will occur, but at a much slower rate controlled by diffusion mechanisms. This slow postcuring of course leads to a decrease in the amount of low-molecular-weight material in the resin. In contrast, degradation reactions will compete with polymer buildup by generating fractions of low molecular weight. These degradative changes will be effected by both the temperature and the presence of water since UF polymers contain a plethora of hydrolyzable amide-type bonds and an abundance of *N*-methylol end groups (*10*). Certainly UF foam used as insulation in homes is exposed to varying conditions of temperature and humidity, and these environmental factors are known to have a significant effect on the durability of the foam and its performance properties (*6*). The chemical structure of the UF polymer also suggests that the inherent acidity of the final foam product will be another important parameter to be considered in the degradation studies of UF resin materials. This acidity is primarily due to the presence of the protonic curing catalyst in the foam-making process.

The foregoing theoretical considerations were the rationale for the experimental technique employed to investigate the degradation of UF foam. Thus, it was expected that a convenient way of following this process and the aforesaid postcuring could be realized through determining the changes in the quantity of low-molecular-weight substances in the UF foam. Since the low-molecular-weight components should be easily soluble, in contrast to the insoluble highly cross-linked network polymer matrix, this experimental approach could be accomplished by extracting samples of the UF foam with hot water and determining the soluble species content by measurement of the carbon content of the extract. This technique seems to have given a fairly good approximation of the actual low-molecular-weight fractions in the tested specimens because the carbon content of the water-soluble foam extract and that of the foam itself did not differ significantly. A series of elementary analyses showed that both the dried foam samples and the dried foam extracts contained carbon in an amount of 33 ± 2%. The contributions of minor amounts of soluble additives present in the studied material, such as modifiers, surfactants, etc., were neglected in these calculations.

Using this analytical technique, we measured the changes of the water-soluble fraction of UF foam when heated at various temperatures and a relative humidity of 90%. The results obtained are collected in Figure 1. It is interesting to note that the foam contains initially a high content of low-molecular-weight water-soluble material which, in the case of the tested product, amounted to ~85% of its dry weight. This is in qualitative agreement with the result predicted from classical gelation theory. The quantity of the soluble species in the foam did not change appreciably at 3 °C even when the foam was stored for several months. However, as shown in Figure 1, when the storage temperature was raised, postcuring reactions leading to high-molecular-weight insoluble products were initiated. As in the rapid foam-curing process, possible pathways of such reactions will involve the formation of methylene bridges between the methylol and amido groups. The formation of ether linkages between methylol groups will also occur, albeit at a slower rate.

The curves depicted in Figure 1 also indicate that the postcuring resulting in an initial conversion of the soluble fraction ($SF_1$) into insoluble material (IF) is apparently accompanied by the degradation of UF polymer which ultimately leads to the augmentation of the low-molecular-weight soluble fraction ($SF_2$). The shape of these kinetic curves suggests that they can be considered as an approximate graphical illustration of the consecutive processes (*13*) of polycondensation and degradation. These reactions can be represented by eq 1

$$SF_1 \xrightarrow{k_1} IF \xrightarrow{k_2} SF_2 \qquad (1)$$

where $k_1$ and $k_2$ are the rate constants for the formation of the water-insoluble fraction and the degradation of UF polymer to the water-soluble species, respectively. It should be understood that the $SF_1$ fraction on the left-hand side of eq 1 represents the low-molecular-weight substances and oligomeric urea–formaldehyde condensation products, whereas $SF_2$ on the right side stands for the mixture of foam hydrolysates and the uncured materials.

For kinetic calculations, it is convenient to consider both the formation of the water-insoluble fraction and the degradation of the foam as first-order processes. The former assumption should not deviate much from reality provided the rate of postcuring is controlled by the diffusive penetration of methylol groups, located mainly at the ends of the oligomeric molecules, in the UF polymer network. The latter is justifiable because the breakdown of the foam is most probably hydrolytic in nature. On the basis of these assumptions, the amount of fraction IF present at time *t* is given by kinetic eq 2

$$IF = IF_0 e^{-k_2 t} + SF_0 k_1 (e^{-k_1 t} - e^{-k_2 t})/(k_2 - k_1) \qquad (2)$$

where $SF_0$ and $IF_0$ represent the initial amounts of the water-soluble species and the insoluble UF polymer, respectively, in the foam. The extreme points ($IF_{max}$, $t_{max}$) on the kinetic curves in Figure 1 will then be given by eq 3 and 4

$$t_{max} = (1/k_2 - k_1) \ln ([k_2/k_1] - IF_0 k_2 [k_2 - k_1]/SF_0 k_1^2) \qquad (3)$$

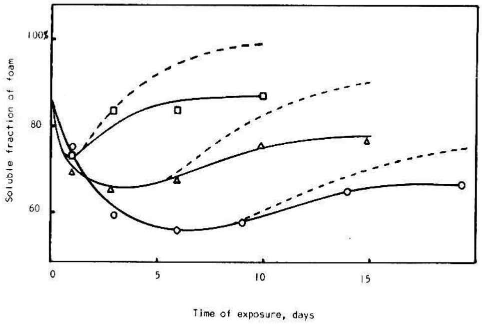

**Figure 1.** A comparison of the experimental results found and the theoretical values (dotted lines) predicted from eq 2 for the amount of water-soluble material in a commercial UF foam exposed at 90% relative humidity to temperatures of 40 (○), 70 (△), or 95 °C (□) for various periods of time.

$$\mathrm{IF}_{\max} = \mathrm{IF}_0 e^{-k_2 t_{\max}} + \mathrm{SF}_0 k_1 (e^{-k_1 t_{\max}} - e^{-k_2 t_{\max}})/(k_2 - k_1) \quad (4)$$

From the obtained solutions for $k_1$ and $k_2$ summarized in Table I, activation energies for each of the two processes were calculated from the Arrhenius plots shown in Figure 2. The value corresponding to the postcuring reaction is 20 kJ/mol, which is consistent with the concept of a diffusion-controlled process. On the other hand, the calculated activation energy for the formation of the soluble degradation products is ~50 kJ/mol, which is the order of magnitude common for acid-catalyzed hydrolyses.

Measurement of the pH values of slurries of foam (2 g, dry weight) in water (150 mL) before (pH 2.7) and after (pH 3.6) heating at 70 °C and 90% relative humidity for 30 days disclosed that the acidity of the parent foam had decreased. One of the reasons for this change is the neutralizing action of the new amino groups generated by the hydrolyses formulated in eq 6. Since the rate of hydrolytic degradation occurring in the UF foam will certainly depend upon the acidity therein, some discrepancy between the experimental data and predictions of eq 2 can be expected. This in fact is observed and the extent of the deviation between theory and practice is illustrated in Figure 1. The differences, however, can also be ascribed to the occurrence of reactions which do not fit into the consecutive scheme represented by eq 1. One such sequence is the hydrolytic cleavage of the methylene linkage between two nitrogen atoms shown in eq 5.

**Table I. Temperature Dependence of the Rate Constants for the Formation of the Insoluble Fraction ($k_1$) and the Soluble Degradation Products ($k_2$) in the Commercial-Grade Urea-Formaldehyde Foam Exposed to Higher Temperatures and Humidity**

| conditions of exposure | | $10^6 k_1$, $\mathrm{s}^{-1}$ | $10^6 k_2$, $\mathrm{s}^{-1}$ |
|---|---|---|---|
| temp, °C | rel hum, % | | |
| 40 | 90 | 2.08 | 1.39 |
| 70 | 90 | 3.24 | 3.36 |
| 95 | 90 | 6.37 | 12.73 |

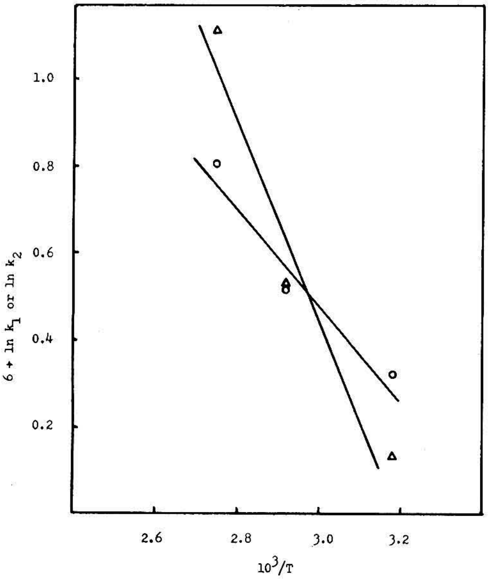

Figure 2. Arrhenius plots of the kinetic data given in Table I; (O) ln $k_1$ = f(1/$T$); (Δ) ln $k_2$ = f(1/$T$).

$$\sim\mathrm{NHCH_2NHCO}\sim + \mathrm{H_2O} \rightleftharpoons \sim\mathrm{NHCH_2OH} + \mathrm{NH_2CO}\sim \quad (5)$$

This is a reversible reaction under acidic conditions which does not necessarily lead to the formation of soluble products. The production of water-extractable material is therefore diminished relative to that predicted by eq 2. However, since the internitrogen methylene linkage is relatively stable, this effect will be most visible under the more drastic temperature regimes and at extended times of exposure. Accordingly, for example, the correspondence between theory and practice shown in Figure 1 is excellent for 10-day exposure of the foam to a temperature of 40 °C. On the other hand, the amido-type linkages between nitrogen atoms and the carbon of carbonyl groups are much more easily cleaved. The cleavage leads to the formation of amino and carboxyl groups, the latter of which is rather unstable when attached to a nitrogen atom. This instability of the carbamic acid moiety can lead to the evolution of carbon dioxide as represented in eq 6.

$$\sim\mathrm{NHCOHN}\sim + \mathrm{H_2O} \rightarrow \sim\mathrm{NHCOOH} + \mathrm{NH_2}\sim \rightarrow \sim\mathrm{NH_2} + \mathrm{CO_2} + \mathrm{NH_2}\sim \quad (6)$$

The occurrence of this reaction as part of the consecutive sequence of eq 1 was validated by comparison of the infrared spectra of undegraded UF foam and of the soluble hydrolysates of the foam reproduced in Figure 3. This comparison discloses a marked decrease in the carbonyl content of the hydrolysates relative to the foam. Furthermore, the actual evolution of carbon dioxide was demonstrated, as shown in Figure 4, by GLC analysis of the volatile decomposition products released from UF foam exposed to hot (55 °C) and humid (90% relative humidity) conditions.

Under the same conditions, the evolution of gaseous formaldehyde gas did not originate from the void space within the foam because the foam structure was destroyed by grinding and flushed with nitrogen before exposure to the degradative conditions. The formaldehyde gas emitted may in part be formed through the intermediacy of methylenediamine formed by hydrolysis of the foam backbone according to eq 7 or, more conventionally, by cleavage within chain-end $N$-methylol groups. The generation of formaldehyde by the depolymerization of short polymethyleneoxy chains is also a possibility, albeit an unlikely one (*10–12*).

$$\sim\mathrm{CO_2NHCH_2NHCO}\sim \rightarrow \mathrm{NH_2CH_2NH_2} \rightarrow \mathrm{HOCH_2OH} \rightarrow \mathrm{CH_2O} \quad (7)$$

Although uncommon, methylenediamine has been isolated as the dihydrochloride from the products obtained by hydrolysis of methylenediformamide (*14*) using concentrated hydrochloric acid. However, the hydrolysis of a closer foam analogue, methylenediacetamide, under similar conditions yielded formaldehyde directly.

It is important to keep in mind that hydrolysis of this type in a UF foam will only occur to a significant extent under the relatively drastic temperature conditions necessary to secure experimental results within a reasonable period of time. Of course, such are not commonly encountered by UF foam insulation in real-life situations.

Under similar high-temperature and humid conditions, the emission of formaldehyde from UF foam followed the kinetic pathways presented in Figure 5 where there is an initial burst of release followed by a slow continuous evolution. The former, in the real-life situation, probably stems largely from unreacted formaldehyde in the foam which was originally present in the parent UF resin. In this study the free formaldehyde

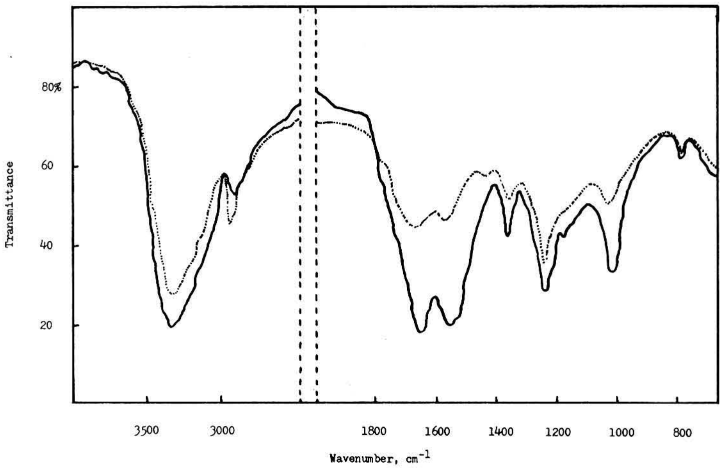

**Figure 3.** Infrared spectra of undegraded commercial UF foam and the soluble hydrolyzates (. . .) derived therefrom.

content of the starting resin was ~0.4% by weight. In these laboratory studies, where this free formaldehyde has been removed, the other substantial contributor to the initial fast release of formaldehyde is chain-end *N*-methylol groups. Once these two sources of formaldehyde are exhausted by emission from or reaction within an installed foam, further release can occur practically only via random degradation of the backbone of the UF polymer. Thus, the degree to which formaldehyde may be emitted from UF foam is directly related to the composition of the precursor resin and the extent of the breakdown reactions in the final foamed product. The former factor can be controlled by the processes of resin manufacture, but the latter will be dependent on the inherent acidity of the foam in situ. It may be noted from Figure 5 that the total emission of formaldehyde from foam samples maintained at temperatures of 55 and 75 °C and 90% relative humidity appears to level off and after 25 days is essentially the same for both exposure regimes.

To ascertain how this acidity might affect the stability of foamed insulation, acid-free and acidic foams were compared. The acid-free type was prepared by washing ground specimens of foam with cold (5 °C) water until the washings had a pH value of 7. The water introduced was subsequently removed by a second washing with acetone which was allowed to evaporate at ambient temperature for 1 day. The acidic foam differed from the acid-free only in that it was not subjected to washing with water. Measurement of the pH values of aqueous foam suspension, before and after washing with acetone, showed that this treatment did not affect the acidity. Using this suspension technique of indirectly evaluating the acidity of foam specimens, we observed that during prolonged heating in nonhumid conditions (Table II) the pH values of the acidic material increase slightly at lower and significantly at higher temperatures. Also, the acidic foam tended to darken even when maintained at a temperature as low as 40 °C. This discoloration was much less in the case of the acid-free foam samples. The development of a straw color in the UF foam on prolonged heating may be a consequence of the reaction of the residual phosphoric acid catalyst with released formaldehyde. The combination of these two chemicals can afford methylene diphosphoric acid which is reported to be light brown in color (*15*). This reaction may make a significant contribution to the overall reduction in the inherent acidity of the UF resin product, particularly when the foam has been exposed to 100 °C heat.

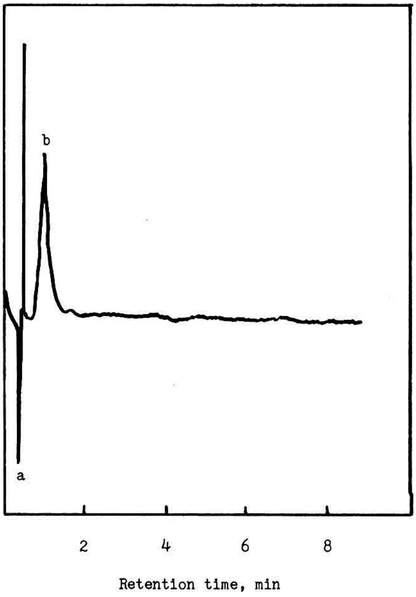

**Figure 4.** GLC spectrum of the gaseous decomposition products (a, $CO_2$; b, $CH_2O$) released from a commercial UF foam.

The acidic and acid-free foams can be further compared with respect to the variation in their content of water-soluble material when the foams are maintained at elevated temperatures and 0% relative humidity. Not surprisingly, the prior removal of water and the nonhumid atmosphere favor polycondensation reactions, inhibit backbone hydrolyses, and cause the content of soluble material in the foam to decrease rapidly, as is apparent from the results collected in Figure 6. At 70 °C this initial drop is subsequently overcome in the acidic foam by an increase in the amount of soluble degradation products formed by hydrolysis keyed by the water created by the condensation reactions and the residual acid catalyst. This behavior of the acidic is not paralleled by its acid-free counterpart at 70 °C presumably because of the absence of

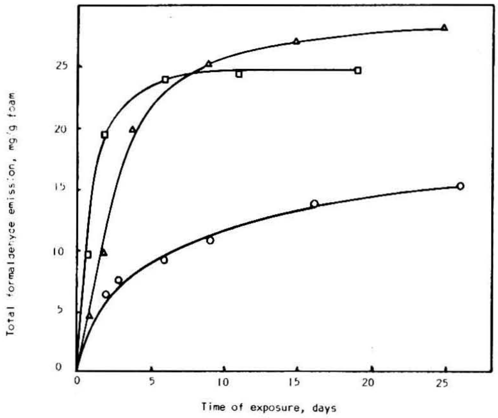

**Figure 5.** The extent of formaldehyde emission from a commercial UF foam exposed at 90% relative humidity to temperatures of 35 (○), 55 (△), or 75 °C (□) for various periods of time.

phosphoric acid. However, these differences are not manifest when the comparison is made at 100 °C. In this situation only the condensation reactions are observed, since the foams are maintained in an essentially anhydrous condition at this temperature and hydrolysis is thereby prevented.

At the lower test temperatures of 40 °C the acidic foam slowly undergoes the postcuring sequence which, after ~4 weeks, loses ascendancy to the solubilizing acid-catalyzed degradation reactions. In conformity with the characteristics noted at 70 and 100 °C, the acid-free foam at 40 °C exhibited no tendency to generate water-soluble material on prolonged heating.

All of these observations mean that the hydrolytic degradation of UF foam is greatly influenced by its constitutive acidity. In contrast, the rate of postcuring self-condensation seems to be relatively independent of this parameter because this process will be diffusion controlled and different kinetically from the analogous reactions in solution (*16, 17*).

It therefore follows that reduction of the acidity in UF polymer networks should lead to some diminution in the emission of formaldehyde. The validity of this view was demonstrated by simultaneously comparing the amount of formaldehyde released from acidic and acid-free UF foams maintained at a relative humidity of 90% and a temperature of 55 °C. Both foams were washed with acetone to remove free formaldehyde. Thereafter, as can be seen from the data depicted in Figure 7, the total quantity of formaldehyde collected from the acidic foam over a period of 30 days was reduced by a factor of ~6 when the foam had been washed to remove residual acid components before testing. Of course, all of these findings are based on a single example of a commercial UF foam. However, since in all UF foams the preponderance of basic structural units are identical, it can reasonably be concluded that other commercial UF foam formulations will exhibit similar long-term stability.

## *Conclusions*

The findings of this investigation of the long-term stability of UF foams define the factors which may under special conditions cause deterioration of this insulation material with the concomitant liberation of formaldehyde. The understanding established thus far provides a sound basis for further research into methods of enhancing the stability of UF foams. Details of how this can be achieved will be the subject of a later communication.

### Table II. Effect of Heating on the Inherent Acidity of UF Foams

| heating temp, [a] °C | inherent acidity of foam [b] | |
|---|---|---|
| | initial pH [c] | final pH [c] |
| 40 | 2.5 | 3.0 |
| 70 | 2.6 | 3.2 |
| 100 | 2.5 | 6.1 |

[a] Heating was performed at a relative humidity of 0% for a period of 30 days. [b] The UF foam was washed with acetone and predried before heating. [c] The pH value was measured on a suspension of ground UF foam (2 g, dry weight) in water (150 mL).

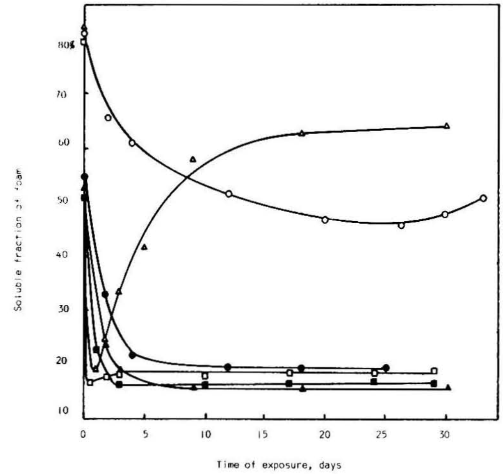

**Figure 6.** A comparison of the amount of soluble material in acid (○, △, □) and acid-free (●, ▲, ■) commercial UF foam exposed at 0% relative humidity to temperatures of 40 (○, ●), 70 (△, ▲), or 100 °C (□, ■) for various periods of time.

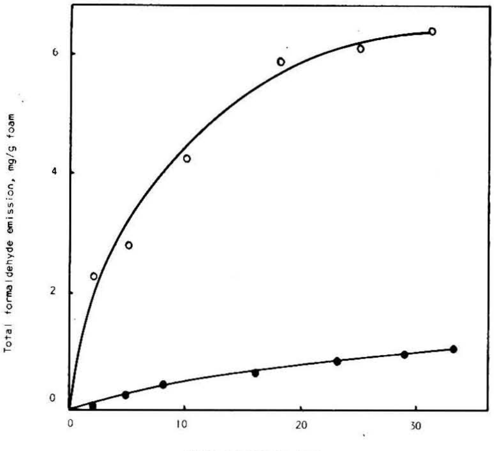

**Figure 7.** A comparison of the extent of formaldehyde emission from acidic (○) and acid-free (●) laboratory foams exposed at 50% relative humidity to a temperature of 55 °C for various periods of time.

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# X-ray Diffractometry Examination of Air Filters for Compounds Emitted by Lead Smelting Operations

**Ronald L. Foster and Peter F. Lott***

Department of Chemistry, University of Missouri—Kansas City, Kansas City, Mo. 64110

■ X-ray diffractometry has been used to characterize particulate pollutant fallout from smelting operations in Missouri. An identification technique has been developed that needs only 1–15 mg of collected material from a Hi-Vol filter. Compound identification reveals changes in the toxic lead compounds after corrective action was taken in the manufacturing process. Typical diffraction patterns are provided.

This investigation on the use of X-ray diffractometry to identify fugitive industrial air particulate pollutants was undertaken in response to the need to identify specific compound emission. Sax (*1*) showed that health hazards depend on the toxicity, solubility, and chemical nature of the pollutant. The environmentalist has long been handicapped by the usual analytical techniques that determine elemental constituents only, thus limiting his ability to assess the hazard.

Pollution enforcement agencies have required blanket installation of expensive control devices based on elemental information alone. Since each step in most industrial processes generates different compound particulates, the identification of a specific operation as a pollution source will benefit industry, as only that particular source need be corrected or regulated. This technique should be invaluable to plant managers in selection of pollution abatement equipment and identification of plant health hazards. Additionally, the identification of process products being generated can be used to evaluate the efficiency of a process or can be used as a guide to the progress of the process. Any deviation from the normal distribution of process particulate compounds serves to identify problems and potential out-of-control situations before or when they occur.

Warner, Saad, and Jackson (*2*) of the Wayne City Department of Health, Detroit, Mich., applied X-ray diffractometry to dustfall samples diluted with powdered glass. They reported finding lime, $CaCO_3$, road salt, coke dust, and "aerosol from sinter emissions". In Japan, Igarashi (*3*) proposed the use of diffraction methods of X-ray analysis for air pollution studies. Davis and Nam-Kun (*4*) investigated the quantitative analysis of Hi-Vol filter segments using an applied reference coating said to correct matrix effects. This involves an aerosol coating chamber to apply the reference. The technique was limited to identification of natural background.

Most X-ray applications to date, however, have applied the X-ray fluorescence methodology to air particulate studies. This simple technique provides valuable insight into the elemental content of pollutants, but advances the knowledge of the investigator no further than traditional instrumental methods.

Hall (*5*), in an excellent article, outlined the seriousness of lead emissions as a health hazard to humans, and discussed the mechanics of lead particulate ingestion. The contamination of vegetation and soil in the vicinity of lead smelters can be great enough to result in the death of horses allowed to graze in proximity to smelter emission sources (*6*). For this reason, the lead smelters were chosen for this study of industrial lead particulate emissions.

## *Experimental Procedures*

The samples were collected by Hi-Vol air filtering devices using fiberglass filters. Samples provided by the Missouri Air Quality Commission were collected over periods normally of either 24 or 48 h, and samples provided by ASARCO, Inc. were collected during 6-h sampling periods.

Samples are prepared for analysis by concentrating the deposit onto Schleicher and Schuell 2.4-cm paper filters. Each Hi-Vol filter is washed with a 5% Duco cement in acetone mixture using a plastic wash bottle. The jet dislodges and washes loose particles into a collection filter cup, where aspiration removes the solvent, leaving a uniform sample deposit on the filter (*7*).

The Missouri Air Quality Commission samples provided deposits of from 4 to 15 mg of material. The ASARCO samples provided only 1.6–4 mg of material. For the ASARCO samples, a reduced deposit area 9 mm × 10 mm was machined in a separate filter cup, as this was found to be the largest area covered by the X-ray beam at the lowest angle scanned. This provides adequate sample thickness for detection of trace constituents (*8*).

The filter disks are mounted on a standard aluminum diffraction sample holder and placed into the analyzing chamber

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of the Philips-Norelco XRG-3000 recording X-ray diffractometer. Instrumental settings are listed in Table I.

A blank filter disk was used to obtain the filter paper background (*9*). Samples from Maryville and Fulton, Mo., were provided to establish natural background for the Missouri Air Conservation Commission material, and samples from Taum Sauk Mountain, the highest point in Missouri, were provided with the ASARCO samples to serve also as a regional background.

**Table I. Instrumental Settings**

| | MACC[a] | ASARCO |
|---|---|---|
| source | Cu K$\alpha$ | Cu K$\alpha$ |
| filter | Ni | Ni |
| voltage | 40 kV | 35 kV |
| current | 25 mA | 15 mA |
| scale | 1 K | 100 |
| time constant | 2 s | 10 s |
| recorder | 30 in./min | 7.5 in./min |
| scan rate | 1°·2$\theta$/min | ¼°·2$\theta$/min |
| pattern number | 5329 | 5136 |
| | 5550 | 5119 |
| | | 5132 |

[a] Missouri Air Conservation Commission.

Smelter dusts from various steps in the process were run to establish the possible fallout compounds observed in the collected samples.

*Results*

A summary of sample observations correlated with weather conditions and plant operation, when available, is given in Table II.

In general, the Glover samples indicate high levels of PbS and associated compounds found in the lead ore concentrate (Figure 1). Nearly all samples from this site reflect varying contributions from this source. Sample 5550 represents the extreme example (Figure 2), even though the sintering operation was the only plant activity during the 24-h sampling period. However, surface weather conditions were very favorable for surface dust suspension, and the indication of $PbSO_4$ would suggest a contribution of sintering dust, which is high in PbS (Figure 3). Because the ore concentrate was

**Table II. Sample Correlations [a]**

| | | smelter operation | | | weather | | | compd rel intensity | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | wind | | | | | | | |
| sample | date | sintering | blast furnace | ore trucking | speed | direction | precpn | dolomite | $CaCO_3$ | $PbSO_4$ | PbS | PbO·$PbSO_4$ |
| 2227G | 9/15/70 | X | X | + | 4–15 | S | L | | H | M | M | M |
| | 9/16/70 | X | X | – | 4–8 | N–S–E–W | | | | | | |
| 2224G | 10/8/70 | X | X | + | 10G20 | SE–E | M | | H | M | M | |
| | 10/9/70 | X | X | – | 10G31 | SW | H | | | | | |
| 2081G | 11/21/70 | X | X | – | 4–20 | SE–S | | | M | VL | M | |
| 2522G | 2/11/71 | X | X | | 12G23 | S | L | | VH | M | L | |
| | 2/18/71 | X | X | | 3–20 | E–S | | | | | | |
| 4943G | 10/6/72 | + | – | – | 3–13 | N–NE | M | | H | M | M | |
| | 10/13/72 | – | + | – | 4–11 | N–E | L | | | | | |
| | 10/20/72 | + | + | + | 2–10 | E–SE | | | | | | |
| 5202G | 2/12/73 | – | – | + | 3–15 | SE | L | | | M | M | |
| | 2/19/73 | – | + | + | 0–10 | W–S | | | | | | |
| 5207G | 2/27/73 | + | + | + | 5–12 | NW–NE | | H | | | L | |
| 5203G | 3/5/73 | + | + | + | 3–12 | W–SE | | M | | M | VH | |
| | 3/12/73 | + | + | + | 5–10 | W–N–SE | | | | | | |
| 5206G | 3/17/73 | + | – | – | 5G30 | NW | T | M | | L | L | |
| | 3/24/73 | + | + | + | 5G32 | SE | L | | | | | |
| 5204G | 3/30/73 | – | – | + | 4–15 | N–E | L | | | VH | L | |
| 5205G | 4/10/73 | + | + | – | 7G35 | W–NW | T | | | M | L | |
| | 4/17/73 | | | | 4–12 | E–N–S | H | | | | | |
| 5113G | 4/24/73 | | | | 4–10 | E–SE | L | VH | | H | H | |
| 5548G | 5/16/73 | + | + | + | 6G25 | SW–N | L | | | VL | H | |
| 5550G | 6/3/73 | + | – | – | 5G30 | S–SW | | H | | M | VH | |
| 2769G | 6/10/73 | + | + | + | 3–10 | W–SE | | | H | M | M | |
| 5527G | 3/6/74 | | | | 4G26 | E–SSW | M | | | VL | H | |
| | 3/13/74 | | | | 8–16 | NE | | | | | | |
| 5119G | 6/9/76 | | | | | SW | | | T | | | |
| 5132G | 9/5/76 | | | | | ENE | | H | M | | | |
| 5136G | 9/14/76 | | | | | SSE | | L | | | | |
| 5327H | 3/28/73 | | | | 6–13 | SE | L | | | VL | T | |
| 5328H | 4/4/73 | | | | 9G23 | NW | M | | | | | |
| | 4/11/73 | | | | 6G28 | SW | T | | | | | |
| 5329H | 4/16/73 | | | | 4G27 | SE–SW–W | M | | | M | T | VH |
| 5330H | 4/22/73 | | | | 5G37 | S–W–NE | H | | | | | |
| 5332H | 5/22/73 | | | | 4–10 | SE–SW–W | M | | | M | VL | |
| 5334H | 6/15/73 | | | | 8–12 | SE–SW–S | L | | | M | L | |
| 5336H | 7/9/73 | | | | 4–8 | W–S–SW | | | | M | L | |

[a] Sample G, Glover, Mo.; sample H, Herculaneum, Mo.; X, strike; +, operating; –, not operating; T, trace; L, low; M, moderate; H, heavy, high; V, very.

stored in mounds in open areas at this plant wind erosion would be expected to produce the observed fallout downwind of the plant during dry conditions.

A similar bleed-off pattern for $PbSO_4$ seemed to continue during an extended period of plant inactivity, except for ore trucking, when the plant was shut down by a strike. While $PbSO_4$ and quartz share two major peak locations in their patterns (Figures 4 and 5), making discrimination difficult, analysis of the linear change in the ratios of the two peaks with changing weight fraction of either compound (as shown in Figure 6) permits calculation of percent contribution by either form. On this basis, calculated $PbSO_4$ contribution to the observed patterns remained fairly constant.

Samples taken after resumption of operations showed, in many cases, no clear correlation between reported activity and resultant fallout. This may be due to the extended sampling periods, usually about 48 h, during which plant operations could vary considerably, as well as changing weather conditions, combining to smear the process events. This produces a composite fallout pattern over periods too long to allow discrimination of specific sources. Selection of shorter sampling times should correct this fault.

The three Glover samples provided by ASARCO reflect a significant difference in composition from the samples collected 3 years earlier by the state agency. While sample 5119 (Figure 7) contains a strong indication for ZnS, no ore con-

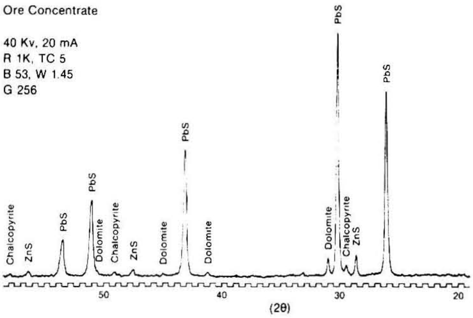

**Figure 1.** Ore concentrate pattern

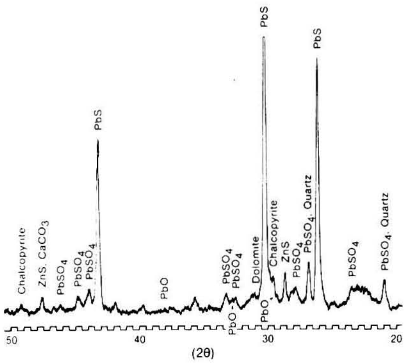

**Figure 2.** Sample 5550 pattern

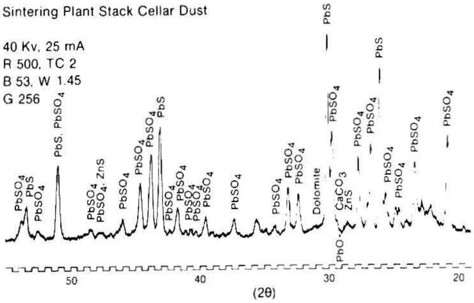

**Figure 3.** Sintering pattern

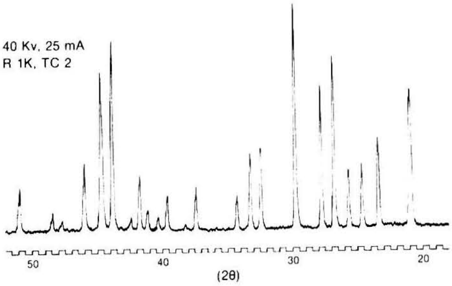

**Figure 4.** $PbSO_4$ pattern

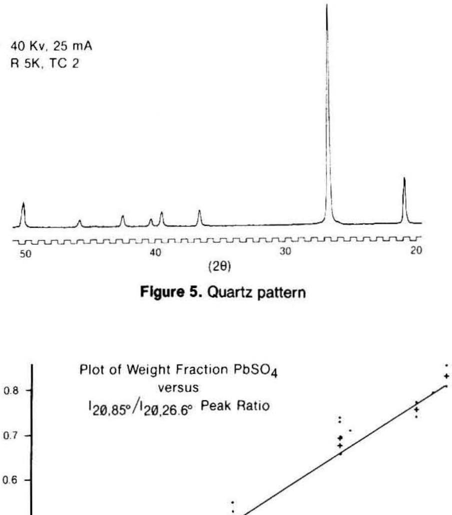

**Figure 5.** Quartz pattern

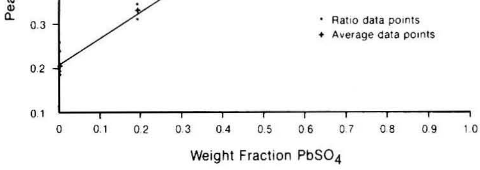

**Figure 6.** Plot of the ratio of observed peak heights of $PbSO_4$ and quartz vs. the weight fraction ($X_{PbSO_4}$) of $PbSO_4$

centrate PbS is indicated. The wind direction at that time was from 197°, or SSW, while the other two samples were taken with winds out of the NNE, sample 5132 (Figure 8), and slightly east of south, sample 5136 (Figure 9). In each sample quartz is an obvious major constituent. In addition, 5132 contains an unusual amount of dolomite, perhaps the contribution of a downwind gravel road. The other two samples may contain only trace amounts of dolomite. Calcium carbonate is observed in 5132 and 5119, and as a possible trace in 5136. A fourth, as yet unidentified compound, indicated by a "?" above the peak, is present in 5132 and 5119, but not observable in 5136. This compound is not observed in the Taum Sauk samples and can be observed in some of the smelter samples from the state study. The pattern, however, does not fit the patterns of expected lead compounds or process-generated compounds containing lead, nor is it found in association with the lead ore concentrate.

Interestingly, these samples contain no observable amounts of the lead compounds found in the earlier sampling conducted by the Missouri Air Quality Commission. This is probably due to the extensive pollution abatement program carried on at the Glover smelter by ASARCO, in response to the identification of an air pollution hazard.

The Herculaneum samples show a striking dissimilarity to those collected at Glover. The low levels of ore concentrate compounds indicate a different ore handling process and, perhaps, a more efficient sintering operation reducing the fugitive PbS emissions. The location of the sampling station atop a school building about 40 ft above ground level may also be a factor. However, as only one sample was available from a period of probably dry surface conditions, it is also possible that the observations are biased by dampness. The most interesting sample of this set, 5329 (Figure 10), indicates an anomalous high fallout of probable blast furnace origin. The unusual ZnO content of this sample is strikingly similar to the patterns observed for fallout from zinc smelters and may indicate the smelting of zinc during this period. The $PbO{\cdot}PbSO_4$ and $PbSO_4$ forms are indicative of the blast furnace operation (Figure 11).

Since plant process dusts were not available from the Herculaneum site, discrimination between emission sources is difficult unless the processes, equipment, and ore composition are the same at both smelters. Indications are, however, that the two situations are not equivalent. The collection of natural background of quartz, dolomite, and $CaCO_3$ seems unimpeded. The very minor contribution of PbS may be due to the elevated sampling site or may be the normal extent of fugitive emissions.

This technique is expected to be capable of quantification in that the areas of the peaks for individual compounds are proportional to the weight fraction composition of the sample. Since interelement effects, particle size distribution, and reflective efficiency vary between compounds, it is felt that a 5% accuracy is not unreasonable.

### *Discussion*

This study shows the feasibility of identifying airborne compounds not naturally present, identifying the source of emissions so that specific corrective action is possible, accurately evaluating the health hazard created by the source, and monitoring the conditions of an emissive process. Source discrimination is observed by examination of the patterns. Pattern 5550, a typical, normal pattern, shows the pressure of the ore concentrate. This indicates that ore handling is a major particulate contributor. In this same pattern, the minor $PbSO_4$ indication implies that the sintering operation is a minor contributor. The absence of the $PbO{\cdot}PbSO_4$ peaks indicates no blast furnace contribution.

Pattern 5329 indicates blast furnace contributors because of the presence of ZnO, $PbSO_4$, and $PbO{\cdot}PbSO_4$. This last compound, $PbSO_4$, clearly indicates a blast furnace contribution. The low PbS level precludes significant ore concentrate or sintering plant contributions.

In contrast, the ASARCO samples 5119, 5132, and 5136, a representative selection from a number of ASARCO patterns which were obtained at high sensitivity settings, showed no

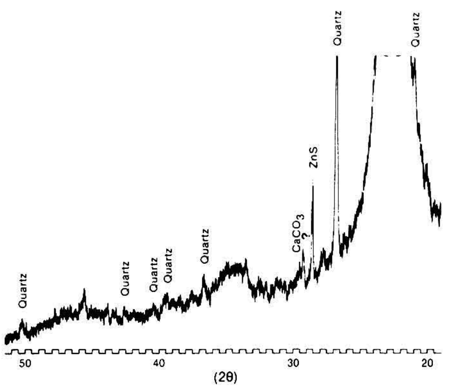

**Figure 7.** Sample 5119 pattern

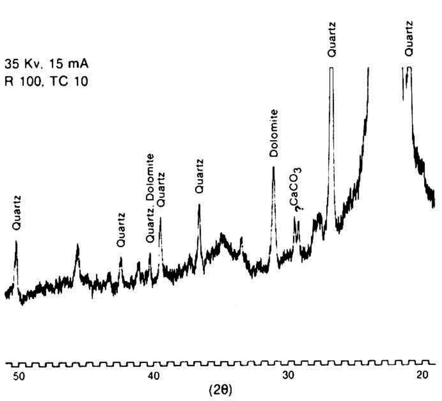

**Figure 8.** Sample 5132 pattern

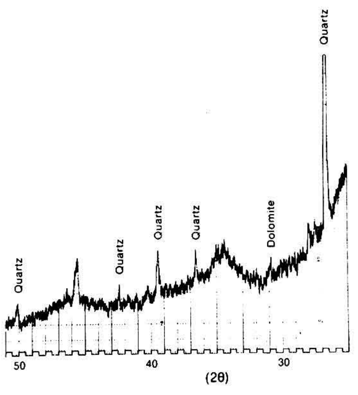

**Figure 9.** Sample 5136 pattern

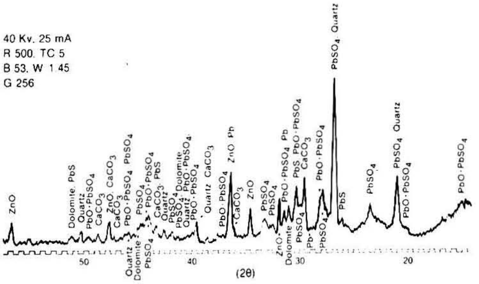

**Figure 10.** Sample 5329 pattern

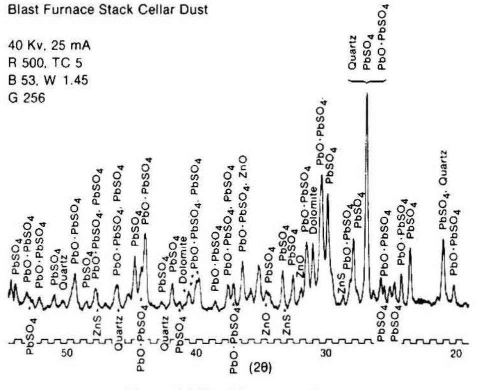

**Figure 11.** Blast furnace pattern

indications of lead compounds. The only compounds observed are attributable to the natural background.

Quantitative evaluation is probably a practical goal, and presently can be applied to simple cases with acceptable accuracy. Further study may solve the problems involved in more complex situations, leading to a universally applicable methodology.

*Acknowledgment*

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# Sulfur Dioxide Oxidation and Plume Formation at Cement Kilns

**Barry Dellinger,* Gary Grotecloss, and Christopher R. Fortune**
Northrop Services, Inc., P.O. Box 12313, Research Triangle Park, North Carolina 27709
**James L. Cheney and James B. Homolya**
U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711

■ The results of source sampling at the Glens Falls cement kiln in Glens Falls, NY, are reported for sulfur oxides, ammonia, hydrochloric acid, oxygen, and moisture content. The origin of a detached, high-opacity, persistent plume originating from the cement kiln stack is investigated. It is proposed that this plume is due to ammonium salts of sulfur oxides ($(NH_4)_2SO_4$, $NH_4HSO_4$, $(NH_4)_2SO_3$, $NH_4HSO_3$) and sulfuric acid that have been formed in condensed water droplets in the plume by the pseudocatalytic action of ammonia.

## *Introduction*

Approximately 80 million tons or 426 million barrels of Portland cement will be produced this year in the United States and Puerto Rico (*1*). Of this total, 44.4% will be produced in the Northeast, 11.2% will be produced in California, and another 11.0% will be produced in Texas (*2*). A problem common to many of these installations is the presence of a detached, high-opacity, persistent plume that emanates from the kiln stack (*3*). The composition of this plume could have considerable impact upon the overall air quality of the respective areas.

The present study was initiated in response to observations of such a plume at the Glens Falls cement kiln in Glens Falls, NY (*4*). The purpose of this study was to determine the origin and nature of this plume and, if possible, propose a suitable method for eliminating the plume.

The Glens Falls cement kiln is typical of a wet-process Portland cement plant (*1, 5*). In this process, the raw materials (limestone, clay or shale, silicates, and ferrous materials) are crushed, screened, slurried, and ground. They are then fed into the kiln where they are first heated to 1000 °C to vaporize the alkalies. At this point, calcium carbonate ($CaCO_3$) is converted to calcium oxide (CaO); combustion of organic material also occurs. After further heating to ~1500 °C, a partial fusion of the raw materials occurs, resulting in "clinker" formation. Once cooled, the clinkers are ground and mixed with gypsum to obtain Portland cement. Sampling was performed on the stack that contained the effluent from the kiln and clinker cooler operations. The Glens Falls plume was observed to be

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persistent, detached, and bluish-white in nature. Although the in-stack opacity was only ~10% and grain loading was very light, the detached plume was observed to have an average maximum opacity of ~85%. The bluish-white nature of the plume indicated the presence of fine particles and, together with the observation of 10% in-stack opacity, virtually negated the possibility that the plume was due to dust or ash from combustion in the kiln. The persistent nature of the plume eliminated the possibility that the plume was solely due to condensation of water. The mystery regarding the origin of this plume was heightened by the observation that the plume began to dissipate at sunrise and had virtually disappeared by 9 a.m.

The stack was sampled for sulfur oxides, ammonia, hydrochloric acid, oxygen, and moisture content. The results and interpretations of the laboratory investigations are presented in this report, as well as the theoretical calculations concerning the chemistry involved in the sampling procedures and the plume formation.

## *Experimental Section*

**Sulfur Oxide Determinations.** The sampling method used to measure sulfur oxides emitted from stationary sources was the controlled condensation system (CCS) (*6*). The CCS typically uses a Goksøyr–Ross-type condensation approach, a heated quartz filter, and a Greenburg–Smith impinger train to collect and separate sulfur oxides belonging to three main categories (*3*): (1) particulate sulfates, (2) sulfuric acid ($H_2SO_4$), and (3) sulfur dioxide ($SO_2$) gas.

The apparatus utilized in the CCS system for this study consisted of a heated quartz-lined probe, a quartz filter and holder, a temperature-controlled glass wool plug and holder, a sampling module, a sampling pump, and a dry gas meter (Figure 1). The sampling module contained an ice bath for the Greenburg–Smith impingers, along with a water bath for the plug holder, and voltage controls for heating the probe and the filter.

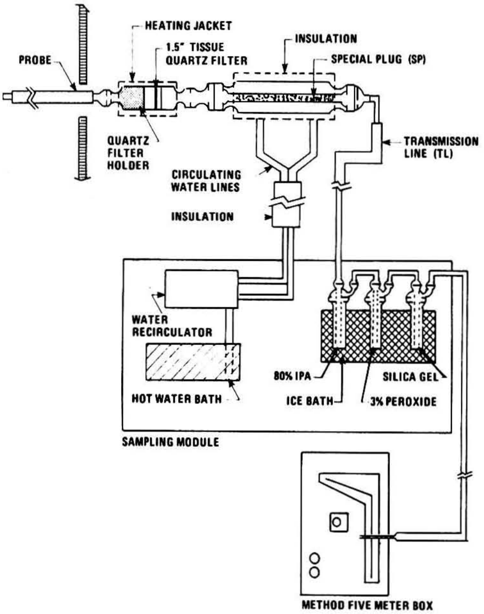

**Figure 1.** Schematic drawing of manual controlled condensation system. A sampling pump and dry gas meter are contained within the meter box. The sampling module contains a constant-temperature bath and circulation pump for the special plug. Temperature controls and readout are also contained in this unit for the probe, the filter, and the special plug.

The system was prepared for sampling by measuring 200 mL of 80% isopropyl alcohol (IPA) in water into the first impinger and 200 mL of 3% hydrogen peroxide ($H_2O_2$) into the second and third impingers; the last impinger was left dry. All components were allowed to reach operating temperature, and the impinger train was leak checked. During sampling, the probe and filter temperatures were maintained at 280 °C to minimize absorption of gaseous sulfuric acid by the particulate matter. The glass wool plug temperature was maintained at 60 °C in order to collect the condensed sulfuric acid but allow the gas-phase water and sulfur dioxide to pass through to the impingers without interference. Care was taken not to allow the plug temperature to rise above the water dew point, since this increase would result in artifact sulfite or sulfate formation due to partial oxidation of sulfur dioxide in the condensed water. The flow controller was adjusted to a flow rate of 10 L/min for a sampling time of 0.5 h. Following the conclusion of each run, the impingers were purged for 15 min at a 10 L/min flow rate.

Each sample fraction was collected and stored in a polypropylene sample bottle and quantitatively transferred to a volumetric flask for dilution to a known volume. The quartz filter was subjected to cold water extraction and diluted to a known volume. The samples were analyzed with a Dionex Model 10 ion chromatograph, employing a 3 × 500 mm anion separator column, combined with a 3 × 150 mm precolumn. Samples were analyzed on the 10 $\mu$mho/cm range by using 0.006 M sodium carbonate ($Na_2CO_3$) as the eluent at a flow rate of 103 mL/h. An external standard method of analysis was used.

**Ammonia Determinations.** Ammonia determinations were made with a standard midget impinger sampling train (*7*). This method as applied to this study utilized the midget impinger train to retain emissions in the flue gas by passing it through a series of impinger solutions of 0.1 N sulfuric acid.

The sampling train was prepared by measuring 15 mL of 0.1 N sulfuric acid into the first two impingers, and 15 mL of 3% hydrogen peroxide into the third impinger. A fourth impinger was kept dry. A piece of Pyrex glass wool was inserted into the inlet of the sampling probe to filter out particulate matter. The impinger solutions were allowed to equilibrate in an ice bath, and the system was leak checked. Each sampling run lasted for ~1 h at a flow rate of 1 L/min. The sample fractions were collected and stored in polypropylene sample bottles. Sulfuric acid (0.1 N) was added to the probe wash and probe plug fractions to retain the ammonia prior to analysis.

All samples were quantitatively transferred to 250-mL volumetric flasks and filtered when necessary. Analysis was accomplished by using the specific ion electrode technique. A standard calibration curve was prepared by making serial dilutions from a $10^{-1}$ M ammonium chloride solution to prepare $10^{-2}$, $10^{-3}$, $10^{-4}$, $10^{-5}$, and $10^{-6}$ M standards. Each sample was analyzed in 50-mL aliquots by adding 1.0 mL of 5 N sodium hydroxide (NaOH) and allowing the solution to stand until a constant reading was obtained on the electrode.

**Hydrochloric Acid Determinations.** The sampling procedures utilized in this method were identical with those used for ammonia except that the first two impingers contained 0.1 N sodium hydroxide (*8*). The samples were analyzed by using ion chromatography (IC) under the same operating parameters as used for the sulfur oxide analyses.

**Oxygen Determinations.** The oxygen level in the flue gas was measured by using a modified Taylor Servomex system

(9). The instrument was set up and operated according to instructions; pure nitrogen and ambient air were used to zero and span the system.

**Moisture Determinations.** The moisture level was determined by trapping moisture in a silica gel tube. The tube was connected to a 3-ft heated probe using a piece of Tygon tubing. Condensation appeared in the transfer line for the first four determinations. During the fifth run, the sample line temperature was increased to the point that condensation did not occur. Thus, it is felt that the 20% value for the last run is nearest the actual stack concentration.

## *Results and Discussion*

Presented in Tables I–IV are the results of in-stack sampling conducted April 25–27, 1979, at the Glens Falls cement kiln for sulfur oxides, ammonia, hydrochloric acid, oxygen, and moisture. The results presented in these tables reveal that significant levels of both ammonia and sulfur oxides exist (an average of 170 and 200 ppm, respectively), as well as unusually high moisture contents (near 20%). The anomolously high levels of ammonia collected on the Pyrex glass wool plug of the ammonia train during the first day of sampling are probably due to condensation of moisture on the plug. Conversely, chloride levels were low (an average of 5.6 ppm). Significant quantities of sulfite were detected by IC in the special plug and IPA impinger fractions (average values of 0.80 ppm and 19 ppm, respectively). Surprisingly, a large quantity of sulfate was detected in the IPA impinger (average value of 56 ppm); the IPA impinger usually traps only sulfuric acid or sulfur trioxide ($SO_3$). Since for the CCS the sulfuric acid should have already been removed and the sulfur trioxide has been shown to be virtually nonexistent (*10, 11*), the sulfate must be due to a reaction that oxidizes sulfur dioxide to sulfite and sulfate either within the IPA impinger or in the transfer line between the special plug holder and the IPA impinger.

**Table I. Glens Falls: Master Sampling Table**

| date | time | CCS run no. | $NH_3$ run no. | HCl run no. | $H_2O$ % | $O_2$ % |
|---|---|---|---|---|---|---|
| 4/25 | 6:00–7:00 | 1 | 1 | 1 | | |
| 4/25 | 7:30–8:30 | 2 | 2 | 2 | | |
| 4/25 | 9:00–10:00 | 3 | 3 | 3 | | |
| 4/25 | 10:30–12:00 | 4 | | 4 | 14 | |
| 4/25 | 12:00–12:40 | 5 | | | | |
| 4/25 | 12:30–2:30 | 6 | 4 | 5 | | |
| 4/26 | 5:30–7:00 | 7 | 5 | 6 | | |
| 4/26 | 7:00–8:30 | 8 | 6 | 7 | | |
| 4/26 | 8:30–9:30 | 9 | | | 16 | 12.2 |
| 4/26 | 9:30–10:30 | 10 | 7 | 8 | | |
| 4/26 | 11:00–12:00 | | 8 | 9 | | |
| 4/26 | 12:00–1:00 | | 9 | 10 | 14 | 12.1 |
| 4/27 | 7:30–9:00 | 11 | 10 | 11 | | |
| 4/27 | 9:00–10:00 | | 11 | | | |
| 4/27 | 9:30–10:30 | 12 | | 12 | 17 | |
| 4/27 | 10:00–11:00 | | 12 | | 20 | |

The determination of the mechanism and rate of oxidation of sulfur dioxide in solution has been the target of many researchers (*12–14*). A mechanism which fits available data and which is generally agreed upon by current researchers is given in eq 1a–d. When sulfur dioxide is introduced into water, the resulting hydrated sulfur dioxide can undergo dissociation into bisulfite and/or sulfite. However, the oxidation of sulfur dioxide depends on the concentration of sulfite ion in solution, thus making the reaction pH dependent. The relative concentrations of these species as a function of pH are depicted in Figure 2.

$$SO_2 + H_2O \rightleftarrows SO_2 \cdot H_2O \qquad (1a)$$

$$SO_2 \cdot H_2O \overset{K_1}{\rightleftarrows} H^+ + HSO_3^- \qquad K_1 = 1.74 \times 10^{-2} \qquad (1b)$$

$$HSO_3^- \overset{K_2}{\rightleftarrows} H^+ + SO_3^{2-} \qquad K_2 = 6.26 \times 10^{-2} \qquad (1c)$$

$$SO_3^{2-} + \tfrac{1}{2}O_2 \rightleftarrows SO_4^{2-} \qquad (1d)$$

Under normal sampling conditions the IPA impinger solution is slightly acidic, preventing sulfite formation and subsequent oxidation. The sulfur dioxide may therefore be removed by purging the impinger with air. However, the presence of ammonia in the flue gas would make the IPA impinger solution basic and allow much of the sulfur dioxide to be oxidized to sulfuric acid or stabilized as bisulfite. Analysis of the IPA and special plug fractions revealed the presence of considerable amounts of ammonia (Tables V and VI); laboratory investigations (Table VII) also verified the effect of ammonia on sulfur dioxide collection. The results of more rigorous investigations into this phenomenon and its effect on wet chemical methods for measurement of sulfur dioxide and into alternative analysis methods will appear at a later date.

The source of ammonia in the process was determined to be the feed stock for the cement-making process (*15*). Kjeldahl nitrogen determinations performed on rock samples of the

**Table II. Condensation System Results (ppm)**

| run no. | sample volume, scf | $(SO_4^{2-})$ probe wash [a] | filter [a] | plug | $SO_3^{2-}$ in plug | $10^{-2}(SO_4^{2-})$ in IPA | $10^{-2}(SO_3^{2-})$ in IPA | $10^{-2}(SO_2)$ in peroxide | $10^{-2}(SO_x)$ (total) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 8.617 | 0.67 | 0.00 | 3.0 | 6.1 | 0.046 | 0.18 | 0.47 | 0.79 |
| 2 | 8.525 | 0.60 | 0.02 | 3.2 | 0.00 | 0.35 | 0.095 | 0.72 | 1.2 |
| 3 | 10.475 | 0.48 | 0.01 | 1.7 | 0.05 | 0.40 | 0.10 | 1.3 | 1.8 |
| 4 | 10.099 | 0.50 | 0.00 | 5.2 | 3.1 | 0.69 | 0.16 | 1.3 | 2.2 |
| 5 | 10.151 | 0.47 | 0.01 | 4.3 | 0.07 | 0.63 | 0.26 | 1.5 | 2.4 |
| 6 | 9.143 | 0.56 | 0.03 | 7.7 | 0.00 | 0.48 | 0.18 | 1.8 | 2.5 |
| 7 | 8.209 | 0.93 | 0.02 | 6.1 | 0.00 | 1.0 | 0.17 | 0.92 | 2.2 |
| 8 | 10.466 | 0.50 | 0.00 | 4.0 | 0.00 | 0.76 | 0.25 | 1.1 | 2.2 |
| 9 | 9.637 | 0.88 | 0.01 | 6.2 | 0.04 | 0.77 | 0.25 | 1.2 | 2.3 |
| 10 | 9.443 | 0.75 | 0.00 | 4.7 | 0.00 | 0.65 | 0.17 | 0.98 | 1.9 |
| 11 | 10.391 | 0.47 | 0.00 | 5.4 | 0.06 | 0.30 | 0.18 | 1.8 | 2.3 |
| 12 | 10.239 | 0.66 | 0.01 | 3.0 | 0.18 | 0.66 | 0.28 | 1.7 | 2.7 |
| av | 9.633 | 0.62 | 0.01 | 4.5 | 0.80 | 0.56 | 0.19 | 1.2 | 2.0 |

[a] Reported as gas-phase $SO_4^{2-}$ in $ppm_{v/v}$.

feed stack yielded an average ammonia content of 2 lb/ton of kiln feed. An emission factor of 0.4 lb ammonia/ton of kiln feed may be calculated from the average stack ammonia concentration of 170 ppm. The discrepancy in the two emission factors may be explained by variations in ammonia content of the raw materials or by the retention of some portion of the ammonia in the clinkers. Also, some of the ammonia may react with nitrogen oxides during combustion.

The observed 10% stack opacity must also be addressed, as it would appear to conflict with the very light or in some cases nonexistent particulate loading on the CCS filter. Any sulfuric acid in this stack would presumably be present as acid mist (the stack temperature is only 106 °C), and the acid mist would react with free ammonia to form ammonium sulfate particulate. However, the filter temperature is approximately 275 °C; since ammonium sulfate decomposes into ammonia and sulfuric acid at 235 °C, any particulate ammonium sulfate collected on the filter would rapidly decompose and pass through the filter (*16*). In this way, ammonium sulfate particulates, which could be responsible for the 10% opacity, would not be collected as particulate.

**Plume Formation.** The results of the in-stack determinations indicate several potential mechanisms for the formation of the plume. The plausibility of these mechanisms may be evaluated theoretically.

One possibility is the presence of seed nuclei upon which water can condense while the plume cools from 106 °C in-stack to ambient temperature. This process would account for the

### Table III. Ammonia Results (ppm)

| run no. | sample volume, scf | probe plug | probe wash | $10^{-2}$(impingers) | $10^{-2}$(total) |
|---|---|---|---|---|---|
| 1 | 3.524 | 68 | 7.7 | 0.078 | 0.84 |
| 2 | 2.616 | 61 | 24 | 0.97 | 1.8 |
| 3 | 1.647 | 48 | 53 | 0.78 | 1.8 |
| 4 | 4.123 | 0.53 | 52 | 1.2 | 1.7 |
| 5 | 2.529 | 0.55 | 49 | 1.4 | 1.9 |
| 6 | 3.111 | 0.25 | 31 | 1.7 | 2.0 |
| 7 | 1.990 |  | 51 | 1.6 | 2.1 |
| 8 | 1.976 | 0.45 | 30 | 1.3 | 1.6 |
| 9 | 1.476 | 0.94 | 55 | 1.0 | 1.6 |
| 10 | 2.822 | 0.68 | 20 | 1.7 | 1.9 |
| 11 | 1.954 | 0.66 | 17 | 1.4 | 1.6 |
| 12 | 1.951 | 1.0 | 26 | 1.5 | 1.8 |
| av | 2.477 | 17 | 35 | 1.2 | 1.7 |

### Table IV. Chloride Results (ppm)

| run no. | sample volume, scf | probe plug | probe wash | impingers | total |
|---|---|---|---|---|---|
| 1 | 2.722 | 0.42 | 0.67 | 5.6 | 6.7 |
| 2 | 2.158 | 0.95 | 0.75 | 1.3 | 3.0 |
| 3 | 2.098 | 0.52 | 0.55 | 5.5 | 6.6 |
| 4 | 2.684 | 0.61 | 0.62 | 3.9 | 5.1 |
| 5 | 4.068 | 0.39 | 0.94 | 2.1 | 3.4 |
| 6 | 3.166 | 0.35 | 0.77 | 3.9 | 5.0 |
| 7 | 3.274 | 0.59 | 0.55 | 3.3 | 4.4 |
| 8 | 3.136 | 0.59 | 0.39 | 3.5 | 4.5 |
| 9 | 2.019 | 0.42 | 0.11 | 5.2 | 5.7 |
| 10 | 1.282 | 1.4 | 0.33 | 9.9 | 11 |
| 11 | 2.699 | 0.20 | 0.39 | 4.3 | 4.9 |
| 12 | 2.215 | 0.62 | 0.51 | 5.0 | 6.1 |
| av | 2.627 | 0.61 | 0.55 | 4.5 | 5.7 |

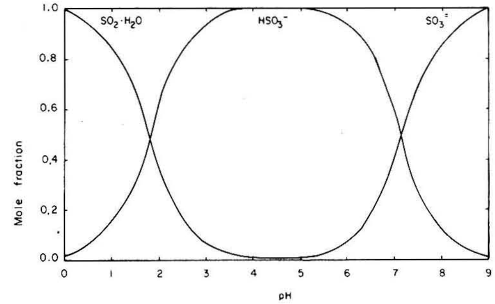

**Figure 2.** Effect of pH on the relative concentrations of the $SO_2$ species in solution (*11*). The figure presents the calculated mole fraction of sulfur(IV) species as a function of pH at 25 °C in aqueous solution. Sulfite is seen to predominate in alkaline solution while bisulfite predominates in the pH range 3–7.

### Table V. CCS Train IPA Impinger Results (mmol)

| run no. | $NH_3$ | $SO_4^{2-}$ | $SO_3^{2-}$ |
|---|---|---|---|
| 1 | 0.25 | 0.047 | 0.19 |
| 2 | 0.62 | 0.35 | 0.096 |
| 3 | 0.99 | 0.49 | 0.13 |
| 4 | 1.8 | 0.82 | 0.19 |
| 5 | 1.8 | 0.76 | 0.31 |
| 6 | 1.1 | 0.52 | .020 |
| 7 | 2.0 | 0.99 | 0.17 |
| 8 | 2.1 | 0.94 | 0.31 |
| 9 | 1.8 | 0.87 | 0.28 |
| 10 | 1.4 | 0.72 | 0.19 |
| 11 | 0.80 | 0.37 | 0.22 |
| 12 | 1.6 | 0.79 | 0.34 |
| av | 1.4 | 0.64 | 0.22 |

### Table VI. CCS Train Special Plug Results (mmol)

| run no. | $NH_3$ | $SO_4^{2-}$ | $SO_3^{2-}$ |
|---|---|---|---|
| 1 | 0.32 | 0.031 | 0.062 |
| 2 | 0.082 | 0.032 | 0.00 |
| 3 | 0.059 | 0.022 | 0.001 |
| 4 | 0.28 | 0.062 | 0.037 |
| 5 | 0.13 | 0.052 | 0.001 |
| 6 | 0.18 | 0.083 | 0.00 |
| 7 | 0.14 | 0.059 | 0.00 |
| 8 | 0.12 | 0.049 | 0.00 |
| 9 | 0.17 | 0.070 | 0.001 |
| 10 | 0.12 | 0.053 | 0.00 |
| 11 | 0.16 | 0.068 | 0.001 |
| 12 | 0.888 | 0.036 | 0.002 |
| av | 0.15 | 0.051 | 0.009 |

### Table VII. Ammonia Interference Laboratory Results (ppm)

| introduced (calcd) |  | collected |  |  |  |
|---|---|---|---|---|---|
| $SO_2$ | $NH_3$ | $SO_4^{2-}$ in IPA | $10^{-2}(SO_3^{2-})$ in IPA | $10^{-2}(SO_2)$ in peroxide | $10^{-2}$(total) |
| 590 | 0 | 0.00 | 0.43 | 0.67 | 0.67 |
| 590 | 0 | 0.00 | 0.00 |  |  |
| 470 | 210 | 9.7 | 2.1 | 2.8 | 5.0 |
| 470 | 210 | 6.1 | 2.7 | 2.6 | 5.4 |
| 470 | 210 | 16 | 2.2 | 2.7 | 5.1 |
| 470 | 210 | 4.7 | 2.2 |  |  |

detachment of the plume since the plume would not form until the effluent temperature has dropped sufficiently for condensation to occur. Assuming the 10% in-stack opacity to be solely due to ammonium sulfate, one can calculate the mass concentration of particulate matter from Bouger's law. If one takes a value of $0.08 \times 10^{-4}$ m$^2$ mg$^{-1}$ for the scattering coefficient, $k_s$, and a stack pathlength of 2 m, a value of 6885 $\mu$g m$^{-3}$ is obtained for the in-stack concentration (*17*).

Ammonium sulfate is deliquescent, and its scattering coefficient increases dramatically with increasing relative humidity. This effect would increase opacity in the plume. The plume cross section, however, was observed to increase by a factor of 50 by the time the plume formed, resulting in a calculated value of less than 10% opacity for the plume rather than the previously reported value of 85%. Admittedly, the scattering coefficient used in this calculation is dependent upon the initial size distribution of the particulate. However, the bluish-white nature of the plume is characteristic of a size distribution with a median diameter of 0.5–0.8 $\mu$m. These particles are not in a size range where the size dependence of the scattering coefficient is sensitive enough to increase the results of the calculation to an opacity of 85%.

The condensation on particulate originating from the stack cannot, therefore, be solely responsible for the formation of the plume. Thus, we conclude that the species responsible for the plume are instead produced in the water droplets that form as the plume cools below its dew point. High-opacity steam plumes are not uncommon, but the persistence of the plume downwind requires the formation of a low-vapor-pressure species for a stable aerosol.

The results of the in-stack investigations indicate a liquid-phase reaction of sulfur dioxide to be the most probable cause. Indeed, the formation of sulfuric acid or ammonium salts of sulfur oxides are likely candidates since either would account for a bluish-white persistent plume which only forms in the presence of water droplets. Solution oxidation of sulfur dioxide thus accounts for dissipation of the plume as the sun rises, since the increased ambient temperature would delay water condensation until the stack effluent had sufficiently dispersed to slow the reaction rate and simply reduce the opacity through dilution. The question to be addressed is whether the oxidation is uncatalyzed or catalyzed by trace metals or involves the pseudocatalytic effects of ammonia.

The water-soluble particulate catch from the CCS system was subjected to X-ray fluorescence analysis for trace metals. The detection limit of the technique was such that sample concentrations corresponding to plume concentrations of $\leq 5 \times 10^{-7}$ M could be detected for all potentially catalytic species such as $Mn^{2+}$ and $Fe^{2+}$ (*12–14, 18, 19*). Since recent studies indicate that concentrations in excess of $10^{-6}$ M are necessary for transition metal catalysis of the reaction, we conclude that trace metal catalysis is not a factor. It has been proposed that ozone and hydrogen peroxide may contribute to atmospheric oxidation of sulfur dioxide (*14*). However, these species have not been reported to be present in stack gas effluents at concentrations anywhere near that which is necessary for sulfur dioxide oxidation at the rate necessary to explain the observed plume formation.

The role of ammonia in aerosol formation was evaluated through oxidation rate calculations. The model used in this calculation is essentially that proposed for oxidation of sulfur dioxide in atmospheric cloud and fog droplets (*20*). This model assumes that sulfur dioxide, ammonia, and carbon dioxide are in equilibrium with the water droplets. The water droplets thus contain species at concentrations which may be determined by Henry's law. The rate of sulfate formation is first order in sulfite concentration which in turn is controlled by the pH of the water droplet for a given sulfur dioxide concentration. In the ambient air, where ammonia concentrations are low, the pH is affected by ammonia, carbon dioxide, and of course the sulfuric acid formed in the reaction. In the plume from this cement plant, however, the high ammonia level can be shown to be the factor responsible for rapid oxidation of sulfur dioxide. By manipulating the various expressions for the solubility of the gases involved and their ionization in solution, it may be shown that the rate of oxidation is inversely proportional to the square of the hydrogen ion concentration. The ratio of the rates for two ammonia concentrations at a constant sulfur dioxide concentration is given by

$$R_{1,2} = \frac{d(SO_4{}^{2-})_1/dt}{d(SO_4{}^{2-})_2/dt} = \frac{(H^+)_2{}^2}{(H^+)_1{}^2}$$

where the hydrogen ion concentration, $(H^+)$, is given by

$$\alpha(H^+)^3 - 2(SO_4{}^{2-})(H^+)^2 - \beta(H^+) - \gamma = 0$$

where $\alpha$, $\beta$, and $\gamma$ are constants related to the solubility and ionization of the species involved. This expression assumes the overall reaction between sulfur dioxide and oxygen to be first order because of the large excess concentration of oxygen. If one uses the data from Tables II and III, the rate of oxidation of sulfur dioxide at the point in the plume where the effluent sulfur disoxide and ammonia are diluted by a factor of 50 is conservatively 500 times as great as if ammonia were not present. Because of the solubility of ammonia in water and its high reactivity with sulfuric acid, it is certainly reasonable to assert that ammonia is reacting with a portion of the oxidized sulfur dioxide to form ammonium sulfate, ammonium bisulfate, or possibly ammonium sulfite and ammonium bisulfite. A mixture of all four of these species along with sulfuric acid is most likely; however, it would be difficult to estimate their relative abundances.

From a stack moisture content of 20%, we estimate the condensed water concentration in the region of initial plume formation to be $3.9 \times 10^2$ g m$^{-3}$. Taking a value of 0.1 min$^{-1}$ for the rate constant of formation of sulfate from sulfite (*21*), we obtain a value of 17 ppm/min for the oxidation rate of sulfur dioxide; under the same conditions, but with ammonia absent, only 0.03 ppm/min is obtained. Thus, under these plume conditions, all of the sulfur dioxide can be oxidized to sulfate in ~15 s. For an equimolar mixture of ammonium sulfate and ammonium bisulfate, the calculated opacity value is 82%, which certainly compares favorably with the observed value of 85%. Because of the slow oxidation rate in the absence of ammonia, a maximum opacity of only 5–15% is predicted for typical values of wind speed of 5 mi/h.

Results of balloon-borne particulate sampling of the plume, performed concomitantly with our source sampling, appear to confirm many of the ideas proposed in this manuscript (*22*). The collected particles were subjected to electron microscopic and X-ray analysis; the results indicated that for these techniques sulfur was the main identifiable material. Assuming that the particles were 100% sulfuric acid, it was calculated that only 4% conversion of sulfur dioxide was necessary to account for the observed aerosol concentration at the point sampled in the plume. This result is consistent with our calculated sulfur dioxide oxidation rates, since this conversion efficiency is easily accomplished in the presence of ammonia but cannot be reached in its absence.

## *Conclusions*

The results of the source testing indicate the primary components of the stack effluent to be ammonium sulfate (4.5 ppm), sulfur dioxide (200 ppm), ammonia (170 ppm), and water (20%), with the numbers in parentheses being the average observed concentrations. Although the possibility that these species exist in other forms cannot be strictly dismissed, an effluent composition of this nature seems most consistent with experiment and theory.

In summary, it appears that the combination of ammonia, sulfur dioxide, high moisture content, low atmospheric temperature, and low stack temperature is necessary for formation of the detached plume. Ammonium sulfate in the stack is responsible for the 10% in-stack opacity, while a secondary reaction involving sulfur dioxide and ammonia in condensed water droplets (forming ammonium sulfoxide salts and sulfuric acid) is responsible for the high-opacity detached plume. This mechanism is consistent with the dissipation of the plume as the ambient temperature increases in that it allows the plume to be diluted before water droplets can condense.

A number of assumptions are clearly involved in this interpretation and warrant additional investigation. However, in light of our results and calculations, we feel secure in asserting that significant oxidation of sulfur dioxide takes place in this plume. Consequently, this reaction not only presents a problem with visibility but also represents a previously undetected source of primary sulfate emissions that may contribute significantly to the sulfate burden of the atmosphere. If the sulfate emission factor obtained for the Glens Falls cement kiln is applied to Portland cement plants, the additional contribution to the total sulfate burden of the Northeast alone would be over 100 000 tons per year.

### *Acknowledgment*

We take pleasure in acknowledging the efforts of our colleague Mr. Mike Pleasant in conducting portions of the source sampling. With equal pleasure we acknowledge the chemical analyses peformed by Mr. Jeff Lorrain, along with his participation in discussions involving data interpretation.

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# Reaction of Epoxides with 4-Nitrothiophenol. Its Possible Application for Trapping and Characterization of Epoxides

**Satish C. Agarwal,* Benjamin L. Van Duuren, Jerome J. Solomon, and Stanley A. Kline**

Laboratory of Organic Chemistry and Carcinogenesis, Institute of Environmental Medicine, New York University Medical Center, New York, New York 10016

■ Reaction of epoxides with the nucleophile 4-nitrothiophenol has been examined. The mono- and diepoxides of aliphatic and aromatic hydrocarbons undergo facile nucleophilic opening by 4-nitrothiophenol to yield the expected 1,2 adducts cleanly and in good yields. The experimental conditions are mild and provide a suitable method for trapping the atmospheric epoxides which may be significant in air pollution carcinogenesis. In the chemical ionization mass spectrum, these adducts have an intense protonated molecular ion which will be extremely useful in their detection and characterization by the technique of single ion monitoring.

The widespread presence of aromatic and olefinic hydrocarbons as environmental pollutants and the carcinogenic effects of some of them in animals have stimulated much interest. Numerous studies to characterize them in ambient atmosphere have been carried out. The hydrocarbons themselves are biologically relatively inactive and require metabolic or photochemical oxidation to more polar oxidized derivatives such as epoxides, peroxides, hydroperoxides, or their subsequent degradation products in order to exert their toxic, mutagenic, and carcinogenic effects (*1–6*). Presently there exists a large body of evidence that implicates arene epoxides as the metabolic intermediates responsible for the carcinogenicity and mutagenicity of polycyclic aromatic hydrocarbons (*7*). This metabolism is mediated by the cytochrome P-450 linked monooxygenase system. Some of the products of benzo[*a*]pyrene (BaP) and other polycyclic aromatic hydrocarbons formed in photochemical reactions are analogous to their metabolites in mammalian cells and may account for the presence of directly active mutagens in urban particulates (*4*). Cobalt-60 $\gamma$ irradiation of BaP in air oxidized the K-region, bay region, and the 6-position of benzo[*a*]pyrene (*5*). BaP dihydro diols, BaP phenols, and other oxidation compounds have been tentatively identified among the mutagenic products formed when a sample of BaP was exposed to ambient smog (*8*). Even though BaP epoxides could not be identified, the presence of dihydrodiols suggests epoxides may have been formed as initial, labile products (*5, 8*). Epoxides and other oxidation products derived from aliphatic hydrocarbons also have mutagenic and carcinogenic effects (*9, 10*). Large amounts of unsaturated aliphatic hydrocarbons are expected to be present in polluted atmosphere. Aliphatic fractions free of aromatic hydrocarbons have been shown to produce skin tumors in mice (*10*). It was suggested that the activity of this fraction may be due to the presence of epoxides.

Despite the obvious health hazards, very little work has been done on the detection and characterization of atmospheric epoxides and other secondary aerosols described above. Styrene oxide has been tentatively identified in air samples (*12*). However, further study is needed for more certain confirmation.

We have recently modified and developed a highly sensitive method for the determination of alkylating agents (epoxides) on a microscale (*13*). This method involved reaction of the substrate with an excess of the potent nucleophile 4-(*p*-nitrobenzyl)pyridine. The absorbance of the product can be measured and correlated with the concentration of epoxides in dilute solutions.

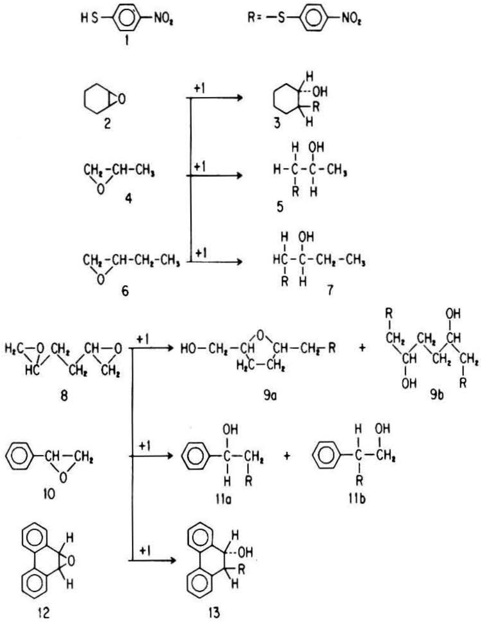
A limiting and serious factor in the characterization of atmospheric epoxides is their relative lack of stability. Most of these compounds are highly reactive and may decompose in the atmosphere too rapidly to be detected (*3*). In view of this, an investigation to detect and characterize photooxidation products of the hydrocarbons, in particular their epoxides, has been undertaken. Exploratory studies have been done to characterize the highly unstable electrophilic epoxides by trapping them with a suitable nucleophile. The experimental conditions for the formation of adducts from known epoxides and the sulfhydryl nucleophile 4-nitrothiophenol have been developed to determine the feasibility of the procedure.

The reaction of epoxides with sulfur nucleophiles has been investigated earlier. Jeffrey et al. (*14*) examined the reaction of thiophenol and thioethanol with benzene oxide–oxepin and naphthalene 1,2-oxide. Posner and Rogers (*15*) reported the formation of *trans*-2-thiophenoxycyclohexanol when the thiophenol doped alumina was allowed to react with 1,2-epoxycyclohexane. Kline and Van Duuren (*16*) have studied the reaction of epoxy-1,1,2-trichloroethane with a number of sulfur nucleophiles including 4-nitrothiophenol.

### *Results and Discussion*

We have found that a solution of 4-nitrothiophenol in 1% aqueous NaOH reacted with a methanolic solution of the epoxide under mild conditions (4 °C). The pale yellow colored adducts could be easily purified by silica gel preparative thin layer or column chromatography. Both mono- and diepoxides of aliphatic and aromatic hydrocarbons have been chosen for this study. Some of them are carcinogenic, and these epoxides may be the products of photooxidation.

1,2-Epoxycyclohexane, **2,** underwent facile nucleophilic opening by 4-nitrothiophenol, **1,** to yield 2-(*p*-nitrothiophenoxy)cyclohexanol, **3.** The structural assignment was supported by microanalysis and by the integrated NMR spectrum. The unsymmetrical 1,2-epoxypropane, **4,** opened regioselectively by 4-nitrothiophenol attack on the less substituted epoxide carbon atom as confirmed by the following data: The NMR spectrum of **5** in deuterated dimethyl sulfoxide showed a one-proton doublet at $\delta$ 5.1 exchangeable with $D_2O$. This hydroxyl proton doublet was consistent with structure **5** rather than its primary alcohol isomer. Similarly, the NMR spectrum of the adduct **7** in $Me_2SO$-$d_6$ confirmed that 4-nitrothiophenol reacted preferentially at the less substituted epoxide carbon atom of 1,2-epoxybutane, **6,** to form the secondary alcohol isomer.



In the case of 1,2:5,6-diepoxyhexane, **8,** a mixture consisting of monoadduct **9a** and a diadduct **9b** was obtained resulting from nucleophilic attack on one or both epoxide moieties. The diadduct separated from the reaction mixture as a yellow precipitate, while the monoadduct was isolated from the filtrate.

The NMR spectrum of the diadduct **9b** in $Me_2SO$-$d_6$ had a doublet (2 H) at $\delta$ 5.2 which disappeared when $D_2O$ was added, thus confirming the presence of secondary alcoholic groups. In addition, the NMR of **9b** showed the presence of a pair of doublets at $\delta$ 7.5 and $\delta$ 8.1 with four protons each. These data are consistent only with the assigned symmetrical structure **9b.** The compound **9a,** however, was shown to be a monoadduct by the mass spectral parent ion, *m*/*e* 269, and elemental analysis. Its NMR spectrum in $Me_2SO$-$d_6$ showed a triplet, exchangeable with $D_2O$, indicating the presence of a primary alcoholic group. Since **9a** was stable to acid, and its yield remained unaffected when the reaction time was increased several times, the presence of an intact oxirane ring was ruled out. These data are most consistent with the five-membered ether structure **9a.**

The reaction of styrene oxide, **10,** and 4-nitrothiophenol went smoothly, yielding only two isomeric adducts. The NMR of the major adduct in $Me_2SO$-$d_6$ exhibited the presence of a one-proton triplet at $\delta$ 4.8, exchangeable with $D_2O$. This confirmed its structure as **11b** and also indicates that the phenyl-substituted carbon atom was preferentially attacked by the nucleophile. Similarly, a one-proton doublet at $\delta$ 5.8 for a hydroxyl group in the NMR of the minor adduct verified its structure as **11a**. When the above reaction was carried out in acetone containing 1 N sodium carbonate at room temperature, the two adducts were formed in almost equal proportion as shown by TLC.

The K-region 9,10-epoxyphenanthrene, **12**, was quite similar in its reactivity to the aliphatic epoxides mentioned above. (K-region double bonds in polycyclic aromatic hydrocarbons are regions of high electron density, e.g., the 9,10-bond of phenanthrene.) The probable trans stereochemistry of the adduct **13** could not be definitely established by the NMR coupling constant ($J_{9,10} \sim 3$ Hz, $Me_2SO$-$d_6$), which is unusually small for a trans isomer. However, this low value of $J_{9,10}$ seems to be consistent with a predominant quasi-diequatorial relationship between these protons (*17, 18*). This is also supported by the acetylation of adduct **13** which further decreased the coupling constant to ~2 Hz and is in accord with the previous observations for analogous compounds (*17, 18*). A similar coupling constant was noted for the adduct of 2-mercaptoethanol, thiolacetic acid, and *tert*-butylmercaptan with 9,10-epoxyphenanthrene and their acetyl derivatives. These compounds were also assigned trans stereochemistry (*17, 18*).

A typical comparison of the EI and CI mass spectra of an epoxide adduct is shown in Figure 1. The molecular ion of the styrene oxide–4-nitrothiophenol adduct **11b** is present in the EI spectra at *m/e* 275 (11%) along with a peak due to the loss of $CH_2OH$ at *m/e* 244 (22%). Under EI conditions most of the ionization is in the low-mass region. Under isobutane CI conditions, the spectrum is dominated by ions in the high-mass region. The base peak is the protonated molecular ion, $(M + H)^+$, at *m/e* 276 and a minor peak due to loss of water, $(M + H - H_2O)^+$, at *m/e* 258 (16%). A small peak at *m/e* 316 (2%) is due to the addition of a reactant ion to the neutral adduct, $M{\cdot}C_3H_5^+$. CI is ideally suited for the detection of these adducts using the technique of selected ion monitoring. The success of this technique depends upon monitoring an abundant ion in the spectrum which is characteristic of the compound.

These results are significant as the experimental conditions are mild for the nucleophilic trapping of epoxides resulting in high yields of stable adducts. This method would be quite suitable for trapping the atmospheric epoxides. For example, a known volume of air might be bubbled directly through a solution of excess of 4-nitrothiophenol in methanol containing 1% aqueous sodium hydroxide and maintained at low temperatures in order to minimize evaporation and decomposition. The reaction mixture might then be worked up and adducts separated from other contaminants by the combined use of column chromatography, TLC, high-performance LC, or GC. Such adducts may then be characterized by their chromatographic retention times as well as CI mass spectrometry monitoring of protonated molecular and $M + H - H_2O$ ions and compared with synthetically obtained adducts of suspected epoxides. This should prove to be a highly sensitive and useful method for the characterization of labile epoxides in the atmosphere or in the industrial environment. For example a minor amount of styrene is converted to styrene oxide in the presence of peroxides when unsaturated polyester resins are processed (*19, 20*). Thus workers in the reinforced plastics industry are exposed directly to both styrene and styrene oxide. This method would be quite useful in the identification and quantitation of styrene oxide in the workroom atmosphere. Under suitable experimental conditions the reagent may also be useful in metabolic studies to trap epoxides, for example, in *in vitro* experiments with animal tissues or in cell culture (*6*).

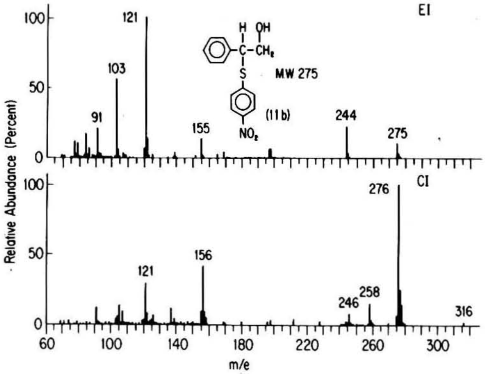


**Figure 1.** Electron impact (top) and isobutane–chemical ionization (bottom) mass spectra of styrene oxide and 4-nitrothiophenol adduct **11b**.

## *Experimental Section*

**Apparatus.** Melting points were taken on a Thomas-Hoover capillary apparatus and are uncorrected. Infrared spectra were determined as a thin film or as KBr pellets by using a Perkin-Elmer Model 137 spectrophotometer. Ultraviolet and visible spectra were obtained with a Beckman Model 25 spectrophotometer. Proton magnetic resonance spectra were recorded on the Varian Associates Model T-60A with $Me_4Si$ as an internal standard and $CDCl_3$ and $Me_2SO$-$d_6$ as solvents. Resonances are characterized as a singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), or broad band (b). Electron impact (EI) and chemical ionization (CI) mass spectra were obtained on a Dupont 21-492 high-resolution mass spectrometer. The source temperature was held at 240 °C, and samples were introduced via the direct probe. CI spectra were acquired by using isobutane (Matheson, instrument grade) as the reagent gas at ~0.5 torr source pressure. The ionizing voltage was 70 eV in all experiments. Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI. Analytical and preparative TLC were carried out on precoated fluorescent silica gel plates in $CHCl_3$ containing a few drops of $CH_3OH$; spots were visualized with a short-wavelength UV lamp. Silica gel (70–230 mesh ASTM) was used for column chromatography. Appropriate precautions were taken to prevent degradation of epoxides.

**Chemicals.** 4-Nitrothiophenol (80%+) from Aldrich Chemical Co., Milwaukee, WI, was purified by silica gel column chromatography and recrystallization from $CH_2Cl_2$–hexane. The epoxides 9,10-epoxy-9,10-dihydrophenanthrene (9,10-epoxyphenanthrene) (*21*), 1,2-epoxycyclohexane, 1,2:5,6-diepoxyhexane, and 1,2-epoxybutane were synthesized according to the literature procedures (*22*). Styrene oxide of Fluka AG, Buchs SG, Switzerland, was obtained from Tridom Chemical, Inc., Hauppauge, NY 11787.

**Reaction of 1 with 1,2-Epoxycyclohexane, 2.** To a stirred solution of 4-nitrothiophenol (0.12 g; 0.75 mmol) in 4.0 mL of 1% aqueous NaOH was added dropwise a solution of 1,2-epoxycyclohexane (0.049 g; 0.5 mmol) in 4.0 mL of methanol, and the solution was kept for 4 h in the cold room with stirring. Cream-colored microscopic needles (0.102 g) separated and were collected by filtration. The residue was washed with $CH_3OH$–$H_2O$ (3:7). More adduct could be obtained by extracting the filtrate with $CH_2Cl_2$. The adduct **3** was purified by silica gel column chromatography. The solvent mixture of hexanes–$CH_2Cl_2$ (4:1) eluted 4,4′-dinitrodiphenyl disulfide while $CH_2Cl_2$ eluted a yellowish band of the adduct. The $CH_2Cl_2$ eluate on evaporation and crystallization from $CH_2Cl_2$–hexane furnished cream-colored needles: mp 89–91 °C; UV max (EtOH) 250 (sh), 346 nm ($\epsilon$ 4600, 12 000); IR (KBr) 3550, 2940, 1580, 1345, 1065, 856, 740 $cm^{-1}$; NMR

($CDCl_3$) $\delta$ 1.3, 1.5, 1.65, 1.9 (bm, 8 H, $CH_2$), 2.4 (s, 1 H, OH, exchangeable with $D_2O$), 3.4 (b, 2 H, CHS, CHO), 7.6, 8.2 (dd, 4 H, Ph H); CI mass spectrum, *m/e* (relative intensity) 254 (100), 236 (21), 206 (9), 156 (17), 81 (39); TLC, $R_f = 0.26$. Anal. Calcd for $C_{12}H_{15}O_3NS$: C, 56.85; H, 5.92. Found: C, 56.76; H, 5.98.

**Reaction of 1 with 1,2-Epoxypropane, 4.** 4-Nitrothiophenol (0.93 g; 6 mmol) in aqueous NaOH (1%, 3.2 mL) and 1,2-epoxypropane (0.23 g; 4 mmol) in 3.2 mL of methanol were stirred in the cold room for 4 h. Water (15 mL) was added, and the solution extracted with excess of $CH_2Cl_2$ (75 mL; 25 mL × 3). The organic layer was first washed with 15 mL of 2% NaOH solution to remove unreacted 4-nitrothiophenol and then with water. The $CH_2Cl_2$ extract was flash evaporated under reduced pressure to yield a pale yellow viscous liquid (0.75 g) which was chromatographed on silica gel. Hexanes–$CH_2Cl_2$ (4:1) eluted the disulfide, and the adduct **5** (0.75 g) was eluted with $CH_2Cl_2$ or $CH_2Cl_2$ containing a few drops of MeOH. At room temperature, the adduct remained as a pale yellow viscous liquid, whereas it solidified in the freezer. It had the following spectral characteristics: UV max (EtOH) 228, 340 nm ($\epsilon$ 7880, 17 200); IR (film) 3350, 1590 (sh), 1585, 1505, 1327, 1085, 853, 738 $cm^{-1}$; NMR ($Me_2SO$-$d_6$) $\delta$ 1.2 (d, 3 H, $CH_3$), 3.13 (d, 2 H, $CH_2$; $J = 6$ Hz), 3.9 (m, 1H, CH), 5.1 (d, 1 H, OH, exchangeable with $D_2O$), 7.5, 8.1 (dd, 4 H, Ph H); TLC, $R_f = 0.34$, Anal. Calcd for $C_9H_{11}O_3NS$: C, 50.64; H, 5.16. Found: C, 50.76; H, 5.27.

**Reaction of 1 with 1,2-Epoxybutane, 6.** 4-Nitrothiophenol (0.93 g; 6 mmol) in NaOH solution (1%, 3.2 mL) was allowed to react with 1,2-epoxybutane (0.29 g; 4 mmol) in 3.2 mL of methanol for 4 h in the cold room and worked up as mentioned in the previous experiment. The adduct **7** was obtained as a pale yellow viscous liquid (0.81 g) which crystallized in the freezer as clusters of pale yellow needles: UV max (EtOH) 226, 342 nm ($\epsilon$ 8060, 16 300); IR (film) 3360, 1580, 1335, 1091, 885, 750 $cm^{-1}$; NMR ($Me_2SO$-$d_6$) $\delta$ 1.05 (t, 3 H, $CH_3$), 1.5 (q, 2 H, $CH_2$), 3.3 (m, 2 H, $CH_2S$; $J = 6$ Hz), 3.7 (tt, 1 H, CHO; $J = 6$ Hz), 5.1 (d, 1 H, OH, exchangeable with $D_2O$), 7.5, 8.1 (d, d, 4 H, PhH); CI mass spectrum, *m/e* (relative intensity) 228 (100), 210 (28), 198 (10), 180 (7); TLC, $R_f = 0.49$. Anal. Calcd for $C_{10}H_{13}O_3NS$: C, 52.82; H, 5.72. Found: C, 52.76; H, 5.58.

**Reaction of 1 with 1,2:5,6-Diepoxyhexane, 8.** 4-Nitrothiophenol (0.28 g; 1.8 mmol) in aqueous NaOH (1%; 3.0 mL) and 1,2:5,6-diepoxyhexane (0.068 g; 0.6 mmol) in 3.0 mL of methanol were stirred in the cold room for 4 h. A pale yellow precipitate separated out and was filtered. The filtrate (A) and the residue (B) were worked up separately.

The filtrate (A) was extracted with $CH_2Cl_2$ several times, and the organic layer washed with water. On flash evaporation of $CH_2Cl_2$ extract, a pale yellow oily residue **9a** (0.035 g) was left and was purified by preparative thick-layer chromatography on silica gel. It was obtained as a light pale yellow viscous oil: UV max (EtOH) 225, 340 nm; ($\epsilon$ 7080, 14 700); IR (film) 3425, 2925, 1580, 1520, 1340, 1090, 856, 743 $cm^{-1}$; NMR ($Me_2SO$-$d_6$) $\delta$ 1.82 (bt, 4 H, $CH_2CH_2$), 3.3 (m, 4 H, $CH_2S$, $CH_2O$), 4.02 (bm, 2 H, CHOCH), 4.68 (t, 1 H, OH, exchangeable with $D_2O$), 7.5, 8.1 (d, d, 4 H, Ph H); NMR ($CDCl_3$) $\delta$ 1.95 (btt, 4 H, $CH_2CH_2$), 2.4 (s, 1 H, OH, exchangeable with $D_2O$), 3.2 (m, 2 H, $CH_2S$ or $CH_2O$), 3.6 (m, 2 H, $CH_2O$ or $CH_2S$), 4.05 (bm, 2 H, CHOCH), 7.4, 8.1 (d, d, 4 H, Ph H). CI mass spectrum, *m/e* (relative intensity) 270 (100), 240 (62), 156 (67), 126 (33), 115 (38); TLC, $R_f = 0.36$. Anal. Calcd for $C_{12}H_{15}O_4NS$: C, 53.53; H, 5.57. Found: C, 53.47; H, 5.66.

TLC showed that the compound **9a** remained unchanged when its solution was treated with a few drops of concentrated HCl at room temperature. There was no change in the yields of **9a** and **9b** when the above reaction was carried out for 60 h.

A solution of the yellow residue (B) in acetone–$CH_2Cl_2$ was chromatographed on a silica gel column made up in hexane. The column was first eluted with hexane–$CH_2Cl_2$ (4:1) to remove the disulfide. $CH_2Cl_2$ eluted the adduct **9b** (0.11 g), which crystallized from acetone–$CH_2Cl_2$–hexane mixture as shiny yellow plates: mp 152–154 °C (starts sintering at 151 °C); UV max (EtOH) 227, 342 nm ($\epsilon$ 14 700, 31 500); IR (KBr) 3520, 1580, 1500, 1330, 1046, 854, 833, 740 $cm^{-1}$; NMR ($Me_2SO$-$d_6$) $\delta$ 1.7 (bs, 4 H, $CH_2CH_2$), 3.2 (d, 4 H, 2 $CH_2S$; $J = 6$ Hz), 3.75 (b, 2 H, 2 CH), 5.2 (d, 2 H, 2 OH, exchangeable with $D_2O$; $J = 6$ Hz), 7.5, 8.1 (d, d, 8 H, Ph H); CI mass spectrum, *m/e* (relative intensity) 425 (7), 407 (100), 377 (18), 156 (63); TLC, $R_f = 0.14$. Anal. Calcd for $C_{18}H_{20}O_6N_2S$: C, 50.90; H, 4.71. Found: C, 50.94; H, 4.72.

**Reaction of 1 with Styrene Oxide, 10.** 4-Nitrothiophenol (0.23 g; 1.5 mmol) in aqueous NaOH (1%; 4.0 mL) was allowed to react with styrene oxide (0.12 g; 1 mmol) dissolved in 4.0 mL of methanol in the cold room for 4 h, and the reaction mixture was worked up as mentioned earlier. A pale yellow viscous liquid (0.28 g) so obtained was subjected to silica gel column chromatography. Hexane–$CH_2Cl_2$ (4:1) eluted the disulfide; hexane–$CH_2Cl_2$ (3:2) eluted the minor adduct **11a** with higher $R_f$ value; hexane–$CH_2Cl_2$ (1:4) eluted first the mixture of isomeric adducts and finally the lower $R_f$ major adduct **11b**. Both of the adducts were further purified by preparative thin-layer chromatography.

The minor adduct isomer **11a** was obtained as a light pale yellow viscous oil which solidified in the freezer: UV max (EtOH) 253 (sh), 342 nm ($\epsilon$ 4870, 15 800); IR (film) 3400, 1610, 1585, 1340, 1045, 1027, 855, 740, 690 $cm^{-1}$; NMR ($Me_2SO$-$d_6$) $\delta$ 3.4 (d, 2 H, $CH_2S$; $J = 6$ Hz), 4.85 (q, 1 H, CHO; $J = 6$ Hz), 5.8 (d, 1 H, OH, exchangeable with $D_2O$), 7.35, 7.5, 8.15 (m, d, d, 9 H, Ph H); CI mass spectrum, *m/e* (relative intensity) 276 (100), 258 (22), 169 (42), 107 (20); TLC, $R_f = 0.27$. Anal. Calcd for $C_{14}H_{13}O_3NS$: C, 61.09; H, 4.73. Found: C, 61.18; H, 5.00.

The major adduct isomer **11b** was obtained as a pale yellow viscous oil: UV max (EtOH) 255 (sh), 343 nm ($\epsilon$ 5220, 13 200); IR (film) 3400, 1610, 1585, 1340, 1045, 1027, 855, 740, 690 $cm^{-1}$; NMR ($Me_2SO$-$d_6$) $\delta$ 3.9 (t, 2 H, $CH_2O$; $J = 6$ Hz), 4.8 (t, 1 H, CHS; $J = 6$ Hz), 5.3 (t, 1 H, OH, exchangeable with $D_2O$), 7.4, 7.6, 8.1 (m, d, d, 9 H, Ph H); CI mass spectrum, *m/e* (relative intensity) 276 (100), 258 (16), 246 (8), 156 (40), 137 (12), 121 (29), 105 (13), 91 (12); TLC, $R_f = 0.21$. Anal. Calcd for $C_{14}H_{13}O_3NS$: C, 61.09; H, 4.73. Found: C, 61.07; H, 4.84.

When an acetone solution of styrene oxide was reacted with 4-nitrothiophenol in 1 N sodium carbonate solution at room temperature for 4 h, both adducts were formed in almost equal proportion as shown by TLC.

**Reaction of 1 with 9,10-Epoxy-9,10-dihydrophenanthrene, 12.** 4-Nitrothiophenol (0.47 g; 3 mmol) in aqueous NaOH (1%; 25 mL) and 9,10-epoxyphenanthrene (0.39 g; 2 mmol) dissolved in a mixture of 25.0 mL of methanol and 12.0 mL of acetone were stirred for 18 h in the cold room. The adduct **13** (0.63 g) crystallized out and was filtered. The residue was purified by silica gel column chromatography. After the disulfide was eluted with hexane–$CH_2Cl_2$ (4:1), the pale yellow band of the adduct was eluted with $CH_2Cl_2$. It crystallized from $CH_2Cl_2$–hexane as cream-colored needles: mp 89–91 °C (decomp); UV max (EtOH) 268, 344 nm ($\epsilon$ 20 900, 13 600); IR (KBr) 3220, 1600, 1580, 1520, 1320, 1095, 990, 853, 764, 738 $cm^{-1}$; NMR ($Me_2SO$-$d_6$) $\delta$ 4.8 (d, 1 H, CHS; $J = 3$ Hz), 5.1 (d, 1 H, CHO; $J = 3$ Hz), 5.7 (d, 1 H, OH, exchangeable with $D_2O$), 7.5, 7.6, 8.2 (m, d, d, 12 H, Ph H); CI mass spectrum, *m/e* (relative intensity) 350 (49), 332 (100), 302 (31), 195 (68), 179 (83), 156 (95), 126 (28); TLC, $R_f = 0.28$. Anal. Calcd for $C_{20}H_{15}O_3NS$: C, 68.69; H, 4.29. Found: C, 68.93; H, 4.05.

The adduct **13** was acetylated in the following way. A solution of 2 mL of dry pyridine in 15 mL of acetic anhydride was heated at reflux for 15 min, cooled to room temperature, and added to the adduct (0.275 g) with stirring. The resulting solution was kept in the cold room for 48 h. At the end, the product was precipitated by the addition of ice-cold water, isolated by filtration, and dried. Purification of the crude product by Florisil chromatography with $CH_2Cl_2$ as the eluent afforded colorless plates (0.27 g; from $CH_2Cl_2$–hexane): mp 133–135 °C; NMR ($Me_2SO$-$d_6$) $\delta$ 1.9 (s, 3 H, $CH_3$), 5.4 (d, 1 H, CHS; $J = 2$ Hz), 6.0 (d, 1 H, CHO; $J = 2$ Hz), 7.5, 7.7, 8.2 (m, d, d, 12 H, Ph H); TLC, $R_f = 0.64$. Anal. Calcd for $C_{22}H_{17}O_4NS$: C, 67.51; H, 4.34. Found: C, 67.41; H, 4.33.

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**NOTES**

# On the Validity of the Codistillation Model for the Evaporation of Pesticides and Other Solutes from Water Solution

**Cary T. Chiou***

Environmental Health Sciences Center, Oregon State University, Corvallis, Oregon 97331

**Milton Manes**

Department of Chemistry, Kent State University, Kent, Ohio 44242

■ Evidence is presented that disagrees with the concept that the rapid evaporative loss of some low-vapor-pressure compounds from water is due to codistillation. The observation that under certain conditions the solute evaporates while the water vapor condenses demonstrates the absence of mechanistic coupling between water and solute transport. These findings suggest that predictions of the solute evaporative loss in terms of water loss would give uncertain results.

To account for the relatively rapid evaporative loss of DDT from water suspensions and solutions, Acree, Bowman, and co-workers (*1–3*) suggested a model analogous to steam distillation, in which the evaporative loss of DDT is coupled to the amount of water loss. They referred to this process as "codistillation". The term and the implication that DDT and certain organic substances show high evaporative loss because of the concomitant water loss warrants careful consideration.

The "codistillation" model was supported by semiquantitative agreement of the results of conventional steam distillation calculations with existing data on evaporative loss rates of pesticides and water. Nevertheless, the idea that one process (the evaporation of one component) may be driven by the thermodynamic driving force of another process (in the absence of mechanistic coupling that makes them a single process) is untenable; it is essentially the "thermodynamic coupling" model (*4*), which has been shown to have trivial physical content (*5, 6*). Therefore, although instances exist in which the "codistillation" model either is mechanistically correct (e.g., direct steam distillation) or gives correct answers (e.g., sparging of mixtures with dry inert gas), one may expect it to fail in other cases as in the evaporation of chemical–water mixtures in highly humid or supersaturated air. We here

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demonstrate experimentally, for example, that DDT and PCB may be lost by evaporation from an aqueous solution that is simultaneously *gaining* weight by moisture condensation and, therefore, that there is no general relation between the evaporative losses of water and of the solute.

The experiment with DDT consisted of passing air at 25 °C and 98% relative humidity over a solution of DDT in water (20 $cm^3$; 0.6 ppb) that was maintained at 13 ± 0.5 °C, so that it would condense moisture. In 64 h the solution *gained* 4.2 g of water and *lost* 76% of its DDT by evaporation. The simultaneous evaporation and condensation of the solute and water may be shown for practically any solutes in water. In a similar experiment, when an unstirred solution of 2,2′-PCB in water (40 $cm^3$; 98 ppb) was cooled to 0–2 °C in ambient air of 25 °C and 36% relative humidity, the solution gained 45 mg of water and lost ~20% of its PCB in 6 h. These experiments demonstrate both the absence of mechanistic coupling between water and the solute and the importance of relative humidity in determining the water/solute loss rates. This is a factor that Acree et al. (*1*) did not report, presumably because it was not considered relevant in their calculations. A more important consequence of independent evaporation is the expectation (not demonstrated here) that relative humidity should have no significant primary effect on the rate of evaporative loss of the solute from water.

Because of the independence of evaporative loss of water and the solute (except in special circumstances), it would be better to use a term other than "codistillation" to describe such evaporative losses, or at least to avoid any implication of a general mechanistic coupling between the two processes.

### Experimental Section

The DDT experiment was conducted by using a Stir-Cool Peltier-effect cooler to control the solution temperature (monitored by a thermocouple). A 6-cm diameter petri dish (with walls insulated) contained initially 20 $cm^3$ of the aqueous DDT solution. The solution was stirred by a magnetic bar (1 cm in length; 0.3 cm in diameter). The sample dish sitting on the cooling plate was enclosed by an inverted 150-mm laboratory funnel fitted with a side-arm for air inlet. The funnel opening served as the air outlet. High-humidity inlet air (1 L/min) was obtained by passage through two spargers in series at room temperature (~25 °C). An Abbeon relative humidity and temperature gauge (enclosed in a Plexiglass box) was connected to the inlet air line for humidity measurement. The inserted Plexiglass box served as an effective trap for eliminating carry-over of bulk water into the sample. DDT was extracted by hexane and analyzed by GC to determine its weight loss.

In the PCB experiment, a beaker with a cross-sectional area of ~12 $cm^2$ was used to contain initially 40 $cm^3$ of the aqueous solution. An ice-water bath was used to cool the sample solution, which was exposed to ambient air at 25 °C and 36% relative humidity. PCB was extracted by hexane and analyzed by GC.

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# General Equation for the Estimation of Indoor Pollution

**Yoshiaki Ishizu**

Central Research Institute, The Japan Tobacco and Salt Public Corporation, 6-2 Umegaoka, Midori-ku, Yokohama 227, Japan

■ When a general equation for estimation of indoor pollution was applied, it was verified experimentally that the usual way of using a mixing factor is erroneous, while a new way is satisfactory. Further, the general equation was extended to be applicable to a more general case in which a generation rate of pollutant is a function of time.

### Introduction

In addition to atmospheric pollution, indoor pollution has become a matter of great concern lately. To estimate a change of indoor pollution quantitatively, it is very helpful to apply a model equation. Turk (*1,2*) has presented a general equation and proposed the use of a mixing factor in an actual case. The mixing factor is usually defined as the ratio of the effective air changes to the theoretical air changes (*3*). This definition, however, is not clear, and subsequent investigators have been confused in using the general equation with the mixing factor. Recently it was pointed out that the usual method in the application of the general equation is erroneous from theoretical considerations (*4*).

Since there has been no experimental verification of the general equation with the mixing factor, experiments were performed to determine the correct use of the mixing factor. Further, a more general equation for indoor pollution is presented when the generation rate of pollutant is a function of time.

### General Equation

When mixing of ventilation air with room air is complete and instantaneous, a general equation for the concentration of indoor pollution can be derived from mass balance as follows (*1*)

$$V\,dC = G\,dt + C_iQ_i\,dt - CQ_i\,dt - CQ_rE\,dt \qquad (1)$$

But mixing is not ideal in many actual cases and is accounted for by utilization of a mixing factor $m$. If the mixing factor is

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defined as the portion of the ventilation air flow which is completely mixed with room air, eq 1 should be modified as follows

$$V\,\mathrm{d}C = G\,\mathrm{d}t + C_{\mathrm{i}}mQ_{\mathrm{i}}\,\mathrm{d}t - CmQ_{\mathrm{i}}\,\mathrm{d}t - CmQ_{\mathrm{r}}E\,\mathrm{d}t \qquad (2)$$

Integrating this differential equation with the boundary condition

$$C = C_0 \qquad \text{at } t = 0$$

we obtain

$$C = C_0e^{-m(Q_{\mathrm{i}}+EQ_{\mathrm{r}})t/V} + \frac{mC_{\mathrm{i}}Q_{\mathrm{i}} + G}{m(Q_{\mathrm{i}} + EQ_{\mathrm{r}})}(1 - e^{-m(Q_{\mathrm{i}}+EQ_{\mathrm{r}})t/V}) \qquad (3)$$

where $V$ = volume of the room (m$^3$), $t$ = time (min), $C$ = concentration of pollutant in the room at any time (mg/m$^3$), $C_0$ = initial concentration of pollutant in the room (mg/m$^3$), $C_{\mathrm{i}}$ = concentration of pollutant of outdoor air (mg/m$^3$), $E$ = efficiency of the air filter in the recirculation loop, $Q_{\mathrm{i}}$ = volume rate of intake of outdoor air (m$^3$/min), $Q_{\mathrm{r}}$ = volume rate of recirculated air (m$^3$/min), $G$ = pollutant generation rate within room (mg/min), and $m$ = mixing factor. This equation was used by some investigators (*4,5*). But, usually, the following equation has been used (*6–8*)

$$C = C_0e^{-m(Q_{\mathrm{i}}+EQ_{\mathrm{r}})t/V} + \frac{C_{\mathrm{i}}Q_{\mathrm{i}} + G}{Q_{\mathrm{i}} + EQ_{\mathrm{r}}}(1 - e^{-m(Q_{\mathrm{i}}+EQ_{\mathrm{r}})t/V}) \qquad (4)$$

The essential difference between eq 3 and 4 is $G$ and $G/m$ in the second term of the right-hand side of these equations.

In the next section, it was shown experimentally that eq 3 can represent the actual concentration of indoor pollutants.

So far, the pollutant generation rate $G$ has been considered to be a constant. When $G$ is a function of time, eq 2 becomes

$$V\,\mathrm{d}C = \mathrm{G}(t)\,\mathrm{d}t + C_{\mathrm{i}}mQ_{\mathrm{i}}\,\mathrm{d}t - CmQ_{\mathrm{i}}\,\mathrm{d}t - CmQ_{\mathrm{r}}E\,\mathrm{d}t \qquad (5)$$

Rewriting eq 5 yields

$$\mathrm{d}C/\mathrm{d}t + PC = Q \qquad (6)$$

where

$$P = \frac{m(Q_{\mathrm{i}} + EQ_{\mathrm{r}})}{V}$$

$$Q = \frac{\mathrm{G}(t) + C_{\mathrm{i}}mQ_{\mathrm{i}}}{V}$$

Since eq 6 is a linear equation of the first order, it can be solved as

$$C = e^{-Pt}\left(\int_0^t e^{Pt}Q\,\mathrm{d}t + C_0\right) \qquad (7)$$

This is a further general equation for estimation of indoor pollution. When $\mathrm{G}(t)$ is expressed by power functions as

$$\mathrm{G}(t) = at^n \qquad (8)$$

where $a$ is a constant and $n$ is an integer (0, 1, 2, 3, . . .)

$$C = \frac{a}{V}\left[\frac{t^n}{P} - \frac{nt^{n-1}}{P^2} + \frac{n(n-1)t^{n-2}}{P^3} - \ldots + (-1)^{n-1}\frac{n!t}{P^n} + (-1)^n\frac{n!}{P^{n+1}}\right] + \frac{C_{\mathrm{i}}mQ_{\mathrm{i}}}{VP} + \left(C_0 - \frac{a + C_{\mathrm{i}}mQ_{\mathrm{i}}}{VP}\right)e^{-Pt} \qquad (9)$$

When $\mathrm{G}(t)$ is expressed by sine functions as

$$\mathrm{G}(t) = b \sin(ct) \qquad (10)$$

where $b$ and $c$ are constants

$$C = e^{-Pt}\left[\frac{b}{V}\frac{e^{Pt}(P\sin(ct) - c\cos(ct)) + c}{P^2 + c^2} + \frac{C_{\mathrm{i}}mQ_{\mathrm{i}}}{V}\frac{e^{Pt} - 1}{P} + C_0\right] \qquad (11)$$

Other forms of $\mathrm{G}(t)$ could be solved by referring to an integral table (*9*).

### *Experimental Section*

Sample cigarettes were commercially available ones 80 mm long with filter tips. They were conditioned in a room at 20 °C and 60% relative humidity for more than 1 week. The concentration of smoke was measured by a recently developed (*10, 11*) respirable aerosol mass monitor (KANOMAX, Model 51-1111) which was placed on a table at the center of a room. The respirable aerosol mass monitor is a very sensitive mass measuring instrument applying piezoelectricity. Room air was sampled for 2 min with a 1.0 L/min sampling flow rate. Then the mass monitor displayed smoke concentrations (mg/m$^3$) printed out by a digital printer. This procedure was repeated throughout each experiment.

The linear velocities of air through a duct were measured at five points across the duct by a hot wire anemometer (Shibata Kagaku Co., Model ISA-31). Then the measured velocities were averaged and multiplied by a cross-sectional area of the duct to determine the volume rate of air.

A cigarette was allowed to smolder statically in a closed 16-m$^3$ room until the butt length became 30 mm (experiment 1) in order to obtain a smoke generation rate. The smoldering period was ~9 min.

Then six cigarettes were allowed to smolder in the same way as mentioned above in a ventilated 71-m$^3$ room (experiment 2). The volume rate of outdoor air intake was 32 m$^3$/min and that of recirculated air was 8 m$^3$/min.

A similar experiment was performed in a huge 268-m$^3$ room by allowing 50 cigarettes to smolder. The volume rate of outdoor air intake was 106 m$^3$/min with no recirculated air (experiment 3).

Further, another experiment was carried out in a 82-m$^3$ room by changing the volume rate of outdoor air intake for 62 and 12 m$^3$/min. The volume rate of recirculated air was 15 and 65 m$^3$/min, respectively (experiment 4). In this experiment, cigarettes were allowed to smolder on a standard smoking machine which was operated to smoke cigarettes with 2-s, 35-mL puffs once every minute. Six cigarettes were allowed to smolder, and smoke generated from the smoldering cone during puff intermissions was left to spread in the room. The smoke generation rate of the smoking machine was also determined from an experiment in the closed 16-m$^3$ room. The smoldering period was ~6 min.

### *Results and Discussion*

The results of experiment 1 are shown in Figure 1. During smoldering, the concentration of smoke increased rapidly. After finishing smoldering, it gradually decreased because of sedimentation or adhering.

Since the volume of the room was 16 m$^3$, and the peak concentration was 0.61 mg/m$^3$, the total amount of the suspended smoke was calculated as 16 × 0.61 = 9.8 mg. The duration of cigarette smoldering was ~9 min, so that the smoke generation rate $G$ was assumed to be 9.8/9 = 1.1 mg/min for one cigarette.

The results of experiment 2 are shown in Figure 2. These results were employed to examine eq 3 and 4. As the particle size of cigarette smoke is as small as ~0.1 μm (*12*), an ordinary air filter hardly entraps cigarette smoke. Therefore, the efficiency of the air filter $E$ was assumed to be zero.

When the mixing factor was unity, experimental results did not agree with the calculated ones. Thus the mixing factor was applied by following eq 3 and 4. With eq 3, calculated values agreed well with the experimental results when the mixing factor was ~0.4, as shown in Figure 3. On the other hand, any calculated values could not represent the experimental results with eq 4, as shown in Figure 4.

The results of experiment 3 are presented in Figure 5. These results were also expressed only by eq 3 with the mixing factor being ~0.6.

The results of experiment 4 are shown in Figure 6. With the smoking machine, the smoke generation rate $G$ was 1.3 mg/min for one cigarette. When the volume rate of outdoor air intake was 62 m$^3$/min, eq 3, again, could represent the ex-

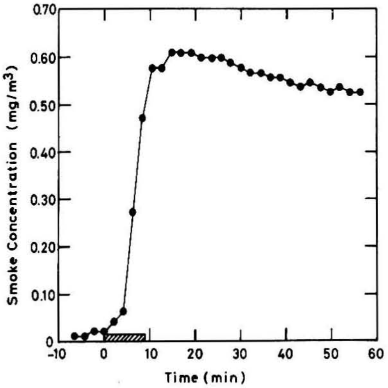

**Figure 1.** The concentration of smoke generated by static smoldering in a closed 16-m$^3$ room: (▨) smoldering period.

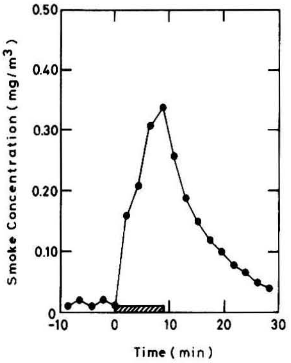

**Figure 2.** The concentration of smoke in a ventilated 71-m$^3$ room: (▨) smoldering period.

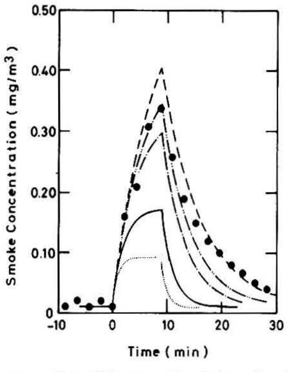

**Figure 3.** The comparison of the experimental results of Figure 2 with the calculated ones from eq 3: (●) measured values; (· · ·) $m = 2.0$; (—) $m = 1.0$; (-·-) $m = 0.5$; (-··-) $m = 0.4$; (- - -) $m = 0.3$

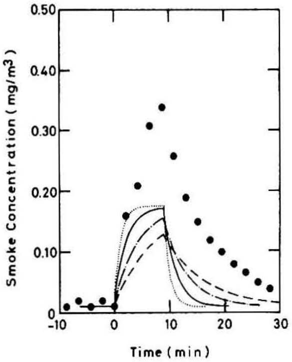

**Figure 4.** The same as Figure 3 from eq 4.

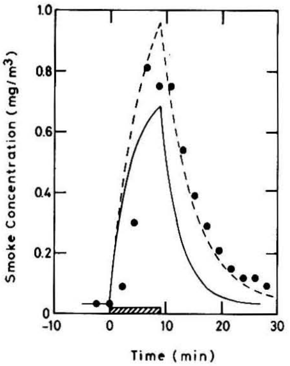

**Figure 5.** The comparison of the experimental results in a ventilated 268-m$^3$ room with the calculated ones from eq 3: (▨) smoldering period; (●) measured values; (—) $m = 1.0$; (- - -) $m = 0.6$

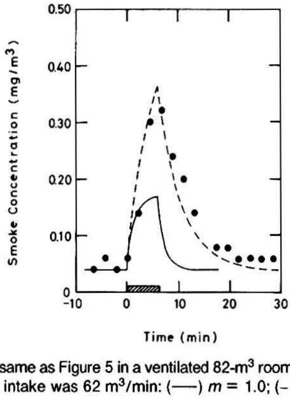

**Figure 6.** The same as Figure 5 in a ventilated 82-m$^3$ room. Volume rate of outdoor air intake was 62 m$^3$/min: (—) $m = 1.0$; (- - -) $m = 0.3$

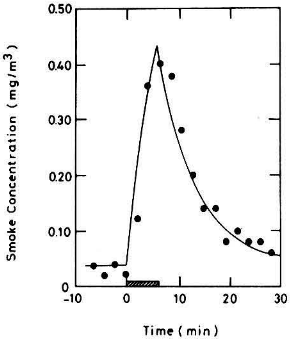

**Figure 7.** The same as Figure 6. Volume rate of outdoor air intake was 12 $m^3$/min: (——) $m$ = 1.0

perimental results with the mixing factor being $\sim$0.3. When the volume rate of outdoor air intake was 12 $m^3$/min, the experimental results were in accord with eq 3 with the mixing factor being unity, as shown in Figure 7. The good mixing may be ascribed to the experimental condition that, in this case, mechanical exhausting of room air was not applied, but room air was made to exhaust spontaneously from small door openings.

It is interesting to note that when a value of the volume rate of outdoor air intake divided by the volume of the room becomes larger, the mixing factor becomes smaller.

From these results, it seems no doubt that eq 3 or more generally eq 7 is an appropriate equation to estimate the concentration of indoor pollutants.

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# Development of an Ozone River Associated with Synoptic Scale Episodes in the Eastern United States

**George T. Wolff*[1] and Paul J. Lioy[2]**
Interstate Sanitation Commission, 10 Columbus Circle, New York, New York 10019

■ The spatial and temporal distributions of ozone in the eastern two-thirds of the United States during three July 1978 episodes are examined. In all three cases, a distinct area of high ozone concentrations was observed flowing northeastward in a "river", extending from the southwest Gulf Coast to New England. The formation, size, and other characteristics of this "river" are discussed.

Typical ozone episodes in the northeastern U.S. are associated with high-pressure systems which originate in Canada and move southeastward into the Midwest en route to the Atlantic Ocean (*1*). As each system moves out of Canada, the air mass contains between 30 and 50 ppb of ozone (*2, 3*). Then as it passes over industrialized and urbanized areas, additional ozone may be formed resulting from precursor emission oxidation and accumulation in the system (*4, 5*). The highest ozone concentrations are usually found on the backside of the high-pressure system presumably because this sector has the longest residence time over areas of high precursor emission densities (*4–6*).

Most of the above results were obtained from sites distributed in 19 states located in the midwestern and eastern U.S. (*1, 2, 4, 5*). Frequently, however, high concentrations of ozone appeared to extend beyond the 19-state area when influenced by southwesterly winds. This high ozone could not be accounted for by emissions in the study area, suggesting that ozone was being transported from areas to the southwest. Consequently, we have expanded the geographic boundaries of the study in an attempt to determine the possible sources of this extraregional ozone. In this note we will discuss the ozone patterns that developed during three such episodes by using data collected in 35 states encompassing all of the U.S. east of the Plains States (Figure 1). The three episodes examined occurred during July 1977 on the following dates: July 12–21, July 21–24, and July 26–30.

## *Results*

**July 12–21 Episode.** On July 12, a high-pressure system was formed in predominantly maritime tropical air over the Gulf of Mexico. This system affected the entire southeastern U.S. and extended from western Texas, northeastward through Illinois, and finally east to the Atlantic Ocean.

By July 14 the southwesterly airflow pattern, which persisted until July 21, began to develop. Trajectories calculated from Heffter's model (*7*) are shown in Figure 2a. Air parcels originating near the Texas–Louisiana area traveled north-northeastward to the lower Midwest and then eastward to the Atlantic Coast. The ozone concentration patterns found within this system are shown in Figure 2b–d. High ozone concentrations were associated with the return flow around the high-pressure system within an ozone river extending from Texas to southern New England parallel to the isobars.

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[1] Present address, Environmental Science Department, General Motors Research Laboratories, Warren, MI 48090.

[2] Present address, Institute of Environmental Medicine, New York University Medical Center, New York, NY 10016.

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The hydrocarbon emission densities for the area influenced by the high-pressure system are illustrated in Figure 3. The Texas and Louisiana Gulf Coast form an area of extremely high emission densities. By comparison, emission densities between this area and the central Midwest are much lower and the source points more diffuse. Consequently, it appears that much of the high ozone observed from Arkansas and Oklahoma to the lower Midwest may have originated from emissions along the Texas–Louisiana Gulf Coast.

The ozone river, averaging ~120–130 ppb, persisted for 1 week and extended northward from the Texas–Louisiana Gulf Coast to the northeastern Atlantic Coast. On almost every day, isolated areas of a few hundred square miles to one thousand square miles experienced higher ozone levels. In each case, the wind speeds within areas of ozone greater than 150 ppb in concentration were significantly lower than areas within the broader band. For example, on July 16, an area which included the southern tip of Illinois, southeastern Missouri, western Kentucky, and most of Tennessee was affected by ozone concentrations of 178–198 ppb. Trajectory analysis indicated that when this air parcel passed over the Gulf Coast on July 13 and moved northward into the Tennessee area on July 15, it contained an average $O_3$ concentration of ~120 ppb. During the next 24 h, wind speeds diminished to less than 6 m/s and the ozone level increased. The wind speed increased to over 20 m/s by July 18, and the small area of high ozone appeared to have been dispersed and assimilated into the air mass.

Figure 1. Location of ozone monitoring sites.

Similar 1-day incidents of $O_3$ concentrations significantly higher than 120 ppb occurred in several other places during the episode. The greatest number of incidents was observed in the Washington D.C.–Baltimore MD area. Ozone concentrations in excess of 150 ppb occurred on July 15 and 16 and in excess of 200 ppb on July 17 and 19. On all of these occasions, the mean wind speed through the mixing layer was <6 m/s. The highest concentration was 328 ppb on July 19. It should be noted that during these 1-day incidents, even though the wind speeds were very low, the daily emissions would still be transported 80–120 km downwind. Thus, it does not appear that local emissions accumulated and persisted over the same area. Consequently, local generation was always less than the ozone transport fraction.

**July 21–24.** Unlike the July 12–20 episode which was associated primarily with a high-pressure system that developed over the southeastern U.S., both the July 21–24 and the July 26–30 episodes began with the typical intrusion of a high-pressure system from Canada. On July 21, a cold front, which marked the leading edge of a cooler Canadian air mass, swept southeastward from Minnesota. By the morning of July 22,

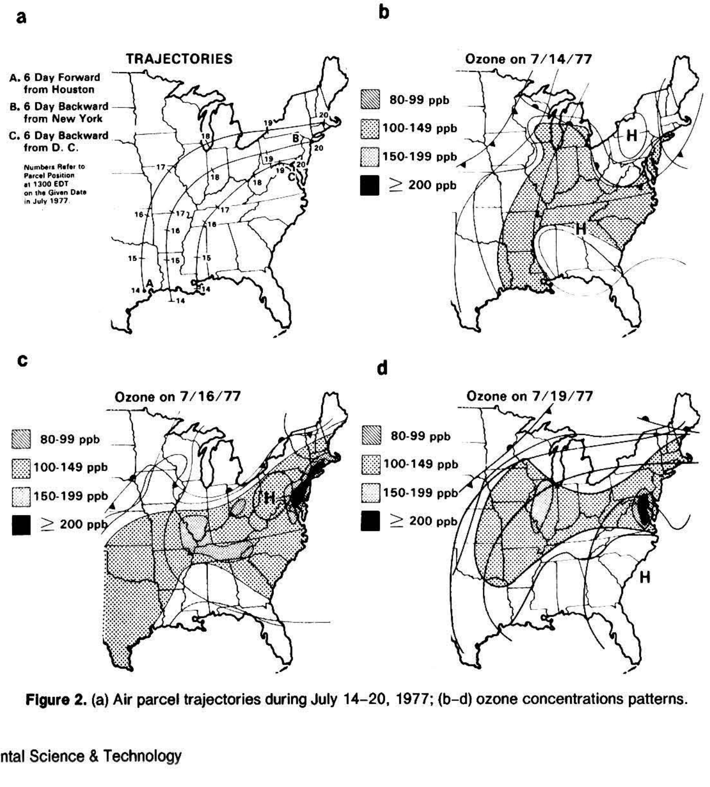

Figure 2. (a) Air parcel trajectories during July 14–20, 1977; (b–d) ozone concentrations patterns.

the cold front moved off the Atlantic Coast and was oriented in a NE–SW line which extended from just east of Maine to the North Carolina coast and then westward through northern Oklahoma. Figure 4a shows that this new air mass replaced the previous air mass over much of the eastern U.S. except in the South. The air mass responsible for the heat wave persisted over the South, and high ozone (~130 ppb) was still recorded over eastern Texas, Louisiana, Oklahoma, and Arkansas.

On July 23 (Figure 4b), the new high-pressure system moved into Pennsylvania and the cold front dissipated from Oklahoma to North Carolina. Consequently, on July 22, the air over the South containing high levels of ozone was rapidly advected into the anticyclonic circulation around the high-pressure center situated in Pennsylvania. The ozone reached southwestern Michigan and western Ohio on July 23. As the high-pressure system moved off the Atlantic Coast on July 24 (Figure 4c), the air containing high levels of ozone reached the Northeast and the ozone river noted during the previous episode was reestablished.

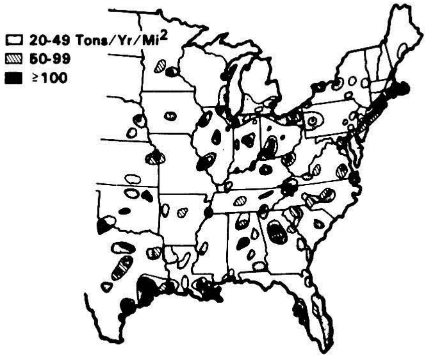

Figure 3. Hydrocarbon emission densities.

Figure 4d was constructed by using trajectories originating in Houston and New Orleans on July 21. In two days, the air containing 130 ppb of $O_3$ over Oklahoma and Arkansas traveled over 2300 km at an average speed of 20 m/s. The air entering the New York City area on July 23 contained ~90–100 ppb of $O_3$, which was 30–40 ppb less than the parcels contained when in the Oklahoma–Arkansas area on July 22. In this case, because of high wind speeds, dilution of $O_3$ must have predominated over accumulation.

**July 26–30 Episode.** The sequence of events during this episode (Figure 5) is almost identical with the previous case. The high ozone contained in the maritime tropical air was suppressed to the southwest Gulf area by a Canadian cold front that moved off the Atlantic Coast by July 26. As the high-pressure system behind this front moved eastward, the ozone river was established once again by July 28. The ozone concentrations, however, were not as high during this episode probably because of scattered areas of precipitation which occurred within the ozone river.

### *Discussions and Conclusions*

The three ozone episodes illustrated in this note indicate that under certain meteorological conditions, high ozone concentrations were transported from the western Gulf Coast area to the Midwest and the Northeast. These incidents were associated with advection of Gulf maritime tropical air via the clockwise circulation of high-pressure systems. Reexamination of previously reported episodes (*1, 2, 4, 5*) suggests that this

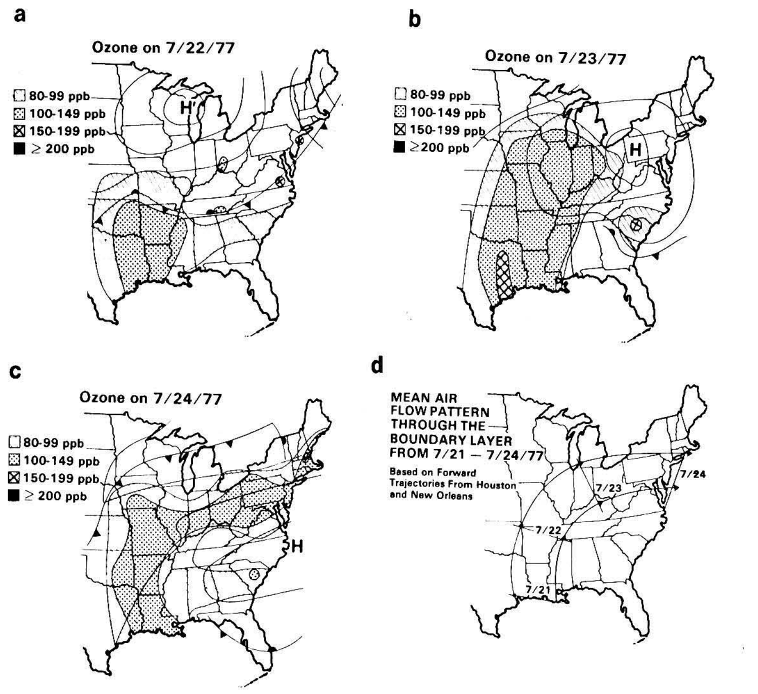

Figure 4. (a–c) Ozone concentrations on July 22–24; (d) air parcel trajectories from Houston and New Orleans on July 21, 1977.

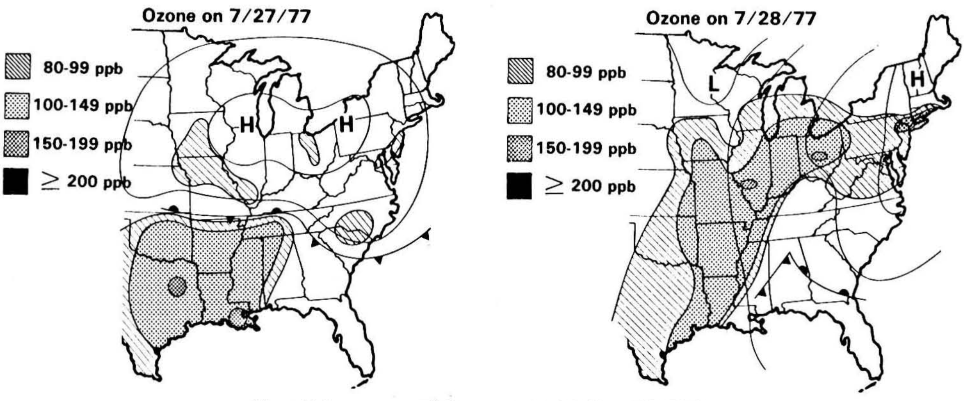

**Figure 5.** Ozone concentration patterns on July 27 and 28, 1979.

phenomenon can account for some of the high ozone which was observed being transported into the Northeast. During most of the final days of these episodes, maritime tropical air (as evidenced by elevated dew point and temperature measurements) was present.

Previous analysis showed that the Midwestern and Eastern U.S. frequently experience the same ozone episodes. The data presented in this paper show an episode which simultaneously affected nearly two-thirds of the U.S., covering an area of ~2 $\times 10^6$ mi$^2$ ($5 \times 10^6$ km$^2$).

The circulation around the high-pressure systems which caused these episodes traveled northward from the Texas–Louisiana Gulf Coast to the Midwest and then eastward to the Northeast and the Middle Atlantic Coast. Ozone concentrations within this river averaged ~120–130 ppb and were as high as 328 ppb in Connecticut.

The first episode was a classic example of a prolonged elevated pollution episode associated with a stagnating high-pressure system. The second two episodes, however, demonstrated that a stagnation in the Northeast is not necessary to produce elevated ozone concentrations. As a new high-pressure system rapidly moved from Canada on July 21, the prolonged ozone episode of July 12–20 terminated in the northern half of the study area but persisted over Texas, Oklahoma, Arkansas, and Louisiana until July 29. For the periods including July 23–24 and July 28–29, the high-pressure system followed the same route, and air containing elevated ozone levels was advected into the backside of each system and transported from the Gulf to New England. During July 22–24, ozone concentrations between 90 and 130 ppb traveled in excess of 2300 km in 48 h. Analysis of hydrocarbon emission density data suggests that the ozone river may originate in the high hydrocarbon emission density areas along the Gulf Coast between Corpus Cristi, Texas, and New Orleans, Louisiana. This area frequently experiences high temperature and ample sunshine which are conducive for ozone formation. The ozone produced is undoubtedly supplemented by emissions into the ozone river en route through the Mississippi and Ohio Valleys to the Northeast. In addition, recent evidence indicates that there is a stratospheric contribution of ozone on the backside of high-pressure systems (*3, 8, 9*). This is based on measurements of a stratospheric air tracer, beryllium-7, which has been found to be the highest on the backside of high-pressure systems (*3, 8*). Although the intrusion of stratospheric air occurs immediately behind the cold front, only rarely does it extend to the ground in the frontal zone (*9*). Instead, it appears that the intrusion reaches the midtroposphere, where it is advected in a clockwise circulation to the backside of the approaching high-pressure system. It is then brought to the surface during good mixing conditions (*8*) which are typical in humid maritime tropical air.

This study has raised many questions regarding the relative importance of both anthropogenic and nonanthropogenic sources of ozone and its precursors along the ozone river. Unfortunately, these questions can only be answered after large regional scale models, which incorporate the complex chemistry and meteorology, are developed.

### *Acknowledgment*

We thank all of the states which made their surface ozone data available. In addition we are grateful to Richard Herrmann of General Motors Research Laboratories for performing the trajectory calculations.

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# Precision of $NO_2$ Photolysis Rate Measurements

**Russell R. Dickerson**[*][1] **and Donald H. Stedman**

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

■ Gas-phase kinetic calculations indicate that actinometric measurements of the rate of solar photolysis of $NO_2$ in nitrogen can be in error by +5 to −15% or more, unless odd oxygen, $N_2O_5$ chemistry, and trace oxygen content are considered. A field experiment confirms that the effect of the quartz tube on the measured photolysis rate is $<1.7\%$.

Solar UV radiation powers photochemical smog formation (*1*). Actinometric techniques (*2,3*) measure rates of solar photolysis of $NO_2$ (Table I, reaction 1) with a precision of a few percent. These photolysis rates are determined from photolysis frequencies, $j(NO_2)$, by chemiluminescent measurement of NO formed from a known amount of $NO_2$:

$$j(NO_2) \equiv [NO_2]^{-1}\, d[NO]/dt \doteq [NO_2]_0^{-1}\, \Delta[NO]/\Delta t \quad (I)$$

where $[NO_2]_0$ is the initial $NO_2$ concentration and $\Delta[NO]$ is the increase in NO after time $\Delta t$. If $[NO_2]_0$ is less than 20 ppm in air or $O_2$, and $\Delta t$ is less than 1.0 s, calculated corrections to eq I never exceed 5% and do not contribute to the uncertainty of final $j(NO_2)$ values (*2*). However, measurements in $N_2$ require corrections to eq I of about 60% (*3*), because, without $O_2$ to remove them, O atoms produced by reaction 1 convert $NO_2$ into additional NO via reaction 3. These corrections have been discussed previously (*3,4*) but need careful reevaluation in order to measure accurate $j(NO_2)$ values. This note presents a new set of calculated corrections on the $j(NO_2)$ measuring system of Zafonte et al. (*3*) including a more complete reaction scheme, updated reaction rates (*5*), and time-dependent calculations. We also present an experimental test of the prediction of Zafonte et al. (*3*) concerning the effect of the reaction vessel on $j(NO_2)$ measurements.

## *Calculations*

Zafonte et al. (*3*) measure $j(NO_2)$ from initial conditions of 1–4 ppm of $NO_2$ and 0.0–0.3 ppm of NO in $N_2$ and an exposure time of 7.5 s. They calculate a quantum yield factor $\phi$ given by the rate of NO appearance over the rate of $NO_2$ photolysis from reactions 1 and 3–6. The mean and extreme of their initial conditions generate a mean and limits:

$$\phi = 1.61 \pm 0.07$$

Calculating $\phi$ by using these initial conditions and reactions and a chemical kinetic model (*6*), we also obtain $\phi$ of 1.61. Addition of $NO_3$ photolysis and reaction 15 of O and $NO_3$ to form $NO_2$ has little effect on $\phi$. However, addition of odd oxygen and $N_2O_5$ chemistry significantly alters $\phi$ values.

Using the full set of reactions listed in Table I and 0.5 ppm of $O_2$, the typical value for "research-grade" $N_2$ (*7*), we calculate a set of exposure time-dependent quantum yield factors (Table II). The new mean value is

$$\phi = 1.69 \pm 0.08$$

or about 5% higher, giving $j(NO_2)$ values 5% lower than previously determined. $N_2O_5$ formation ties up $NO_3$ and prevents loss of NO via reaction 6. Using 300 ppm of $O_2$, the typical value for "extra-dry" $N_2$, we calculate quantum yield factors from 3.6% higher to 17.5% lower:

$$\phi = 1.56 \begin{array}{l} +0.18 \\ -0.25 \end{array}$$

Note that symmetry about the mean is lost. A concentration of 300 ppm of $O_2$ can generate as much as 10 ppb of $O_3$ via reaction 2 which rapidly oxidizes NO to $NO_2$ and lowers $\phi$. Intermediate grades of $N_2$ give intermediate quantum yields. These results are insensitive to changes in temperatures from 273 to 305 K.

## *Experimental Section*

In these measurements of photolysis rates, some question naturally arises concerning attenuation and reflection of sunlight by the walls of the reaction vessel. Zafonte et al. (*3*) calculate the optical properties of spherical and cylindrical vessels for use in solar photolysis rate measurements and conclude that reflections on the outer surface are exactly compensated for by internal reflections. To test their calculations, we set up a $j(NO_2)$ measuring system (*2*) on Niwot Ridge near Nederland, CO. From one to three additional tubes were slid over the initial tube and $j(NO_2)$ was measured. An Eppley UV radiometer monitored the slight changes in solar radiation so that $j(NO_2)$ values could be normalized to a standard solar intensity. Three or more readings were recorded with each set of tubes, and within the ±5% precision of the experiment, the additional tubes had no effect on the measured $j(NO_2)$. If one assumes that the effects of each tube are cumulative according to the following equation

$$(1 - X)^n = (1 - \sigma)$$

where $X$ is the fractional loss of light due to each tube, $n$ is the number of additional tubes, and $\sigma$ is the precision of all of the

**Table I. Reactions Involved in $NO_2$ Photolysis Rate Measurements at 293 K**

| | reactions | rate constants |
|---|---|---|
| (1) | $NO_2 + h\nu \rightarrow NO + O$ | $5.0 \times 10^{-3}$ [b] |
| (2) | $O + O_2 \xrightarrow{M} O_3$ | $1.5 \times 10^{-14}$ [a] |
| (3) | $O + NO_2 \rightarrow NO + O_2$ | $9.1 \times 10^{-12}$ |
| (4) | $O + NO_2 \xrightarrow{M} NO_3$ | $2.0 \times 10^{-12}$ [a] |
| (5) | $O + NO \xrightarrow{M} NO_2$ | $2.8 \times 10^{-12}$ [a] |
| (6) | $NO_3 + NO \rightarrow 2NO_2$ | $1.9 \times 10^{-11}$ |
| (7) | $NO + O_3 \rightarrow NO_2 + O_2$ | $1.5 \times 10^{-14}$ |
| (8) | $NO_3 + h\nu \rightarrow NO_2 + O$ | $0.5 \times 10^{-1}$ [b] |
| (9) | $NO_3 + h\nu \rightarrow NO + O_2$ | $2.0 \times 10^{-2}$ [b] |
| (10) | $NO_2 + NO_3 \rightarrow N_2O_5$ | $2.8 \times 10^{-12}$ |
| (11) | $N_2O_5 \rightarrow NO_2 + NO_3$ | $6.3 \times 10^{-2}$ |
| (12) | $N_2O_5 + h\nu \rightarrow NO_2 + NO_3$ | $0.5 \times 10^{-5}$ [b] |
| (13) | $O_2 + 2NO \rightarrow 2NO_2$ | $2.3 \times 10^{-38}$ |
| (14) | $NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$ | $5.0 \times 10^{-16}$ |
| (15) | $O + NO_3 \rightarrow NO_2 + O_2$ | $1.0 \times 10^{-11}$ |
| (16) | $O_3 + h\nu \rightarrow O_2 + O$ | $2.0 \times 10^{-4}$ [b] |
| (17) | $O_3 + NO_2 \rightarrow NO_3 + O_2$ | $2.8 \times 10^{-17}$ |

[a] Equivalent two-body reaction rate for a number of density of $2.5 \times 10^{19}$ molecules $cm^{-3}$. [b] Photolysis rates for half sun.

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[1] Presently at the National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO 80307. (The National Center for Atmospheric Research is sponsored by the National Science Foundation.)

**Table II. Comparison of Quantum Yield Factors Using Initial Conditions of Zafonte et al. (*3*) and Reaction Scheme from Table I**

| initial $NO_2$, ppm | initial NO, ppm | $\Delta t$, s | $\phi$ (this work) | $\phi$ (ref 3) | difference, % |
|---|---|---|---|---|---|
| | | Research-Grade Nitrogen, 0.5 ppm of $O_2$ | | | |
| 4.0 | <0.01 | 1 | 1.81 | 1.68 | 7.7 |
| 4.0 | <0.01 | 5 | 1.78 | 1.68 | 6.0 |
| 4.0 | <0.01 | 10 | 1.74 | 1.68 | 3.6 |
| 2.5 | 0.15 | 1 | 1.74 | 1.61 | 8.1 |
| 2.5 | 0.15 | 5 | 1.71 | 1.61 | 6.2 |
| 2.5 | 0.15 | 10 | 1.68 | 1.61 | 4.3 |
| 1.0 | 0.30 | 1 | 1.57 | 1.54 | 1.9 |
| 1.0 | 0.30 | 5 | 1.56 | 1.54 | 1.3 |
| 1.0 | 0.30 | 10 | 1.54 | 1.54 | 0.0 |
| | | Extra-Dry Nitrogen, 300 ppm of $O_2$ | | | |
| 4.0 | <0.01 | 1 | 1.74 | 1.68 | 3.6 |
| 4.0 | <0.01 | 5 | 1.70 | 1.68 | 1.2 |
| 4.0 | <0.01 | 10 | 1.64 | 1.68 | −2.4 |
| 2.5 | 0.15 | 1 | 1.63 | 1.61 | 1.2 |
| 2.5 | 0.15 | 5 | 1.59 | 1.61 | −1.2 |
| 2.5 | 0.15 | 10 | 1.53 | 1.61 | −5.0 |
| 1.0 | 0.30 | 1 | 1.40 | 1.54 | −9.1 |
| 1.0 | 0.30 | 5 | 1.34 | 1.54 | −13.0 |
| 1.0 | 0.30 | 10 | 1.27 | 1.54 | −17.5 |

$j(NO_2)$ measurements (5%), the effect of the initial tube must be less than 1.7%, as predicted by Zafonte et al. (*3*).

## *Discussion*

One of the most important results of these new calculations is the dependence of the quantum yields on exposure time, as shown on Table II. Commercial $NO_x$ detectors often have a time lag due to the volume of the plumbing between sample inlet and reaction chamber. This time lag can be as long as 30 s, and during this time the composition of the sampled gas can change. For example, if $j(NO_2)$ is measured in "extra-dry" $N_2$ by using the mean initial conditions described previously, a 30-s delay will reduce the apparent $j(NO_2)$ by ~5%. Thus measurements of $j(NO_2)$ in $N_2$ should include careful consideration of trace $O_2$ content, $N_2O_5$ chemistry, and exposure time effects on quantum yield. The new quantum yield, 1.69 ± 0.08, is accurate to at least 5% for $O_2$ contents from 0 to 50 ppm. Alternatively, measurements should be made in air or $O_2$ with a $NO_x$ detector modified to give appropriately fast response (*2*).

## *Acknowledgment*

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# Synthesis of Peroxyacetyl and Peroxyaroyl Nitrates. Complexation of Peroxyacetyl Nitrate with Benzene

**Tina M. Kravetz, Steven W. Martin, and G. David Mendenhall***
Battelle Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201

■ Convenient procedures are given for the condensed-phase synthesis of peroxyacetyl nitrate (PAN), peroxybenzoyl nitrate, and *m*-chloroperoxybenzoyl nitrate from the corresponding peracids, sulfuric acid, and sodium nitrate. The position of the $^1H$ NMR signal from peroxyacetyl nitrate in $CCl_4$–benzene mixtures depended on the solvent composition in a way consistent with complex formation between PAN and benzene, with $K_{eq} = 0.095$ at 27 °C.

Peroxyacyl and peroxyaroyl nitrates are highly reactive compounds of considerable interest because of their physiological and chemical action in polluted atmospheres (*1–4*). Samples of such compounds are routinely needed for calibration of analytical instruments for their detection, and several syntheses have been published (*1, 5–8*). The procedure of Louw et al. (*5*) is particularly convenient because the reaction is carried out in the condensed phase, although rather corrosive reagents are required.

Stephens (*1*) reported that mixtures of nitric and sulfuric acids gave only traces of peroxyacetyl nitrate (PAN) from peracetic acid. We find, however, that yields of PAN comparable to those from other procedures in the condensed phase (*5*) can be obtained from peracetic acid with sulfuric acid when the nitric acid is produced in situ by addition of sodium nitrate or (in initial experiments) anhydrous calcium nitrate (Table I). The method works equally well for the conversion of two peroxybenzoic acids to the corresponding peroxybenzoyl nitrates.

## *Experimental Section*

A typical procedure was as follows. A 50-mL 3-necked flask equipped with an inlet for nitrogen, a thermometer, and a magnetic stirring bar was flushed with $N_2$ and charged with 30 mL of nitrogen-flushed pentane (Burdick and Jackson). The flushing of the flask with nitrogen could be omitted if the room air was relatively dry. The flask was placed in an acetone bath, and its contents were stirred under nitrogen while sufficient dry ice was added to the bath to cool the pentane to 0 °C. Peracetic acid (40% in acetic acid, FMC Corp., 4.0 mmol) was added with stirring at this temperature, followed by concentrated sulfuric acid (3.6 g, 2.0 mL) and then finely powdered sodium nitrate (0.85 g, 10 mmol, Baker) at a rate such that the temperature remained <5 °C (**Caution! Exotherm!**). After stirring at 0 °C for 30 min, the mixture was poured onto ~30 g of ice in a separatory funnel and shaken until the ice had melted. The lower layer was separated, and the organic layer was washed three times with 30 mL of ice water and dried over anhydrous $MgSO_4$. The IR spectrum of the solution displayed strong bands (*1*) from PAN at 1830 and 1725 $cm^{-1}$ and no absorptions in the OH stretching region or from other carbonyl species.

Solutions of PAN in pentane or hexane, prepared in this manner, have been stored over $MgSO_4$ at −18 °C for several months without evidence of significant decomposition (IR). A new peak in the gas chromatogram of a pentane solution did appear on standing under these conditions, and the intensity of this peak grew with time. Its retention time was nearly coincident with that of PAN under our column conditions, and the retention time was identical with that of a synthetic sample of 2-pentyl nitrate (*9*). Solutions in carbon tetrachloride, on the other hand, were qualitatively observed to be much less stable under the same storage conditions, although the reasons for this difference are not known.

**Table I. Conditions for Synthesis of PANs**

| precursor,[a] g | solvent, mL | $H_2SO_4$, mL | $NaNO_3$, g | temp | time | yield, % |
|---|---|---|---|---|---|---|
| 40% $CH_3CO_3H$ in $CH_3COOH$ | | | | | | |
| 0.76 | *n*-pentane, 30 | 2.0 | 0.85 | 0 | 30 min | 35–40 |
| 1.54 | $CCl_4$, 60 | 4.3 | 1.71 | −5 | 30 min | 35 |
| 0.60 | chlorobenzene, 30 | 3.9 | 1.7 | −5 | 30 min | 0 |
| 80% *m*-chloroperbenzoic acid[b] | | | | | | |
| 1.58 | *n*-pentane, 30 | 5.6 | 2.31 | −10 | 3 h | 33 |
| 1.15 | $CCl_4$, 50 | 1.03 | 0.408 | −10 | 3 h | 30 |
| perbenzoic acid[c] | | | | | | |
| 0.096 | *n*-pentane, 20 | 0.31 | 0.39 | −20 | 3 h | 45 |

[a] Weights are given for the amount of pure peracid present. [b] Aldrich. The remaining 20% of the material is largely *m*-chlorobenzoic acid. [c] From benzoyl chloride and $H_2O_2$ (*16*). The aqueous peracid product was extracted into pentane.

For calibration purposes, PAN was transferred from the pentane by bubbling dry $N_2$ through the solution into a Teflon bag. The concentration in the bag was determined by Fourier transform infrared analysis (*10, 11*) (pentane spectrum substracted) with a 1.0-m cell. Simultaneously, samples of PAN were withdrawn from the bag with glass/Teflon gas-tight syringes and diluted with a known volume of clean air in a second, evacuated Teflon bag. Multiple dilutions were used to derive a calibration curve concentration vs. detector response in the gas chromatogram (*4*). Losses of PAN either in the original or in diluted bags were detectable over a few hours, although substantial losses have been observed over a weekend (cf. ref *10*). The pentane solution could also be injected directly onto the chromatographic column for analysis.

The concentration of PAN in solution was measured by addition of an aliquot of solution (30–60 μL) to excess 3 M KOH, followed by colorimetric (*11, 12*) analysis of the extract for nitrite ion. Analysis by iodometric methods gave values ca. 20% higher than with this method, but the results were not very reproducible. The concentration of PAN in carbon tetrachloride could also be determined conveniently by addition of a known amount of benzene to a weighed aliquot followed by comparison of the integrated peak heights of PAN and the standard by NMR. We have not attempted to isolate the PAN from solution (*1, 7*).

No PAN was formed by our procedure when chlorobenzene was the solvent, and perbenzoic acid itself did not yield any peroxybenzoyl nitrate under the conditions described above. We reasoned that both of these results were due to a competitive, oxidative attack on aromatic rings by the peracid moiety under strongly acid conditions. A reasonable yield of peroxybenzoyl nitrate was then subsequently obtained simply by changing the order of addition, so that the peracid was added to the other ingredients stirred at −20 °C. Under these conditions, the destructive side reactions are not competitive with the desired reaction (Table I).

The washed and dried ($MgSO_4$) organic solutions of the peroxyaroyl nitrates showed only infrared absorptions which could be ascribed to solvent and to the desired products. In particular, they were free from aromatic acid ($\nu_{CO}$ at ~1700 $cm^{-1}$) and anhydride ($\nu_{CO}$ ~1770 $cm^{-1}$). One preparation of peroxybenzoyl nitrate contained an impurity with $\nu$ = 1760 $cm^{-1}$, which was removed by concentrating the solution under reduced pressure and below 25 °C to an oil, and selectively extracting the desired product by stirring with *n*-pentane at −20 °C. The aromatic PANs do not appear to be prone to sudden decomposition, although they were never stored in the pure state, and handled with suitable care in amounts less than 200 mg.

The yields of peroxyaroyl nitrates were determined by evaporating the solvent from an aliquot at aspirator pressure and weighing the residue. The absence of decomposition during this procedure was established by dissolution of the residue in the original volume of solvent and by comparison of the IR spectra (*5*) of the original and reconstitued solutions.

NMR spectra were recorded at ambient temperature with a Varian EMI-360. Chemical shifts were measured downfield from internal tetramethylsilane.

## *Discussion*

Nicksic et al. (*13*) reported values of 78 and 137.5 cps, respectively, for the H NMR chemical shifts of PAN in benzene and carbon tetrachloride. The magnitude of this difference surprised us and suggested that the signal in one case may have been due to a decomposition product. Nicksic's assignments are correct, however. We found that the chemical shift of the methyl group decreased regularly when a solution 0.045 M in $CCl_4$ was diluted progressively with benzene (Figure 1).

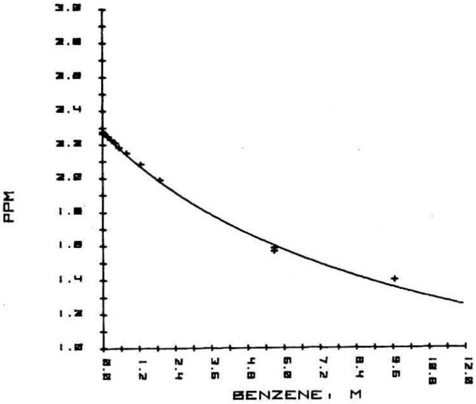

**Figure 1.** Proton chemical shift of peroxyacetyl nitrate (initially 0.045 M in carbon tetrachloride) as a function of added benzene at 27 °C.

The data were analyzed by standard methods (*14, 15*)

$$\underset{2.28\ \text{ppm}}{C_6H_6 + CH_3COO\text{-}ONO_2} \rightleftarrows \underset{\lambda\ \text{ppm}}{\text{complex}}$$

with the assumption that the observed signal position represented an average of free and complexed PAN. The curve through the points in Figure 1 corresponds to the least-squares fit of the data to the equation $(\delta_{\text{obsd}} - \delta_{CCl_4})/(\text{benzene}) = K_{\text{eq}}\lambda - K_{\text{eq}}\delta_{\text{obsd}}$, which gave $K_{\text{eq}} = 0.095\ M^{-1}$ and $\lambda = 0.356$ ppm. The observed value of the methyl resonance in pure carbon tetrachloride ($\delta_{CCl_4} = 228$ ppm) and the calculated value in pure benzene at 11.2 M (1.288 ppm) correspond to shifts of 136.8 and 77.3 cps, respectively, for a 60-MHz instrument. These values are in good agreement with the reported ones (*13*). The upfield shift of the methyl resonance is presumably due to deshielding of the methyl protons in a face-centered complex by the $\pi$-orbitals of the benzene molecule. Similar phenomena have been observed from the H NMR spectra of benzene–acetonitrile mixtures (*17*). The resonances of PAN were very sharp at all concentrations of benzene, implying a complex with $t \lesssim 10^{-7}$ s, which is consistent with the small value of $K_{\text{eq}}$. Upfield shifts of the methyl resonance were also obtained with benzene-$d_6$ in place of benzene.

## *Acknowledgment*

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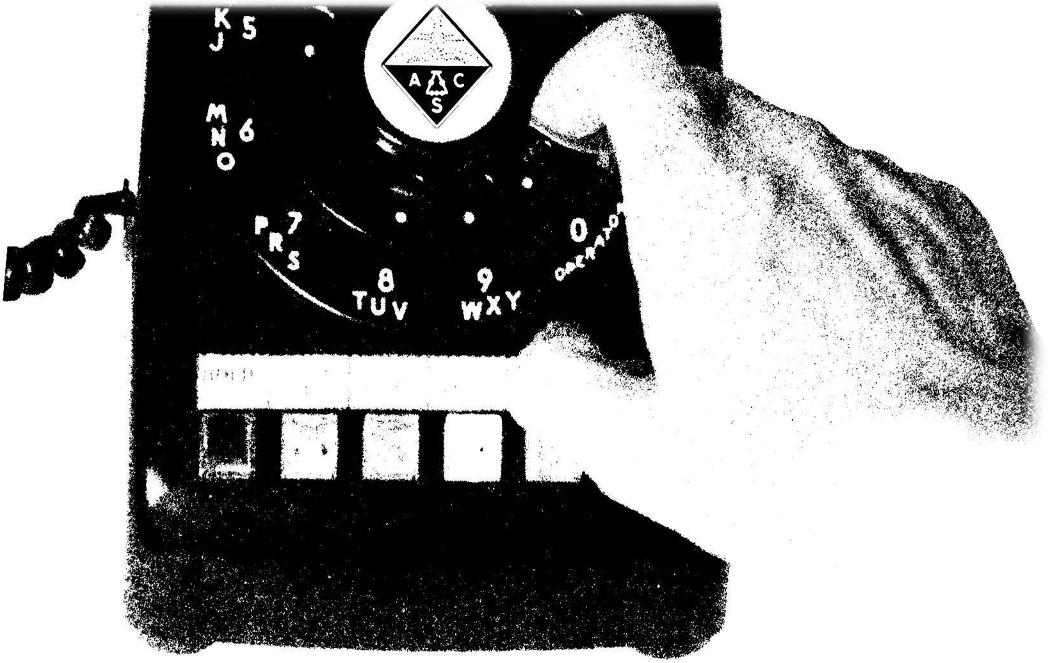

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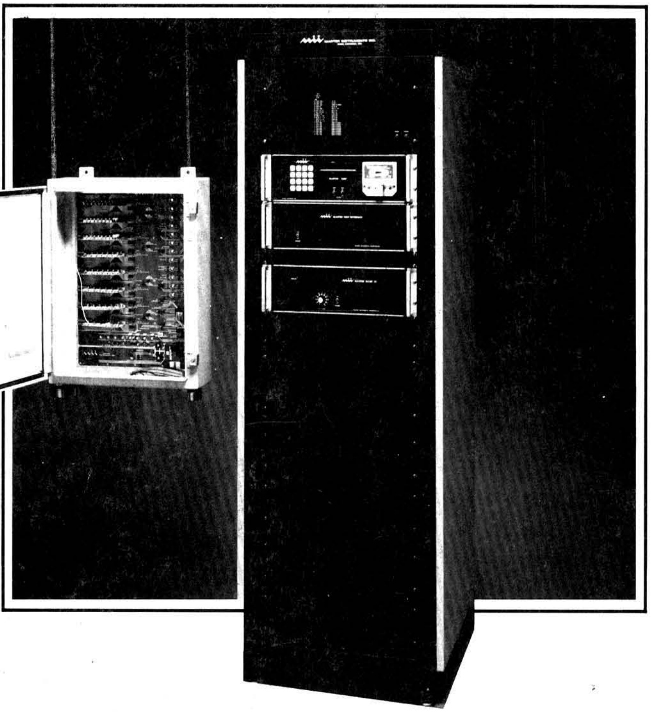

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