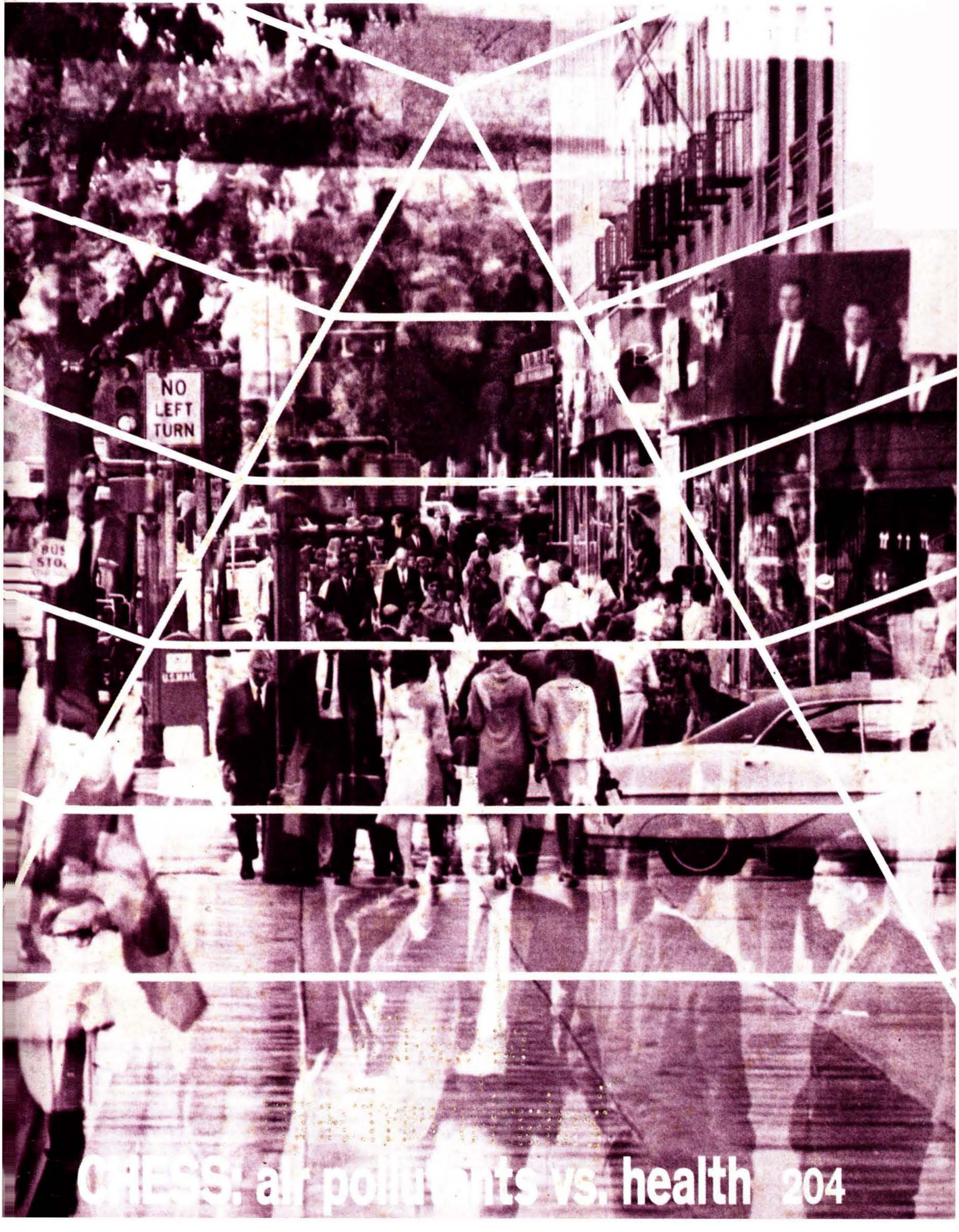
Environmental
Science & Technology

MARCH 1973



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Science & Technology

Volume 7, Number 3, March 1973

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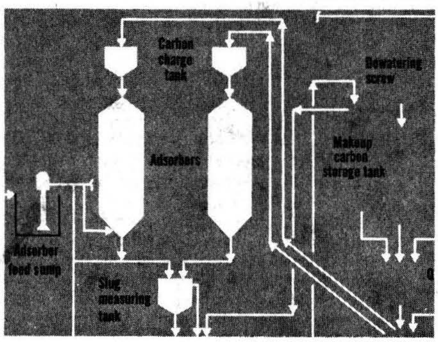

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RESEARCH BRIEFS

Formation of hydrocarbons and oxides of nitrogen in automobile engines is discussed by John Heywood and James Keck of the MIT Department of Mechanical Engineering 216

It is estimated that there are 100 million motor vehicles on the road today and that each car annually emits 1200 pounds of carbon monoxide, 320 pounds of hydrocarbons, and 140 pounds of nitrogen oxides. Basic mechanisms responsible for the production of the latter two pollutants from spark-ignition engines are now understood. Nitrogen oxide formation is rate controlled in the high temperature burned gases inside the engine cylinder; important processes have been demonstrated for hydrocarbons' formation.

Du Pont Petroleum Laboratory's Kamran Habibi characterizes the particulate matter in vehicle exhausts 223

Lead salts, iron as rust, base metals, soot, carbonaceous material, and tars make up the complex mixture of particulate matter emitted from present-day automobiles. Factors including mode of operation, age and mileage of car, and type of fuel affect both the composition and total particulate emission rate. Sampling and analytical techniques are reviewed.

Chemical element balances and identification of air pollution sources is summarized by Sheldon Friedlander of the CIT W. M. Keck Engineering Laboratories 235

By solving a set of simultaneous linear algebraic equations on carbon balance, one can readily obtain the individual contribution of pollution sources. The method has been applied to the particulate matter in the air over Pasadena, Calif. but elemental concentrations by themselves are not sufficient to define the state of a polluted atmosphere or its effect on public health, weather modification, and so on.

CIT W. M. Keck Engineering Laboratories' Rudolf Husar and Minnesota Department of Mechanical Engineering's Kenneth Whitby discuss growth mechanisms and size of spectra of photochemical aerosols 241

The importance of various physical mechanisms, including nucleation, coagulation, and condensation, was shown from a series of photochemical aerosol-aging experiments. From a comparison of smog chamber results and those in a real atmosphere it was found that the size distribution of aerosol in an initially particle-free smog chamber and that during smog formation in a real atmosphere is quite different.

Vertical distribution of photochemical smog in the Los Angeles Basin is discussed by James Edinger of the U. of California Department of Meteorology 247

Oxidant concentration and temperature have been measured by aircraft soundings in the vertical section from the California coastline to the mountains (from Santa Monica to San Bernardino). Perhaps the most striking feature of the distribution is the occurrence of oxidant concentrations within the inversion of the same magnitude as those beneath it.

Robert Lamb and John Seinfeld of the CIT Department of Chemical Engineering present a general theory for the mathematical modeling of urban air pollution 253

A fundamental modeling theory has been developed which includes the requirements for simulating photochemical smog formation in an urban area, wind conditions, and conventional model. An equation has been developed which under certain limiting conditions represents a valid urban air pollution model for photochemical smog formation.

Credits: 183, C&EN's Dermot O'Sullivan; 189 (upper and lower right), Uniroyal Inc.; 189 (center), Maxwell Photos; 191, Kile Studio; 194 (upper), MacMurray College; 194 (lower), Austen Field; 199 (left), Mike Gordon; 199 (right), EPA-Documerica—Belinda Rain

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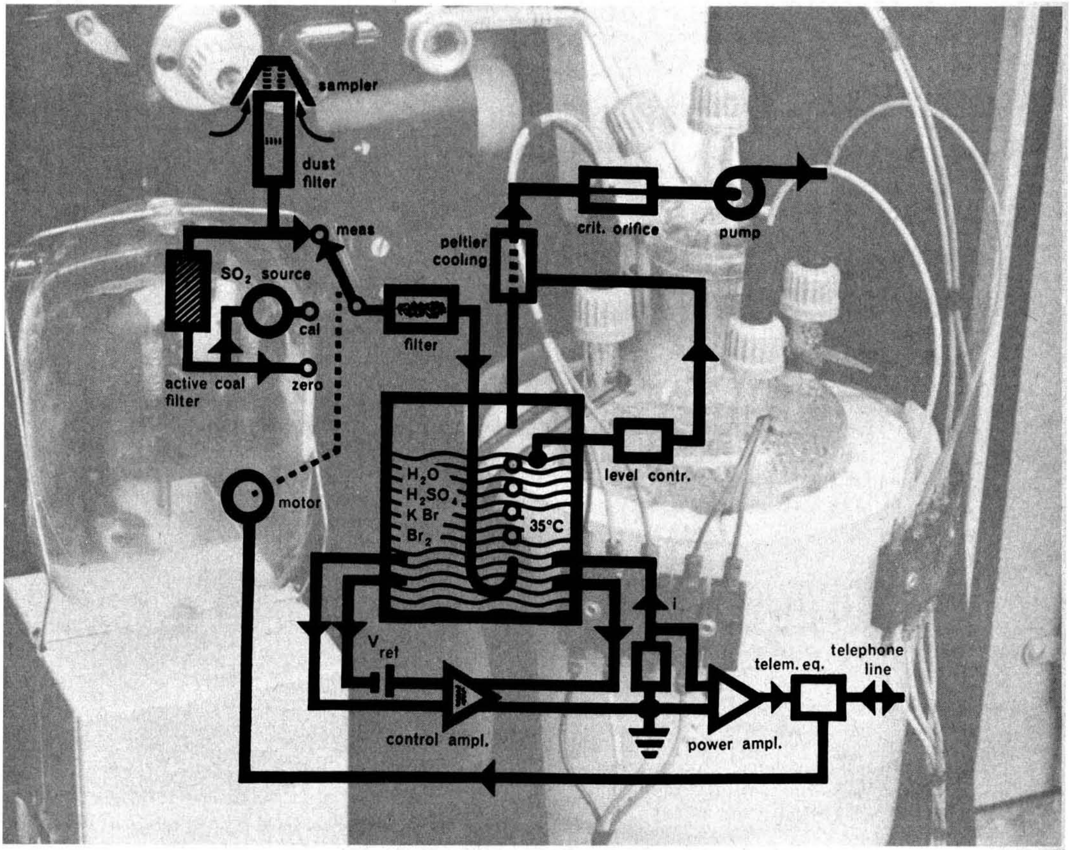

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In each paper with more than one author, the name of the author to whom inquiries should be addressed carries a numbered footnote reference.

But dad, how will you get to work?

Simplistic questions from children have very few answers these days, if indeed they have any at all, and it is especially true with this one. Perhaps the transportation question could be answered years past, but recent air pollution control laws certainly ensnarl one's options.

Early this month, the Los Angeles area plans to hold no less than a series of nine public hearings on the transportation controls that have been proposed to reduce air pollution level in that city's intrastate air quality control region. And although the problems in California area may be more difficult than in other areas, all told there are 28 urban areas in 18 states that are faced, once again, with telling the federal Environmental Protection Agency precisely what each area plans to do to meet the requirement of clean air by 1975. Of course, in the law extensions can be secured up to a period of two years, and in the past, the EPA administrator has granted some.

But early last month, the U.S. Court of Appeals for the District of Columbia rescinded the earlier-granted extensions, requiring the states once again to reconsider these incredibly difficult decisions.

What are the options? Obviously, the list is endless—mass transportation, annual inspection and maintenance programs, conversion of fleet vehicles to natural gas, private bus lanes, rationing of gasoline—certainly you can add others yourself to the seemingly endless list. But that is not the task at hand. The real test is coming forth with a winning combination, one which at the best will not only achieve the standard but one which is viable and somewhat palatable to the public. Perhaps when the public realizes that it is its health that is at stake, perhaps then it will proceed in a rational decision-making process to get on with the cleanup.

By the middle of next month public hearings will have been held in each of the 28 areas and again state control strategies will be formulated. The answers are in the offing.

Stanton S Miller

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LETTERS

Phosphorus in runoff

Dear Sir: The editorial "Runoff poses next big control challenge" in the September 1972 issue correctly points out that more attention should be placed on the role of diffuse nutrient sources as a factor in the eutrophication of natural waters. At the University of Wisconsin Water Chemistry Program, the fertilization of lakes by diffuse nutrient sources has been under investigation for several years. Recently, it has been estimated that about 50% of the total phosphorus annually entering Lake Mendota is derived from rural runoff.

However, preliminary results of studies currently conducted at this laboratory indicated that a significant portion of the total phosphorus in runoff may not be biologically available. The fraction of organic and particulate phosphorus that becomes available in natural waters is extremely important in designing meaningful eutrophication control programs for diffuse sources of nutrients. There would be little point in attempting to control a source of phosphorus if it is known that most of the phosphorus does not become available for biological growth under conditions existing in receiving waters.

As the emphasis in eutrophication control shifts to diffuse sources of nutrients, a much better understanding of the aqueous environmental chemistry of particulate, inorganic, and organic forms of phosphorus and other nutrients must be achieved in order to ascertain the real significance of nutrients derived from diffuse sources in rural and urban areas in stimulating the growth of aquatic plants.

William Sonzogni
G. Fred Lee
University of Wisconsin
Madison, Wis. 53706

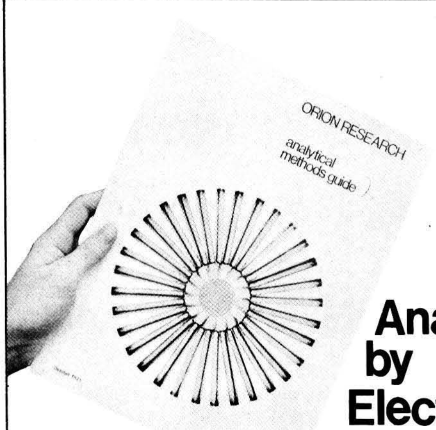
Filtration theory

Dear Sir: Arnold L. Cohen's paper entitled "Dependence of Hi-Vol Measurements on Airflow Rate" (ES&T, Jan. 1973, pp 60–1) reveals a serious misunderstanding of filtration theory and, as a consequence, he reaches an erroneous conclusion concerning the sigificance of his observations. His statement that "an 8 X 10-in. glass fiber filter [is] capable of removing nearly 100% of all particulates 0.3 μ[m] in diam or greater" carries his implication that the filter has a significantly lower efficiency for particles less than 0.3 μm. Mr. Cohen makes this implicit in his conclusion by adding, "Although the glass fiber filters are reported to be extremely efficient for 0.3-μ[m] diam particles."

The error arises from the fact that the filter papers in question are customarily guaranteed by their manufacturer to have a minimum efficiency of 99.97% for monodisperse dioctylphthalate (DOP) mist having a particle diameter of 0.3 μm. The DOP test was recommended by Nobel laureate, Irving Langmuir, who studied the fundamental processes involved in the filtration of chemical smokes for the U.S. Army Chemical Corps during World War II and arrived at the conclusion, based on theoretical considerations, that a 0.3-μm particle is the most difficult to capture because inertial separating forces are ineffective for particles less than 0.3 μm in diameter while diffusional separating forces are ineffective for particles greater than 0.3 μm. More recently, others have performed experiments to test Langmuir's hypothesis and found that particles somewhat smaller than 0.3 μm are harder to filter. Regardless of the exact minimum filterable particle diameter, it represents a minimum point in a particle size curve, and not a cutoff point. It does not mean that everything less than 0.3 μm (or even a significant fraction) passes through.

Therefore, an a priori conclusion that a reduction in dust collection by the Hi-Vol sampler must result from a loss through the paper of "a larger proportion of particles in the lower submicron range" is unwarranted. A more likely explanation of the observed reduction in total collected dust mass is loss of the largest particles by impaction on the inlet louvers of the filter housing at the highest sampling rates studied.

Melvin W. First
Professor of Environmental
Health Engineering
Harvard University
Boston, Mass. 02115



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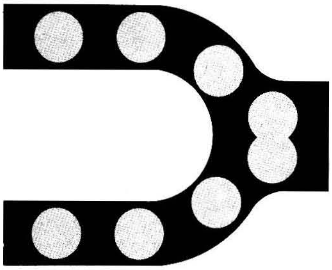

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CURRENTS

INTERNATIONAL

A Governing Council for Environmental Programs has been established by the United Nations General Assembly (UNGA). Elected for a 4-year term, Maurice Strong has been named first executive director. The council has approved 58 nations for membership—Africa (16), Asia (13), Latin America (10), Western Europe and others (13), and Eastern Europe (6). Another item that has been referred to the governing council includes the action plan of more than 100 recommendations for international action adopted at the Stockholm conference. In addition, UNGA decided to locate the Environment Secretariat at Nairobi, Kenya, and called for observance of June 5 as World Environment Day.


Council chairman Strong

WASHINGTON

EPA must review formerly approved transportation control strategies to meet the clean air deadlines. Last month, the U.S. Court of Appeals for the District of Columbia ruled that EPA must rescind the extensions granted 18 states to meet the national air quality standard. Earlier in the approval of state implementation plans, EPA had granted 2-year extensions (till 1977) on such controls.

CEQ finds that better pest controls are not completely reliant on chemical pesticides. Natural integrated techniques of pest management in many cases can offer better pest control at lower costs and with significantly reduced environmental problems. CEQ chairman Russell Train says, "We must let nature work with us in controlling pests, rather than depending on persistent and often toxic chemicals as our only means to meet rising food needs. We must continue to find better ways to control pests if we are to meet our food and fiber needs." Former Secretary of Agriculture Earl Butz says that the concept of integrated pest management is embraced, practiced, and encouraged by the department. Butz was recently appointed Counselor for Natural Resources to the President.

"The President's budget for environmental programs is absurd," says Sen. Edmund Muskie (D-Me.). "This is not a commitment. It is a retrenchment." According to the estimates of this congressional critic, air pollution will be funded at less than one third the authorized levels; waste water construction facilities less than half; solid waste less than 3% of the level intended by Congress; and noise slightly more than 50%. For solid waste, Congress authorized $216 million for development of resource recovery and recycling programs, but the fiscal year 1974 budget virtually abolished the program (see p 197).

The role of recycling in the conservation of material needs be increased, according to the second interim report of the National Commission on Materials Policy. The formation of this commission stems from a requirement of the Resource Recovery Act of 1970. The trends reveal that

- no industrialized nation or area is completely self-sufficient in all materials essential to build a modern industrial society
- the position of the U.S. as predominant producer of metals, minerals, and fuels has declined considerably during the 1950–1970 period
- with the exception of the USSR, major industrialized areas of the world are becoming increasingly dependent upon other developed countries and lesser developed countries for raw materials.

Commerce begins an environmental study of coastal waters off northern Florida, Georgia, South Carolina, and North Carolina. Dubbed Project SCOPE (Southern Coastal Plains Expedition), the expedition will collect data which will enable coastal zone planners to predict the consequence of both natural and man-made activities in these areas. It also promises data which will enable planners better to cope with coastal water pollution. Field work will terminate in December 1974.

STATES

The California Bay Area Air Pollution Control District rescinded its October 1972 decision to ban the construction of new gasoline stations in the San Francisco area. Construction permits were denied on the basis of increased air pollution resulting from gasoline vapors emitted from service stations, but the ban imposed economic hardships and did little to reduce air pollution, the district concluded. However, construction permits will be issued only to new stations equipped to recover at least 90% of the fumes emitted when underground storage tanks are filled. Also, the stations will have to install, by January 1, 1974, equipment to control 90% of the vapors emitted when vehicle tanks are filled with gasoline.

Fume controls required

A picnic pavilion "that ecology built" is under construction in Denver, Colo. The $60,000 pavilion will consist of panels made from used container glass and urban demolition rubble such as bricks and masonry. The glass-rubble panels were developed by the Colorado School of Mines Research Institute (CSMRI), and the pavilion is financed by CSMRI, the Glass Container Manufacturers Institute, the Colorado Soft Drink Association, and several Denver industries. Approximately 1500 panels will be needed to build the shelter and will require about

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We don't claim Chiyoda has all the answers. But we do feel our 1,700 engineers and scientists, and those at other technology-minded companies around the world provide hope. And with community support we can make technology solve the problems caused by technology.

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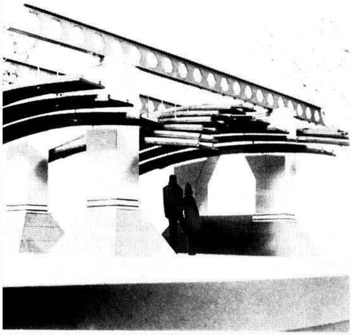


Denver's "waste" pavilion

29,000 lb of demolition rubble, 15,000 lb of reclaimed container glass and 2800 lb of clay. The reclaimed glass and rubble are ground up and mixed with clay. The mix is then cast into panels by a vibration process and fired in kilns.

Colorado standards for waste discharges, adopted by its Water Pollution Control Commission, became effective in January. With the exception of storm water runoff and agricultural return flows, the standards apply to all waste water discharged into any classified waters of the state or any tributaries of such classified waters. Restrictions are placed upon settleable solids, suspended solids, turbidity, color, pH, fecal coliform, dissolved oxygen, residual chlorine, and oil and grease. The commission also has the option to establish more stringent restrictions if deemed necessary.

Ohio's EPA has ordered the Chemline Corp. (Lisbon, Ohio) to cease and desist its industrial waste disposal operations at an abandoned strip mine because liquid wastes were leaking into nearby state waters. The firm must reclaim the land within 17 months or pay a $450,000 fine to the EPA. Also, Chemline's water discharge permit will not be renewed by the state in view of violations of applicable regulations.

An algae-eating fish, the amure, which originates in Asia is being tested in Ohio waters to control algae growth. However, New York's Commissioner of Environmental Conservation, Henry Diamond, says the fish has little effect on algae and may compound eutrophication since its system only partially digests its food, thus enriching the water.

Texas' Gulf Coast Waste Disposal Authority (GCWDA) and five industries—Atlantic Richfield Co., Air Products & Chemicals, Inc., Champion International, Crown Central Petroleum Corp., and Petro-Tex Chemical Corp.—located on the Houston Ship Channel signed an agreement for waste water treatment in January. As a result, the first regional approach to the operation of waste water treatment plants in the U.S. will be completed in early 1975. The $25 million waste water treatment facility, to include a collection system, primary and secondary treatment, and sludge handling and disposal, will treat the wastes from the five participating industries. GCWDA purchased Champion International's waste water treatment plants plus additional land adjacent to the Channel. Pipelines will be constructed from the plants to the treatment facility, and the complex will be expanded to include sludge incineration.

In cooperation with the City of San Antonio, Tex., Southwest Research Institute and the federal EPA are operating a 500,000-gpd pilot-scale sewage treatment plant to remove viruses from municipal waste water. Removal or inactivation of potentially hazardous viruses is desirable at some stage of water treatment if water conservation practices involve direct water reuse. In the pilot plant, lime coagulation, usually a third treatment step after conventional biological treatment, is moved to the primary treatment stage specifically for virus removal.

TECHNOLOGY

Removal of mercury from chlorine plant effluents is now possible. The process is available for commercial licensing from the FMC Corp. Protected by U.S. patent, the process requires only standard mercury cell chlorine plant engineering facilities and equipment. FMC reports that its process does not require exotic resins or catalysts; all reagents necessary for their process are generally available at chlorine plants. Originally developed for the company's Canadian 175 tpd chlorine–caustic plant in Squamish, B.C., the process yields, on the average, liquid effluents with 3 ppb mercury, solid effluent with 28 ppm mercury, and a total mercury discharge averaging less than 1.5 lb of mercury per week.

Recovering mercury from chlorine plants

A new aluminum smelting process uses less energy, less labor, and less space than today's conventional potline production method. Developed by Alcoa, the revolutionary method is the first basic change in the electrolytical process that was discovered independently by Hall and Heroult in the latter half of the 19th century. In the old process, alumina is dissolved in an electrolyte of molten cryolite whereas in the new process, alumina is combined with chlorine first to form an aluminum chloride which is then dissolved in an electrolyte. The process is said to have taken 15 years and $25 million to develop; Alcoa is planning to build a small plant in the U.S. by 1975.

Contaminated gas is being turned into usable natural gas at the first commercial gas conditioning plant of Systems Capital Corp. (Phoenix, Ariz.). The plant uses a three-bed molecular sieve process system developed by SCC and is in full operation. The Phoenix plant receives gas, containing up to 30% carbon dioxide, from the Salt Lake Field of Seaboard Oil & Gas Co., located in the Los Angeles basin area. Don Benscoter, chairman of SCC says, "The new, patented three-bed processing system appears to be one of the most economical ways of removing carbon dioxide. In addition, this system can be used to remove other contaminants such as water and hydrogen sulfide from natural gas."

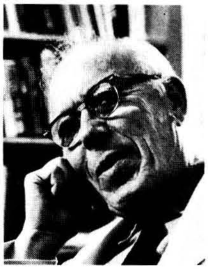

PORTABLE OPACITY METER

CURRENTS

In practical incinerator tests, polyethylene wastes have been burned resulting in lower emissions than those specified under New York City statutes. High-density polyethylene milk bottles in normal residential garbage produce no trace of carbon monoxide and about one third the particulate emissions permitted under the city statute. Tests were conducted by the New York Testing Laboratories, Inc., for the Celanese Plastics Co., producer of Fortiflex, high-density polyethylene resins. On the average, municipal refuse contains 2–5% by weight of plastics. When a charge of 25% high-density polyethylene and 75% garbage was used, actual particulate matter emissions in two tests were 0.13 and 0.17 lb/hr; permissible emissions were 0.38.

VIEWPOINT

Rene Dubos discussed certain limitations of the 4th law of ecology —Barry Commoner's "Nature knows best"—in the 1972 B. Y. Morrison Memorial Lecture delivered at the AAAS meeting (Washington, D.C.) late last year. The professor emeritus of Rockefeller University said, "Most surprising is the fact that even without environmental changes caused by human interference or accidental cataclysms, nature fails in many cases to complete the recycling processes which are considered the earmarks of ecological equilibrium. Examples of such failures are the accumulation of peat, coal, oil, shale, and other deposits of organic origin . . . . Just as it is erroneous to claim that nature has no waste, so it is erroneous to claim that it has no junkyards. The science of paleontology is built on them. . . . The solid waste problem has become grave because we produce more wastes than in the past, and they are commonly of a chemical composition not found in natural ecosystems."


Lecturer Rene Dubos

INDUSTRY

Petrochemical industry giants, including Union Carbide, Celanese, Du Pont, Dow, Hercules, Monsanto, and other chemical and rubber companies, have taken steps to see that the industry has adequate supplies of feedstocks. The companies have formed a Petrochemical Energy Group (PEG) which will serve as a "community of interest" to push for liberalized import tariffs on crude earmarked for chemical feedstocks. PEG says such liberalized quotas would stimulate domestic refiners to build more refining capacity—a step the oil companies are not anxious to take in the face of uncertain government policy on crude supply. Relying upon foreign refining capacity would add additional uncertainties to the already existing instability of imported crude sources, PEG believes.

Rust Engineering will construct a pilot plant for coal gasification by the Synthane process; the company was the lowest of eight bidders for a BuMines contract. Key to this process is a patented coal pretreatment step which makes it possible to use all grades of coal, including "caking" varieties generally not considered applicable to gasification processes. Scheduled to be on stream by mid-1974, the pilot plant will convert 75 tpd of coal to pipeline quality gas. Value of the contract is $9.65 million. Rust, a member of the Environmental Systems Group of Wheelabrator-Frye, has just recently been awarded an $18 million contract to build a pilot plant to make low-sulfur, low-ash, solvent-refined coal.

Members of the electric utilities industry have joined forces to create the Electric Power Research Institute (EPRI) which will carry out a unified R&D program aimed at solving technical problems unique to the industry. EPRI's first president is Chauncey Starr, former dean of the UCLA School of Engineering; William Meese, president of Detroit Edison Co., is EPRI's chairman and chief executive officer. Primary R&D goals include development of coal gasification, safety designs for nuclear power plants, and improvement of transmission efficiency of power lines. Some projects under study by the Edison Electric Institute, including research on fusion reactor design, fuel cells, and breeders, are scheduled for transfer to EPRI, according to Starr.


EPRI's Chauncey Starr

Combustion Engineering is moving into the supplemental boiler fuel picture in a bigger way. C-E has completed a study for the U.S. Department of Agriculture on the advantages of burning wood residues mixed with municipal solid waste for generating electric power. C-E estimates that the country's 400 million tons of refuse and wood residue could produce some 30 million kWh when fired as a primary or supplementary fuel in steam-generating units. The study comes hard on the heels of an agreement among C-E, the federal EPA, and the City of St. Louis to study the use of municipal refuse as a supplementary fuel for producing electricity from steam. On this project, C-E is cooperating with Union Electric Co. and the consulting engineering firm of Horner and Shifrin.

Expenditures for water pollution control and noise pollution control made mandatory by recent legislation will soar by the end of the current decade, according to two new studies from Frost & Sullivan, a technological market research organization (New York City). Capital expenditures for municipal and industrial water pollution control will rise to $4.8 billion by 1980 from the 1970 level of $2.9 billion. Additionally, expenditures for noise control products and materials, design improvements, and consulting services will rise to $1.8 billion by 1980, up from the 1971 figure of $700 million.

OUTLOOK

Scrap tires can yield marketable products

The 200 million tires thrown away annually could be recycled into asphalt, fish havens, or even protein

Recycling is the key word in environmental circles these days—federal and state officials, environmental groups, and the public are all clamoring for reclamation programs for any number of wastes. In spite of this apparent support, certain problems continue to hamper effective, economical recycling. So it is with reclaiming rubber.

Approximately 11 billion lb of rubber products are produced annually in the U.S. Tires constitute the largest segment of these goods, and waste rubber—more than half of the rubber produced annually—is 70% tires.

Tires have certain characteristics, lauded when in use, that create inherent problems associated with their disposal. For example, tires are a heterogeneous combination of materials (fibers and metals) made in various sizes and shapes. They are scattered throughout the U.S., are not easily degradable and will not compact in landfill operations and, although readily combustible, they create air pollution problems when burned in ordinary, low-quality incinerators. Of course, open burning, in most instances, is prohibited.

The tire disposal problem will continue to grow as more than 211 million tires for passenger cars, trucks, buses, motorcycles, and off-the-road vehicles and equipment are manufactured annually, and, at the same time, more than 200 million old tires are discarded each year. Since tire manufacturing is growing at a rate of 5% annually, these numbers will increase. Also, new tire depth and tread regulations are shortening the highway life of tires.

What to do with millions of tires

Backyard swings, boat bumpers, and flower planters obviously cannot consume 200 million tires each year. However, for the past 70 years or so, rubber reclaimers have been taking old discarded tires and producing quality pliable rubber for use in new tires or other rubber products. In fact, these reclaiming companies formed the Rubber Reclaimers Association (RRA) some 40 years ago. However, business is far from good. Twenty years ago nearly two dozen member companies reused nearly 303,000 long tons (2240 lb/ton) of rubber per year; now the seven remaining reclaiming rubber companies reuse only 190,000 long tons annually.

RRA members—Uniroyal, Inc., U.S. Rubber Reclaiming Co., Midwest Rubber Reclaiming Co., Centrex Corp., Goodyear Tire and Rubber Co., Nearpara Rubber Co., and Goodyear in Canada—attribute the decline to economics. It's more and more difficult to compete with inexpensive synthetic rubbers and plastics, and natural rubber is selling at a lower cost now than several years ago. In reclaiming, however, energy, manpower, and equipment costs are continuing to rise.

Another contributor to the declining reclamation business is aesthetics. Reclaimed rubber is black, which was great for floor mats, trunk mats, and running boards in cars 20–30 years ago. Now, auto interiors contain brightly colored vinyls or fiber carpets. Black is not beautiful for reclaimed rubber.

Nevertheless, reclaimed rubber is presently used in a number of goods (see box), but the amounts are small—accounting for only 5% of the waste rubber in the U.S.—and uses are not expected to increase significantly. However, RRA is backing a special use for reclaimed rubber, which, according to RRA vice-president Walter Markiewicz, would eliminate unsightly mounds of discarded tires dotting the countryside. The answer—using reclaimed rubber in asphalt for road surfacing.

Reclaimed rubber uses

- **Tires, tire repair material**
- **Inner tubes**
- **Hard rubber battery boxes, covers, vents, steering wheels**
- **Auto mats, mechanical goods**
- **Heels, soles, footwear**
- **Cements and dispersions**
- **Hose, belting, packing**
- **Mechanical goods, not auto**
- **Rubber surfacing materials**
- **Other—toys, proofing, insulated wire, etc.**

Sure, says John Q. Public, put rubber in roads along with glass, plastics, and the rest of the garbage. That's everybody's answer. Not so, replies RRA. Asphalt pavement consists of two components—aggregate and binder. Glass, plastics, and other solid waste (including ground rubber) could substitute for the aggregate. However, reclaimed rubber enhances the properties of the binder in several ways. The resilience of the road would be increased in the winter, and flowing characteristics of asphalt would be reduced in the summer months when road bed temperatures can reach 140°F. Rubber reduces the tendency of asphalt to bleed to the road surface where it presents a skidding hazard; rubber in the mix allows more asphalt to be added for better aging and reduced raveling tendencies (and no bleeding from the excess asphalt).

The road would have greater resistance to compaction due to "rebound" of the rubber in the mix; also, increased resiliency reduces surface cracking. The asphalt-rubber mix would cost more, granted, but the increase in road paving costs would be offset by less repair and longer life of the roads. Another economic advantage of using reclaimed rubber in roads is little or no transportation costs—roads are all over the country as are tires.

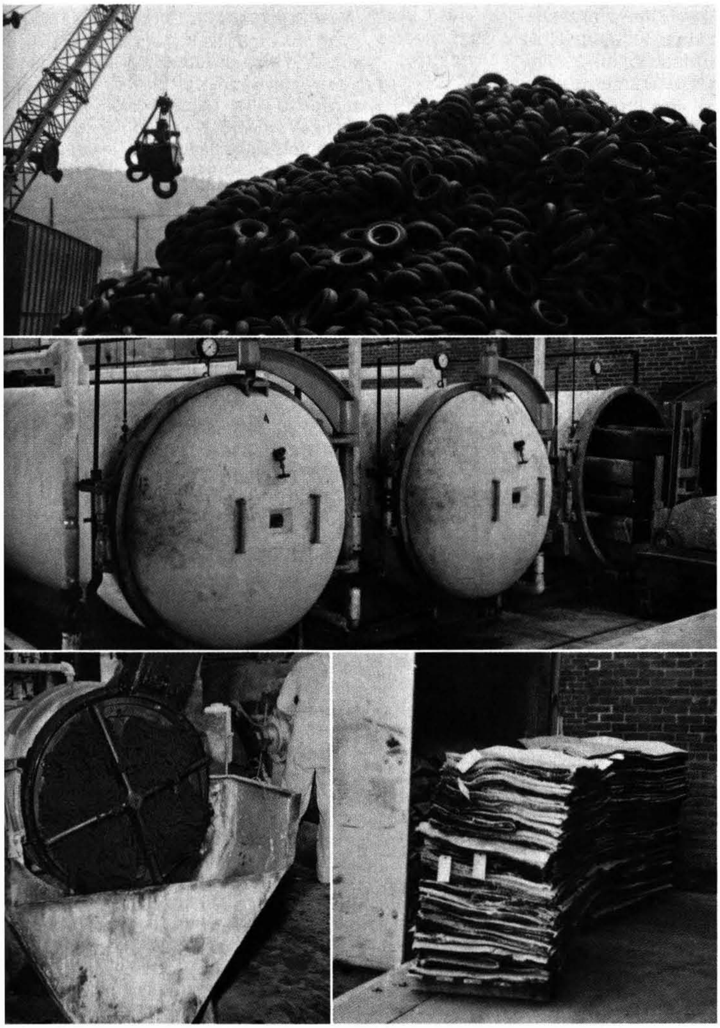
Both laboratory and field testings of the asphalt-rubber mixture have yielded favorable results. All tire manufacturers have been experimenting with rubber in road pavement, and the University of Connecticut received a grant from RRA to further test this use. If 1–2% reclaimed rubber in roadbeds became common practice, 60% of the nation's waste tires then would be utilized usefully each year. RRA is now seeking federal EPA and Federal Highway Administration blessing for reclaimed rubber in asphalt to become eligible for federal funding of projects.

New York state is using reclaimed rubber with hot asphalt to seal cracks and joints in highways. "The mix lasts twice as long as ordinary asphalt, penetrates deeper into cracks, and doesn't get as brittle in freezing weather," says State Transportation Commissioner Raymond Schuler. The improved sealant is expected to last 2–3 years rather than the one-year life span of ordinary asphalt sealants.

Reprocessing old tires

Reclaimed rubber is produced by treating vulcanized waste rubber with chemical agents, heat, and intensive mechanical working to produce a uniform consistency. Tires or waste rubber first passes through crackers for size reduction. Crackers are machines with two rolls rotating at different speeds to create a friction ratio for shearing. As the tires pass into the cracker, the slower roll holds the tire while the faster roll corrugations shear, slice, crush, and abrade the tire. Bead wire, which holds the tire firmly to the rim of the wheel, is removed after the tire passes through the cracker.

Rubber particles from the crackers then pass through a fiber separation process to remove tire-reinforcing materials such as cotton, nylon, rayon, polyesters, fiber glass, and metal from the rubber. This involves use of hammer mills (high-speed rotating drum with bars or knives mounted on the periphery of a drum), sifters, or beaters which complete fiber removal. The fiber waste is baled, and the "clean" rubber particles are finely ground to 30-mesh size.



Reclaiming rubber. Scrap tires (top above) are first ground into small pieces which are reprocessed by autoclaving (above). After softening, the reclaimed rubber is strained (left) and refined into slabs or bales for shipping (right)

This finely ground rubber can be reprocessed by three different methods: the digester or wet process, devulcanizer or dry process, and mechanical process. In digesting, rubber particles are placed in a vessel with water and softening chemicals, heated, and then discharged as a slurry. The now-softened rubber is mechanically dewatered and dried.

In devulcanizing, fine rubber particles are premixed with softening chemicals and placed in an autoclave. After this steam pressurization treatment, rubber is cooled and ready for further processing.

The mechanical process, unlike the other two processes, is a continuous rather than a batch-type operation. Fine-ground rubber is fed into high-temperature shear machines with the softening chemicals. The discharged rubber needs no drying and is ready for further processing.

The rubber from all of the softening processes is intimately mixed with compounding ingredients which give the finished relcaimed rubber special physical properties. The softened product is afterward strained and refined into a thin film by huge rollers. It can then be formed into slabs or bales for shipping.

Other ways to recycle

Tires can also be crumbed—just ground into fine particles—for use as aggregate or in products where devulcanized rubber is not required. The city of Tucson, Ariz., currently uses rubber crumb in asphalt patching mixes. Also, crumb can be used under house foundations as a cushioning agent.

Goodyear is installing a furnace (built by Lucas American Recyclers, Inc.) at its Jackson, Mich., tire plant that will use old tires as fuel to generate steam for new tire production. Whole unshredded tires will be fed continuously bv conveyors onto a rotating hearth. As the tires move in a spiral toward the center of the hearth, the temperatures (up to 2400°F) will oxidize even the wire bead.

The incinerator is not yet operating and will not save money for Goodyear, although tires have 50% more Btu value than coal. The special incinerator is more expensive than conventional units, and company officials think it will be more expensive to run. However, it can use 3000 tires daily that would otherwise pose disposal problems.

Firestone has developed a destructive distillation process for reclaiming hydrocarbons and carbon black from tires. In this process, tires are shredded, fed into a reactor, and heated. As many as 50 different chemicals have been identified and collected in the gases driven off. The economics of this process will probably depend on the carbon black produced which may compete with carbon black now on the market. A process developed by Cities Service and Cabot Corp. to recover carbon black from tires is also plagued with economic problems.

RRA does not view incineration as the answer for waste tire disposal for two reasons. First, the economics of the equipment and the process itself have not been favorable on any concept yet developed. Second, burning the tires as a fuel eliminates any value added to the tire when processed from the original petroleum products into rubber. Any reclaimed tire used as a rubber will recover some of the value in the material.

Scientists at Rutgers University (New Brunswick, N.J.) have isolated about 50 organisms that not only reduce the size of rubber particles, but also remove most of the oil. Oxygen added to the rubber gives it exchange properties making it useful as a soil conditioner. For example, when the aerated rubber is mixed with sand, water retention is increased, and when it is mixed with clay, water passes through.

Other scientists claim that shredded tires mixed with shredded polystyrene can effectively clean up oil spills. Others say that high-protein foodstuffs and water purification material can be produced from tires. Goodyear, University of Cincinnati, and Texas Transportation Institute have tested scrap tires as crash barriers for stationary highway hazards (bridge piers, abutments).

Every major rubber company is involved in one or more artificial reef programs. More than 80 reefs from artificial scrap tires are being built along the East and Gulf coasts. Proponents of tire reefs cite the abundant supply of tires, low total cost, nonmagnetic properties, crevices for fish "homes," marine organism growth potential, and long-lasting materials.

RRA and others agree that using tires in reefs is feasible, but only so many reefs can be built. Reefs will not solve the tire disposal problem year after year, and transportation costs to coastal areas could cause financial difficulties. Also, the long-term effects of slowly disintegrating tires has not been proved.

The only economically sound and effective method yet evaluated for tire disposal, in the opinion of RRA, is using reclaimed rubber in asphalt pavement. Unless this is undertaken on a large scale, says T. H. Fitzgerald, another RRA official, rubber reclaiming will stay at its present low level or slowly decline. CKL

EPA's technology transfer: now geared to industry

Through capsule reports, seminars, and design manuals, EPA publicizes available waste control techniques


Seminar. *Experts thoroughly explain available pollution control technology*

Over two years ago, EPA began a technology transfer program for marketing the products of federal research, development, and demonstration activities. Technology transfer (TT) was aimed at making an impact on the construction of municipal waste treatment facilities, with plans for expansion into other fields (ES&T, April, 1972, p 314).

EPA activated its industrial technology transfer program to disseminate information to industry on the technology now available for the control and treatment of air, water, and solid waste pollutants. In the past nine months technology transfer staff members have covered a great deal of ground in providing plant management with information of the available pollution control and treatment technology.

The industrial pollution control branch, headed by Paul Minor and assisted by Dennis Cannon for EPA in Washington, D.C., publicizes the latest industrial waste treatment technology in three ways: technical capsule reports, seminars, and design manuals. Capsule reports are concise technical documents, usually 6–8 pages, which describe successful pollution abatement projects proved reliable in either demonstration or full-scale operation. In some cases, they involve non-EPA projects. The purpose of the capsule reports, explains EPA's Minor, is to bring to light the in-plant control and treatment methods available for industrial waste control when the knowledge is first revealed.

Six capsule reports are either distributed or being printed: recycling zinc in vicose rayon plants by two-stage precipitation (American Enka), dry caustic peeling of peaches (Delmonte), hot air blanching of vegetables (National Canners Association), aerated lagoon treatment of sulfite pulping effluents (Crown Zellerbach), color removal from kraft pulping effluent by lime addition (Interstate Paper), and process changes for waste abatement in brass wire mills (Volco Brass & Copper).

Eight other capsule reports are scheduled for completion by the end of June. Potential topics include molecular oxygen used in black liquor oxidation (Owens Illinois), by-products from brewery wastes (Coors), regeneration of sulfuric acid pickle liquor, and total recycle in a coal-fired power plant; others are still under consideration.

Industrial seminars

The industrial seminars, one of the most important phases of the technology transfer program, usually consist of a two- to three-day technical meeting. The seminars are geared to provide plant management (usually smaller manufacturers) with a thorough understanding of available pollution control technology. EPA officials as well as pollution control and plant processing experts participate in the seminars. EPA aims to present the best treatment alternatives without emphasizing or recommending any specific method of pollution abatement.

The seminars are pulled together by EPA's Minor and Cannon who draw upon the expertise within EPA as well as industrial experts in that area of process design and pollution control. Seminars are scheduled at the request of any of the 10 federal regions. In this way, EPA can respond to industrial needs and questions.

Eight seminars on five topics—poultry processing, metal finishing, meat packing, dairy products, and seafood processing—are scheduled before the end of fiscal 1973. At press time, six such seminars had been held and enthusiastically received.

A seminar on a particular industry's waste problem consists of several individual sessions. A general session covers regulatory aspects for this industry—the permit program, effluent guidelines, pretreatment requirements, the new water bill—and some basic technology in that area. Then two detailed technical sessions are held, one on in-plant process changes for pollution abatement and the other on waste treatment. Technical handouts explaining in-plant processing control and treatment alternatives are given to each attendee.

The final session includes a management consultant to discuss financial alternatives including any assistance from the Small Business Administration and the Internal Revenue Service. EPA officials encourage questions and discussion (sometimes heated) to become familiar with industry's problems in meeting environmental requirements.

Design manuals

Technology transfer's industrial waste group is now preparing design manuals which are developed under contract. A water monitoring manual—a guide for instruments for waste water sampling—will be out by June. An air monitoring manual is scheduled for fiscal 1974. Design manuals for various industrial sectors, aimed at design engineers in one particular industry, are also in the works. The iron and steel and the pulp and paper industries will be covered first. Other areas under consideration for detailed coverage in the manuals include the power and textile industries. The industrial waste program will continue full steam ahead by updating its past works and continually looking into new sources of industrial pollution. CKL

The environment in Illinois

Three state agencies plus the attorney general's office join hands to protect the environment and nail polluters

When it comes right down to the nuts and bolts of pollution control, it's sometimes pretty hard to tell just who is responsible for what. Pollution, so it is often argued, knows no boundaries and must therefore be controlled on a regional or a national basis.

But even a national program bogs down if it is too much centralized because there is seldom enough manpower to keep tabs on the individual polluter. Surely, the counterargument runs, state and local governments are closer to the source of pollution and should therefore be more effective in solving day-to-day problems as they arise.

And so the national tennis games go. After a couple of years of frenetic federal activity, the ball seems once again to be back on the states' side of the net.

And it seems likely to remain there for some time. The word is out from Washington that state governments will have the major responsibility for implementing environmental protection measures across the country. Most of the states have responded by reorganizing their bureaucracies to handle the load.

Some use the one-from-column-A, one-from-column-B, Chinese-restaurant approach, taking "environmental" duties away from boards of health, water supply, and the like, and coordinating them under the framework of a new state agency.

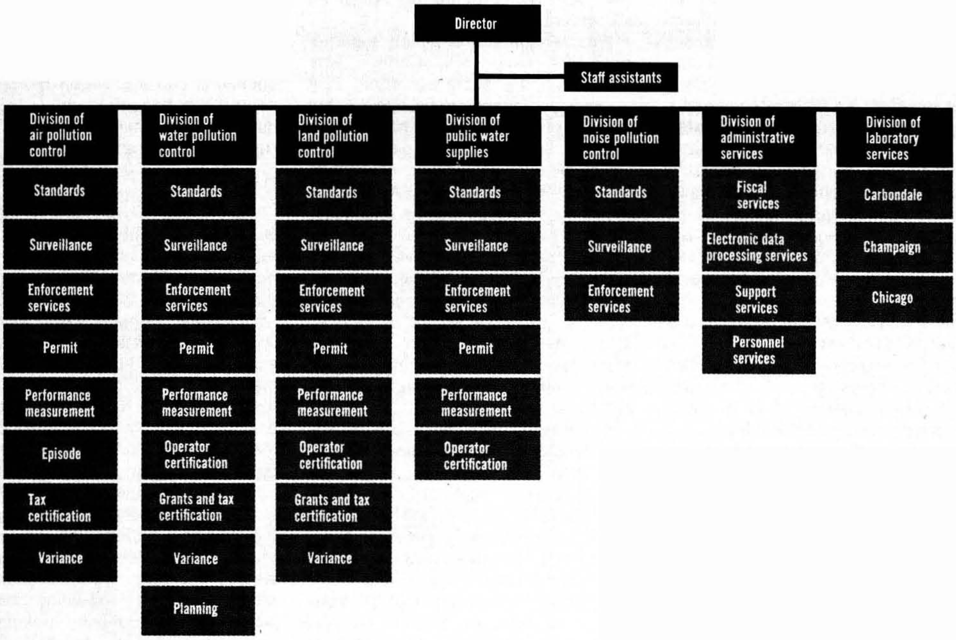
Others go all the way and design new agencies and programs more or less from the ground up. Illinois' scheme for protecting the environment stands as a unique example of the ground-up approach.

New environmental act

In July 1970, the Illinois General Assembly passed the Environmental Protection Act, the state's landmark piece of environmental legislation. Prior to 1970, Illinois had a number of boards and agencies, each dealing with various pollutants or aspects of pollution. There was, for example, an Air Pollution Control Board, made up of nine unpaid members with various professional qualifications but limited jurisdiction relating to enforcement of air pollution laws and some power to adopt new regulations.

Illinois also had a Sanitary Water Board which had limited power to

Organization of Illinois EPA



Governor appoints Leahy EPA director

Illinois' new Environmental Protection Agency Administrator Mary Lee Leahy, a 32-year-old Chicago lawyer, is no newcomer to environmental matters. Leahy was instrumental in incorporating the state's Environmental Protection Act into the new state constitution in 1970 and spearheaded the *qui tam* section of the law which gives private citizens the right to sue polluters on their own behalf.

Leahy, who was very active in the gubernatorial campaign of Illinois' new Governor Dan Walker, was a Fulbright Scholar and holds a Master's degree in political science from the University of Manchester in England in addition to her law degree from the University of Chicago.

Before joining EPA, she was an assistant professor of law at the Illinois Institute of Technology—Chicago Kent College of Law.

At press time, Leahy had been in her post only a week and had issued no major policy statements. No additional changes in personnel or agency organization had been announced.

Leahy is widely regarded as "tough and businesslike," at least by the Illinois media, and she is expected to keep a close watch on the state's polluters. Most agency employees are "enthusiastic" about their new boss, according to an EPA spokesman, and don't expect any radical changes in the agency's operations or goals.

Outgoing EPA director William Blaser, meanwhile, will keep his hand in environmental matters in the private sector. Blaser has formed a new consulting firm, Blaser, Zeni and Co., specializing in governmental and environmental affairs.

adopt water quality standards within the state and similar limited enforcement powers. The state's effluent standards covered only BOD and suspended solids; technical guidelines dealing with other contaminants were not legally enforceable. (The Chicago Metropolitan Sanitary District, had somewhat tougher standards.) Other agencies were responsible for water supply, landfill operations, and the like, but Illinois lacked a centralized agency which could coordinate a state-wide, all-out attack on pollution.

With the passage of its Environmental Protection Act, however, state government got into environmental protection for keeps. The act set up three separate but interrelated agencies responsible for curbing pollution. Two of the agencies—the Illinois Environmental Protection Agency (EPA) and the Illinois Institute for Environmental Quality (IEQ)—were established as part of the executive branch of government. The third agency—The Pollution Control Board (PCB)—is independent, although its members are appointed by the governor, subject to specific professional qualifications and advice and consent of the state senate.

The Environmental Protection Agency is the state's permit, inspection, and enforcement branch. The Institute for Environmental Quality is the research arm of the state for environmental matters. The Pollution Control Board is both quasilegislative and quasijudicial; it both adopts regulations of environmental import and sits as a sort of pollution court to hear alleged violations of regulations and the Environmental Protection Act.

A fourth agency dealing with environmental protection—although not specifically so designated under the Environmental Protection Act—is the office of the state attorney general. The attorney general has some prescribed duties as legal counsel to the PCB, but he has even broader powers which make him, in effect, a free agent in pollution cases. The scope of his power makes his office loom large—some say too large—in pollution control in Illinois.

Pollution Control Board

As defined by the Environmental Protection Act of 1970, the state's Pollution Control Board consists of five members with three-year terms each appointed by the governor with the advice and consent of the state senate. During their tenure, board members are relatively immune from political pressure. The act states that no more than three board members may be a member of any one political party and specifies that PCB members must be "technically qualified."

The board's first chairman was David Currie, a professor of law at the University of Chicago, and one of the chief architects of the Environmental Protection Act. Currie recently resigned his position on the PCB to resume teaching at the University of Chicago Law School and was replaced by acting chairman Samuel Lawton. During the interim between the departure of former Governor Richard Ogilvie and the inauguration last January of current Governor Dan Walker, the PCB lacked a quorum. Governor Ogilvie had appointed two members to fill vacancies on the board but the senate had declined to consent to their nominations, feeling that Governor Walker would like to name his own board members. At press time, Walker had renominated Ogilvie nominee Donald Henss, a Rock Island, Ill., lawyer and former state legislator, to the PCB. Walker had not renominated John Parker, a temporary appointee whom Ogilvie had tapped to fill the balance of the term of Samuel Aldrich, an original member of the PCB. The senate has not yet confirmed the Henss appointment, but is expected to do so. In the meantime, Henss has authority to act as a member of the PCB.

The board, which now has a quorum, consists of acting chairman Lawton, Jacob DuMelle, an engineer, and Henss. When the PCB reaches its full complement of five members, Governor Walker will presumably appoint a chairman.

Duties and authority

The duties of the PCB are essentially three-fold, Lawton explains. First, and perhaps foremost, the PCB has power to enact environmental regulations within the framework provided by the legislature. Second, the PCB sits as a court to hear matters relating to violations of environmental regulations or provisions of the Environmental Protection Act. Third, the PCB has power to grant one-year variances and it also has jurisdiction to hear appeals from polluters who are denied various permits by the state's EPA.

Originally, the PCB had jurisdiction over operating permits for nuclear steam-electric generating facilities and fuel processing plants, but recent federal court decisions have held that the Atomic Energy Commission preempts states' rights to regulate nuclear facilities, Lawton points out.

Legal challenges

The power to draft environmental legislation is an important one, Lawton notes, since it represents authority that is usually reserved by state legislatures. That fact is being used as the basis for appeal in a number of important cases in Illinois by polluters who contend that such law-making power without direct election by the voters is unconstitutional.

In its capacity as an environmental court, the PCB hears cases brought by the EPA although Lawton points out that private citizens may also bring actions before the PCB.

The board has authority to enter cease and desist orders and penalties as high as $10,000 plus $1000 a day for each day of violation, according to Lawton.

The legal status of the PCB is also unique in that it is the only state agency whose decisions, under the Illinois Administrative Review Act, are appealed directly to the apellate court. Since the PCB's orders are not self-executing, enforcement in cases of noncompliance becomes the responsibility of the attorney general or the state's attorney in the circuit court.

"The breadth of authority granted by the statute to the Pollution Control Board has created a substantial number of legal issues dealing with the Board's jurisdiction as an administrative Agency, the delegation of legislative authority to the Board, the capability of imposing fines, the right to impose fines without jury trial and the pervasive issue of what subjects have been preempted by the Federal Government," Lawton says.

In virtually every case appealed to the appellate court, the defendants have contended that the Environmental Protection Act unconstitutionally delegates legislative authority to the board. There have been no definitive rulings on this constitutional argument by either the appellate court or the state supreme court, but the PCB is confident that the courts will find in favor of the act. "Legislators are too busy and government too intricate for any one body to prescribe precisely the particular rules of every aspect of human behavior that requires regulation," Lawton says. "Predecessor agencies in Illinois have all acted pursuant to rule-making authority delegated by statutes containing similar provisions and cases decided by our supreme and appellate courts have upheld these grants."

The power to levy fines is also defended by Lawton. "Since the right of trial by jury is assured only in civil suits or criminal actions, a fine imposed by an administrative body does not conflict with the constitutional guarantees," Lawton says.

For all the difficulties arising from uncertain legal status and manpower vacancies, the PCB has heard and decided about 700 enforcement and variance proceedings since its inception. Besides imposing penalties, the PCB has, in some cases, ordered installation of pollution abatement equipment by specified dates. One important principle, affirmed by the PCB, is that delay in receiving federal construction grant money is no excuse for continued pollution. And in cases where companies had already begun adequate treatment facilities but had not begun them soon enough, the PCB granted variances but imposed penalties for the delays.

Although the PCB has made "impressive progress" in the regulatory and enforcement fields, Lawton says, much depends on the way the courts handle the pending appeals. "The future of the pollution control program in Illinois will be dependent on the outcome of these pending cases," Lawton says.

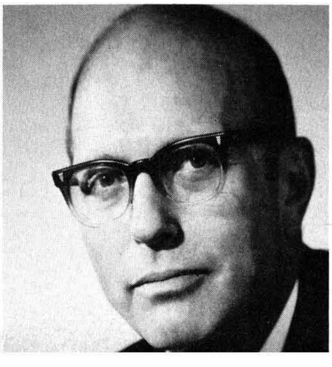
Environmental Protection Agency

The Environmental Protection Agency, the permit, inspection, and enforcement arm of the state, employs several hundred engineers, geologists, scientists, and other pollution control specialists. In its capacity as enforcement agency, EPA has responsibility for prosecuting violators before the PCB although nearly two years ago, a "Memorandum of Understanding" between the EPA and the attorney general's office transferred responsibility for litigation before the PCB to the attorney general's office. That memorandum has drawn fire from some quarters on the grounds that the attorney general who also represents the PCB, is wearing one too many hats.

Until recently, EPA's director was William Blaser. (At press time, Governor Dan Walker had only just appointed a new director. See box, page 193.)

Blaser, a former state legislator and professional company president (he had rebuilt four ailing companies before coming to EPA), had the task of organizing the fledging agency to carry out its legislative mandate. The agency now has seven divisions—Air Pollution Control, Water Pollution Control, Land Pollution Control, Public Water Supplies, Noise Pollution Control, Administrative Services, and Laboratory Services—each with a full complement of sections dealing with enforcement, monitoring, standards, and similar assigned tasks (see chart).

PCB's Lawton
No constitutional conflict



Attorney General Scott *gets a lesson in pollution monitoring equipment from MacMurray College professor Dr. Bruce Campbell*

The structure is important, according to Blaser. It is carefully planned to do the job in the best way possible. It is an outgrowth of Blaser's background in corporate management and reflects his management philosophy. The system works, says Blaser with a characteristic lack of affected modesty, "because Bill Blaser put his mind to it—because Bill Blaser thought this all out on paper before putting it into action."

Organization is key

There are two obvious ways to have organized the agency, Blaser points out. One was by function—permits, enforcement, and similar categories. The other is by type of pollutant—such as noise, solid waste, air. Blaser chose the latter because of his belief that the agency, above all things, must be responsive to the citizen. "If the public has a problem, they have to know where to go," Blaser says. "They know that their problem is air pollution or water pollution; the public has to find its way through the organization." He draws an analogy from his corporate background. "If you don't please your customers, you go out of business," he says. In Blaser's business, pleasing "customers" means giving them a clean environment. And in the two years he has been director, Blaser says, the agency can point to some specific advances. Blaser points out that the state has cleaner air, cleaner water, and fewer open dumps than it did a year ago largely because each of the operating pollution control divisions has personnel involved in monitoring, detection of violations, standards, and regulatory activities.

Shortly before leaving office last January, Governor Ogilvie announced that measurable airborne particulate matter in Illinois' most populous Chicago and Metro East areas had been reduced about halfway toward meeting the federal and state goals for air quality standards. In the Peoria area, Illinois is "virtually meeting those tough standards today," reported Ogilvie. "Present downward trends in particulate matter, if continued, will enable Illinois to meet the National Clean Air Goals well ahead of the 1975 target date," he predicted.

Gains have been made along the water pollution and solid waste fronts as well, according to Blaser. EPA's monitoring teams now sample all 15 river basins in the state, landfill sites, and public water supplies. Air quality is monitored in five air quality regions and monitoring samples have increased by 85% in fiscal 1972 over 1971. Water sampling has jumped 25% in the same time period.

EPA's Blazer
Worked it out on paper

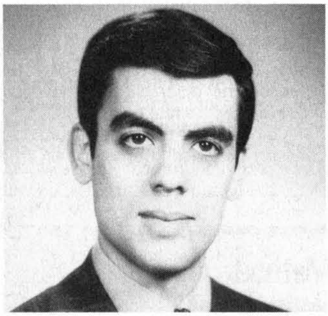
Illinois has closed some 400 illegal dumps in the state. Blaser credits stepped-up surveillance and enforcement programs with the success EPA has had in closing dumps. The number of legal actions recommended by surveillance sections to EPA enforcement sections jumped a whopping 385% to 645 in fiscal 1972 from 133 in fiscal 1971. EPA has also been busy issuing permits to municipalities and industries for construction and operation of pollution control equipment, public water supplies, landfills, and sewage treatment plants.

Financing authority

One of EPA's most important functions is administration of Illinois' Anti-Pollution Bond Act of 1970 which aids municipalities in construction of waste water treatment facilities. More than $80.3 million in grants has been offered to municipalities by EPA, and municipalities had already received some $20 million by the end of fiscal 1972.

Where lack of promised federal funds is causing a delay in treatment facilities, Illinois also advances money against federal commitments to get the project going. A typical example is the delay caused in building facilities for upgrading a sewage treatment plant for the Village of Mundelein, Ill. Mundelein's projected $2.95 million cost was eligible for federal share-funding programs. The state agreed to pay $737,000 under the Anti-Pollution Bond Act, and advanced the municipality an additional $1,622,500 against the federal obligation. Federal officials have agreed to the Illinois advance funding plan—the first of its kind in the nation, according to Blaser—and will reimburse Illinois for grants awarded.

In its capacity as watchdog for the environment in Illinois, EPA's responsibility tends to be of the day-to-day type. Because of its day-to-day mission, "it was thought that the agency would get so immersed in short-term administrative details that it would be difficult to look out for long-term policy," Blaser says.



IEQ's Schneiderman
Still in the saddle

Institute for Environmental Quality

To guard against that possibility, the Environmental Protection Act set up a separate Institute for Environmental Quality. The IEQ bridges the scientific knowledge gap that might otherwise exist between the PCB and the EPA. It is not concerned so much with monitoring as with monitoring techniques. Its bailiwick is the research necessary to back up new regulations.

By its constitutional mandate, the IEQ investigates "practical problems" and implements "studies and programs relating to the technology and administration of environmental protection."

The institute also acts as a data bank for obtaining, storing, and processing relevant environmental data. IEQ cooperates with the PCB, EPA, the Illinois State Geological Survey, the Illinois State Natural History Survey, and the Illinois State Water Survey in developing integrated, problem-oriented R&D programs.

The IEQ is largely prohibited from undertaking "abstract scientific research." In addition to its function as research arm of the environmental protection apparatus, the institute cooperates with the state Board of Higher Education and with colleges in the state in developing interdisciplinary approaches to environmental problems.

The IEQ is part of the executive branch of state government and the director serves at the pleasure of the governor. The institute's current director is Michael Schneiderman, a 33-year-old Chicagoan appointed by former Governor Ogilvie. At press time, no new director had been appointed by Governor Walker and it is widely expected that Schneiderman will keep his post for the foreseeable future.

Attorney general's role

Although Illinois' triple agency environmental protection scheme makes it unique among the states organizationally, what makes the antipollution program more interesting is the role of the state's attorney general in setting the machinery in motion.

Illinois' attorney general is William Scott. Scott, a Republican, was the single largest vote getter in the state during the last election, a statistic which attests to his enormous popularity with the people of Illinois. He professes a vital interest in cleaning up the environment—he was President Nixon's personal envoy to the Stockholm Conference on the Human Environment last June—and enjoys being in the thick of environmental battles in the state.

Under the Environmental Protection Act, the attorney general is legal counsel to the PCB. Under a less formal arrangement with EPA, his office also prosecutes polluters before the PCB. That arrangement was made, some of Scott's critics charge, because the attorney general, for political reasons, was reluctant to give up his role as environmental protector. Officially, the explanation lies in law which holds that the attorney general is the legal representative of the state and that under the constitution, no one except the attorney general is empowered to sue on the state's behalf.

That, some observers feel, adds a new dimension to the constitutional questions surrounding the Environmental Protection Act of 1970. The act specifically gives authority to prosecute polluters to the legal staff of the EPA in the same way as it gives legislative power to the PCB. Quite apart from philosophical discussions centering around division of powers, the constitutional questions of whether the legislature can give legislative or judicial powers to bodies other than those specifically set up by the constitution remain to be tested.

David Dinsmore Comey, director of Environmental Research for Chicago-based BPI (formerly Businessmen for the Public Interest, Inc.) is one critic of the present arrangement. "I wrote to the governor when this . . . [the legal machinery under the Pollution Control Act] . . . was proposed and I told him I thought it was a hell of a way to proceed," Comey says.

As an example of the difficulty that can be encountered under the present system, he cites a settlement reached between U.S. Steel's South Works and the attorney general's office. In that case, according to Comey, although there was already a suit against U.S. Steel's South Works to make the company stop polluting Lake Michigan, Scott filed his own suit and the court consolidated the two actions. "We got worried and tried to intervene because we were afraid that Scott might negotiate a deal that wouldn't be completely in the public interest," Comey says. The court refused to let BPI intervene, saying, in effect, that BPI's lawyers had no standing to sue and could not be private attorneys general.

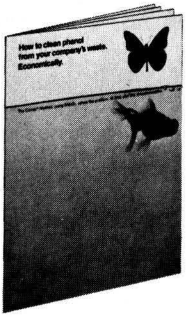
"The negotiations were completely underground for six months; Scott wouldn't talk to anyone," Comey charges. What came out of the suit, Comey says, was a "Swiss cheese agreement—full of holes and kind of stinky."

One "hole" was a clause in the agreement which bound all partners in the agreement—both lawyers for U.S. Steel and the attorney general's office—to defend the settlement before any agency that wanted to impose more severe sanctions. "Suppose the Pollution Control Board says the standards were too low, or the timetable isn't fast enough, says Comey, "Scott is the PCB's lawyer and yet he is bound by the agreement to defend the agreement against himself. Somehow he would have to be on one side of the courtroom saying clean up faster, and then on the other side of the courtroom saying it's fast enough."

Although that particular situation is unlikely to arise, Comey sees other instances where there could be potential conflicts of interest. As lawyer for both the PCB and the EPA, where would the attorney general be if EPA wanted to take a PCB ruling to the apellate court? "Which body would Scott represent?" he asks. Or what would happen if the attorney general differed with the PCB over an interpretation of the Environmental Protection Act and the PCB wanted to go to court for a ruling. Which hat would the attorney general wear, Comey asks.

What bothers Comey more, however, is that such legal shenanigans may have already taken place. In such an instance, he asks, what's to keep the parties from simply getting on the phone and agreeing not to take things any further, thereby circumventing the appeal process which is designed to give a definitive answer to such questions?

The Pollution Control Board's Lawton agrees that such cases could arise, but thinks the likelihood of serious problems arising from conflict of interest is not particularly great. And while he may not agree with Comey on that issue, nearly everybody—BPI, Lawton, and Blaser among them—agrees that the Illinois system is a good one and very likely to succeed. HMM



Government ups environmental funds

Despite cutbacks in other programs, its environmental funds show continual growth

Overall, the federal budget request of the U.S. Government for fiscal year 1974 is $268 billion, up from $250 the previous fiscal year. The projected deficit is $12 billion, less than half the $25 billion deficit of fiscal 1973. President Nixon promises to hold the Federal Government to this level of spending, so that no tax increase is necessary.

By now, federal environmental programs each year are the subject of special analysis in the Official Budget of the U.S. Government. Budget authority for the 1973 and 1974 periods is nearly seven times that appropriated in 1970, the first year of the environmental decade.

The Environmental Protection Agency, the lead federal agency in the U.S. cleanup efforts, has requested $3.515 billion in fiscal year 1974, up from $2.447 billion last fiscal year. But the total figures are not to be misleading. Understandably, the largest share of the EPA figures goes for the construction of municipal waste treatment facilities. (The new contract authority totaling $5 million—less than half the Congressional authorization of $11 billion under. P.L. 92-500—for the fiscal years '73 and '74 was announced last November.) Excluding the funds earmarked for construction of waste treatment facilities, EPA has a $44 million increase in its operating budget and an increase in 703 personnel positions, half of which have already been absorbed in 1973.

Within EPA

All told, the water activities program increased; the air activity decreased a small amount; but the major decrease is in the area of solid waste. In water there is:

- a doubling of the financial backing for the state program grants (to $40 million in 1974 from $20 million in 1973)
- contract authority totaling $25 million for area-wide planning grants under the new water bill (Section 208)
- $3.2 million for development of effluent guidelines which are now due on October 18, 1973.
- $3.1 million for implementation of the permit program.

EPA has an additional series of responsibility under the other three pieces of environmental legislation which were enacted in the waning days of the last session of Congress—the new laws for noise, pesticides, and ocean dumping. Other increases in EPA budget request for fiscal 1974 include $4.4 million for its pesticides program, $1.6 million increase for its noise program, and a $4 million item for the development of a toxic substances office to handle that area as it evolves and legislation is introduced.

By functions within EPA, enforcement is up $11.8 million. The activity in the air category goes for enforcing state implementation plans, all of which are in by now but not all of which have been finalized. In the water category, the step-up on enforcement goes for the permit program, and in the pesticides category, additional enforcement is called for under the new law.

Now for the bad news: EPA decreases are shown for the solid waste and air categories. In air, the decrease of $10 million stems from the fact that the agency has completed the first generation of SO_2 control technology and is now moving into the second generation of control technology which is in the R&D phase and hence less costly.

The major decrease in the agency's activities in solid waste program (to slightly less than $6 million, from $30 million last fiscal year) stems from several considerations. The first, and probably the more significant reason is that the "replacement" solid waste legislation (the present legislation expires this June 30) has not as yet been finalized and at this time EPA simply is not sure what its recommendation to Congress will be. The questions that the Executive branch of Government asks are the same that it asked in the early round of hearings on the Resource Recovery Act namely, what level of government should be handling the solid waste program and how? The Executive branch thinks the problems need be addressed at the local and municipal level.

Within the nearly $25 million decrease in the solid waste effort is a $9 million reduction in the resource recovery effort, a phase-out of state and local planning grants (all states with the exception of 10 have submitted their plans which have been approved), and a reduction in technical assistance to cities and municipalities. Nevertheless, the solid waste management program hopes to come to grips with the handling and disposal of hazardous materials.

Again and again it has been emphasized that the problem with solid waste is certainly not technology. The technology is here today, and the fact that EPA is not funding any technology is due to the fact that other problems are the hurdles. These hurdles include the freight rates issue and the problem of tax structure. One nagging question is whether the recycled material that comes out of the front end of a resource recovery system is marketable. Another question is the balance of incentives for the use of recycled materials vs. the incentives for the use of virgin materials.

At the end of the EPA press briefing, decreases in other federal agencies environmental programs were made obvious but to what extent these programs will be shifted to EPA activity was not known. SSM

EPA Operating Budget

	Change from 1973	'74 Request
	(Million of dollars)	
BY FUNCTION		
Agency and regional management	+$ 4.6	$ 50.8
Research and development	−24.4	148.7
Abatement and control	+52.1	264.1
Enforcement	+11.8	47.4
Scientific activities overseas	Same	4.0
Total	**+$44.0**	**$515.0**
BY PROGRAM		
Air	−$ 6.1	$146.4
Water quality	+53.2	192.4
Solid waste	−24.2	5.8
Pesticides	+4.5	25.5
Radiation	Same	7.1
Noise	+1.6	4.0
Water supply	+0.1	4.4
Intermedia and program support	+10.6	74.7
Agency and regional management	+4.6	50.8
Scientific activities overseas	Same	4.0
Total	**+$44.0**	**$515.0**

EPA's Office of Research and Monitoring is conducting a nationwide survey of more than 1100 lakes in order to answer . . .

How fast are U.S. lakes aging and why?

The National Eutrophication Survey is the largest water field-sampling program in the history of the Environmental Protection Agency. Literally, as many as 200,000 water samples will be collected from about 1100 lakes in the U.S. According to the best information available today, there are some 3800 municipal sewage treatment plants that have an impact on these lakes, and the survey is the first nation-wide attempt to learn what effect they have on the aging of our lakes. All told, the survey will cost about $5 million over four years, with all samples to be collected by the end of calendar year 1975.

Can you recall all the controversy over phosphate removal from detergents that gained national headlines a few years ago? Do you remember the joint CEQ, EPA, FDA, HEW position on the matter? Members of the Washington press corps certainly do. It was at that time, September 15, 1971, that EPA administrator William Ruckelshaus committed his agency to the fact-finding task of identifying those lakes in the U.S. that were being threatened by the addition of phosphorus-containing materials from municipal sewage treatment plants. Although the lakes survey was not officially announced until three months later, even then, on December 15, 1971, the agency had neither the manpower nor the funds to begin the program.

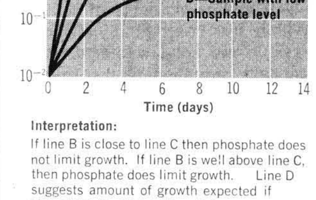
Within the early months of 1972 plans for the survey were generated within the EPA Office of Research and Monitoring and then submitted to the Office of Management and Budget (OMB). EPA received the go-ahead sign on March 28 for funds and 50 personnel. Of the 50 people approved for EPA, two are assigned to the Office of Water Programs, three to the Office of Research and Monitoring at EPA headquarters in Washington, D.C., 22 at the Corvallis National Environmental Research Center (NERC), leaving 23 persons at the Las Vegas NERC, including 14 members of the helicopter team that surveys and collects samples.

Basically, the major objective of this ambitious survey is to determine, once and for all, if increased phosphate removal at sewage treatment plants would significantly improve the water quality of a lake or impoundment that receives sewage effluent. But before this fundamental and legitimate question can be answered, three tasks must be performed:

- to determine the trophic conditions of the lakes and impoundments
- to determine the growth-controlling nutrient in each lake
- to identify the influence of nutrients on each lake

Obviously the logistics of the survey and sampling strategy are staggering. Robert Payne, EPA's program element manager for the survey says, "They could not all be done immediately." Therefore, the strategy calls for dividing the lakes in the U.S. into three distinct geographic areas —one for each of the three calendar years 1972, 1973, and 1974. The initial survey operation for 1972 was limited to 10 states in the northeast —New York, Michigan, Wisconsin, Minnesota, and the six New England states. Within this area, efforts on some 220 lakes were begun in 1972, with results to be in final form by this June.

In the 1973 survey area, now getting under way, 300-350 lakes in the remaining 17 states east of the Mississippi River will be surveyed. At press time, eight of the 17—Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, and Tennessee—had their plans ready to go.


Algal assay specific growth

Interpretation:
If line B is close to line C then phosphate does not limit growth. If line B is well above line C, then phosphate does limit growth. Line D suggests amount of growth expected if phosphate is removed from lake.

Then beginning in 1974, the survey moves west of the Mississippi River and although the schedule is not final, the remaining 21 of the contiguous 48 states will have their lakes and impoundments surveyed in the next year or two.

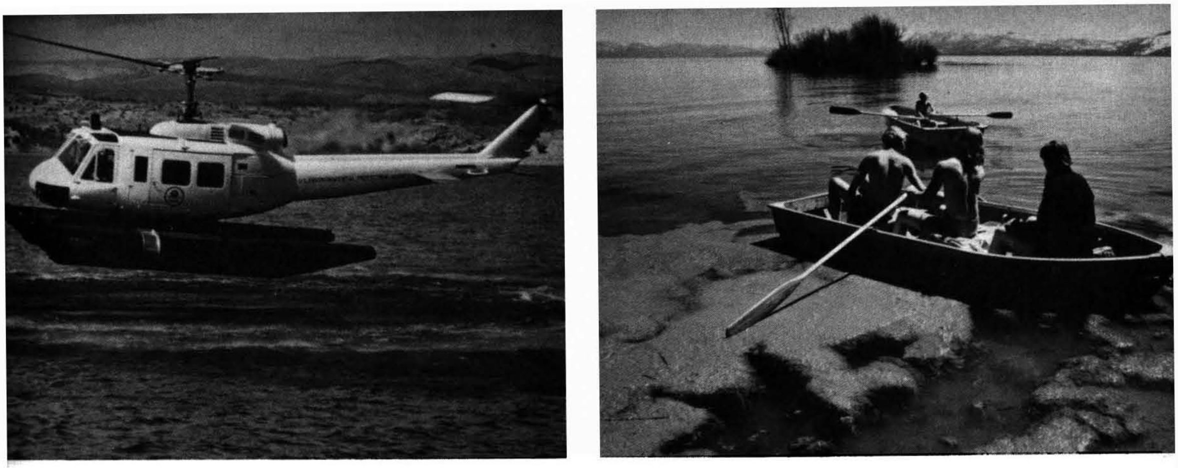
How it's done

There are really several parts of the survey. Samples are collected by a helicopter team, National Guardsmen, and operators at municipal sewage treatment plants. Although most samples are analyzed at the Corvallis NERC, and some work is done at the Las Vegas NERC, the number of analyses is still staggering. In fact, part of the information collected on the first 220 lakes fills a computer printout book that is more than half a foot thick!

To undertake the first task—to determine the trophic condition of the lake—the survey has three Huey helicopters on loan from the Department of the Army. Each is equipped with sophisticated water-sampling and analytical equipment.

The helicopter team drops an instrument package into the lake, and the instruments record depth, temperature, pH, dissolved oxygen, and conductivity. Data on these parameters are relayed to the helicopter where an on-board analog recording device automatically plots any one parameter against any other. In this way, the plots of temperature vs. depth, dissolved oxygen vs. depth, and the like are generated. On the average, about a half dozen sites are sampled on each lake, and three complete circuits are made on each site for any one lake. In addition, water samples can be taken at different depths in order to get a composite water sample to send back to the Las Vegas NERC for additional analyses—usually total phosphorus, dissolved phosphorus, nitrogen as ammonia, nitrate-nitrite, Kjeldahl, and alkalinity.

A remarkable fact about this helicopter team of 14 dedicated personnel, including helicopter pilots, lim-



Algae. *In 1972, EPA's helicopter team surveyed 220 lakes; growth is readily visible on Lake Tahoe, Calif.*

nologists (lake scientists), and others is that in a mere 35 days after OMB approved the lake survey program (March 28), the team sampled its first lake in New York state on May 2, 1972! Then from early May through early November (the team even took off in a snow storm in Michigan) of last year, the team collected samples and data from dawn to dusk six to seven days a week and sometimes holidays. In recognition of their contribution to the EPA effort, the team members each received a gold group medal award at EPA's second annual award ceremony. Leslie Dunn at the Las Vegas NERC was responsible for coordinating much of the initial effort.

Basically, the team surveyed the first 220 lakes, obtaining the data necessary to determine the trophic state of the lakes. This year, the helicopter survey team will cover 300–350 lakes in the Southeast, and will wing its way westward sometime early next year.

The second element

The second charge—to identify the controlling nutrients in each lake—is fulfilled by the 22-member team at the Corvallis NERC. One of the samples collected by the helicopter is a large composite sample of water from each lake. The composite is made up of an integrated sample from different depths, at the various half dozen sites, taken during the spring- or fall-sampling circuit.

At Corvallis, the composite is analyzed by the algal assay procedure that was developed jointly by EPA and The Soap and Detergent Association. The composite is split into a number of samples, each of which is inoculated with a test species of algae. Phosphate is added to one sample, phosphate plus nitrogenous materials are added to another, a third acts as a control (no additions), and the fourth one is stripped of any phosphorus materials by passage through an alum column. Then each of the four cultures is allowed to grow under controlled conditions in the laboratory for a period of 14 days. From the curves (see art) one can readily see the effect that phosphate has on the ability of that particular lake to grow algae.

Other information needs

As well as checking on nutrients which enter streams via sewage treatment plant effluents, the survey team also wants to determine how other nutrients are entering U.S. lakes. The team does this in two ways: one involves the National Guard and another centers around plant operators at the sewage treatment plants affecting the lakes.

The first program involves sampling the mouths of the major streams entering the lake at a monthly frequency for one year. Additional sampling (twice monthly) is performed during the two months of highest runoff. This, too, is an ambitious sampling plan since there are, on the average, five to seven streams coming into each lake.

The National Guard play a key role here. Endorsement to use the Guard on a state by state basis was obtained from the Office of the Secretary of Defense and the National Guard Bureau. Their first duty, a pilot test program, occurred in Vermont last July 15, and later, approval for their use became possible in the first 10 states.

The Guard volunteers are collecting samples from streams entering each of the 220 lakes in the first 10-state area of 1972. All told, more than 1100 water samples are being collected each month by the National Guardsmen. Again, the samples are being analyzed by continuous techniques for total phosphorus and ortho-phosphate and nitrogen—ammonia, nitrate-nitrite, and Kjeldahl.

Last month, when the 1973 survey sampling got under way in 17 states east of the Mississippi River, it was anticipated that the National Guard would help with the survey, although approval for their use must be given on a state by state basis. Nevertheless, sampling started in Florida last month; and the 17-state program is scheduled to end in the spring of 1974. Six states—Alabama, Florida, Georgia, Kentucky, North Carolina, and South Carolina—have already endorsed the use of their National Guard to participate in the sampling.

Another series of samples is being collected by plant operators of the effluent from waste treatment plants on the particular lakes. This program has the endorsement and approval of the state water pollution control agency involved.

This year, all series of samples are being coordinated and scheduled so that sampling by the helicopter team, the National Guardsmen, and the plant operators is performed on a consistent time basis. In this way, the information is consistent for one growing season in the lake.

Despite the fact that sampling and analysis began in 1972, the results on the first 220 lakes will not appear before mid-June, shortly after completion of all sampling activities.

How will these results be used?

As the final data are analyzed and interpreted, survey personnel will prepare comprehensive reports of findings lake by lake. These results will be received by state environmental authorities and will serve as the basic input for information of joint state-federal control strategies for lakes found to have serious water quality problems caused by municipal effluents. EPA's Office of Water Programs will aid each state in the planning and financing of upgraded waste treatment facilities where warranted. SSM

P–C treatment gets industrial trial

Activated carbon cleans up effluent to meet state standards at reasonable capital and operating costs

Physical/chemical treatment using large-scale activated carbon adsorption technology is getting a major industrial test at the Tuscaloosa, Ala., plant of Reichhold Chemicals, Inc. Just how well it does may determine, to a large extent, the future of physical/chemical plants in industrial waste treatment and what part activated carbon will play in industrial waste water cleanup.

Reichhold's Tuscaloosa plant is located on the Black Warrior River, part of the Warrior-Tombigbee River system which enters the Gulf of Mexico some 358 river miles south. The plant, along with several other manufacturing operations, including paper making, foundry, by-product coking, asphalt, and chemicals, is on the Warrior Pool, an eight-mile section between Oliver and Holt Lock and Dams.

The Tuscaloosa plant, which began operations in 1943 with synthetic phenol production, makes sufuric acid, formaldehyde, pentaerythritol, sodium sulfite, sodium sulfate, orthophenylphenol, and a number of synthetic resin and plastics in its production units. Its effluent streams, therefore, represent a diverse combination of types and poses a complex.

In 1966, in conjunction with the Alabama Water Improvement Commission, Reichhold determined that its effluent loading 16,444 lb/day BOD, 26,718 lb/day COD, 1540 lb/day phenols and had an average pH or 9.8 with a range of 5.4–12.3. Effluent volume from all plant sources ranged from 10–15 million gpd.

In accordance with an agreement between the company and the Alabama Water Improvement Commission, a target reduction of 90% was agreed upon. (Although legislation and regulations applicable under current law required a 75% reduction, the industries in the Tuscaloosa area were requested to achieve an 85% minimum reduction.) In addition, because of special conditions surrounding operation of a peak-load hydroelectric generating plant immediately upriver, Reichhold, along with all other industries on the Warrior Pool, was required to install capacity for holding its entire discharge for five days.

Getting started

Reichhold then started work to find out how the proposed reduction in discharge could be met, according to its regional vice-president T. P. Shumaker who is in charge of the Tuscaloosa plant. The program attacked the problem from three directions: reducing the effluent loading by in-plant process and/or equipment improvements, reducing the hydraulic loading by segregation and separation of effluent-bearing streams from once-through streams, and seeking the most economical and efficient means for effluent treatment.

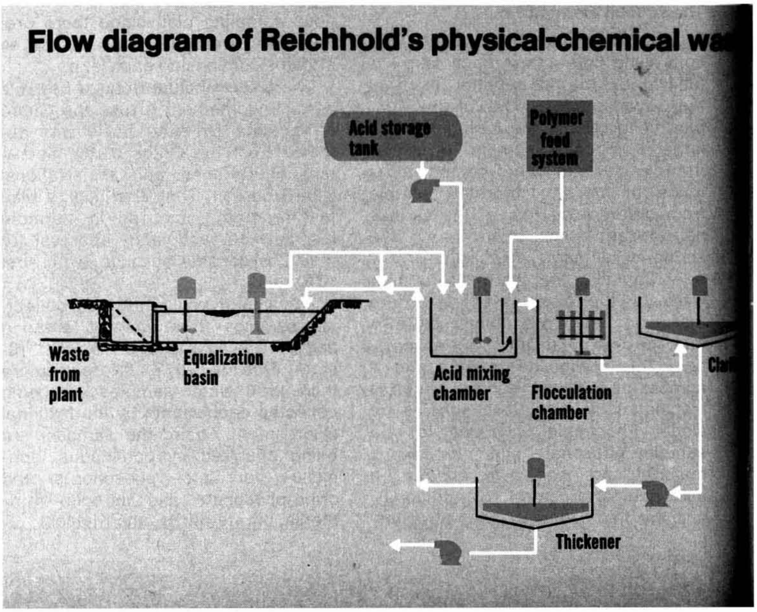
In-plant improvements included redesign and replacement of caustic concentrators where entrainment had added 4000 lb/day of caustic soda to the effluent stream. The loss has been reduced to fewer than 40 lb/day. Sodium sulfite, previously washed from returning rail cars in a cleaning process, now has been returned to the process water rather than to the effluent.

The program to reduce hydraulic loading included a complete rebuilding of the entire plant sewer system where once-through cooling waters were separated from effluent streams. The volume of effluents to be treated was reduced from 15 million gpd to half a million gpd.

Looking for an answer to its treatment problems, Reichhold found there was no "off-the-shelf" technology then available which would fill the bill. The company looked at several alternatives, Shumaker notes.

Municipal treatment by the City of Tuscaloosa was impossible since the city did not have secondary treatment facilities, nor would secondary treatment be available in time for compliance deadlines to be met.

Reichhold studied the possibility of concentration and incineration of the wastes but found that incineration could not handle the entire problem. Certain process effluent streams had relatively high levels of alkali metals (such as sodium formate and sodium



Flow diagram of Reichhold's physical-chemical wa acetate), and concern for refractory life led Reichhold to drop evaporation/concentration plans.

Deep well injection

A preliminary feasibility study of deep well injection was done and looked pretty good, according to Shumaker. So a program was established with the Environmental Protection Agency, the Geological Survey of Alabama, and Alabama Water Improvement Commission to drill, monitor, and conduct an extended research program on applicability of deep well injection. A research test well, drilled to a depth of 8097 ft, has been completed at the Tuscaloosa location and continues to be studied.

Although deep well injection holds potential for future application and possibly total elimination of discharge, it was not considered a part of the primary process for meeting the current discharge standards, according to Shumaker.

Reichhold mounted a major effort in process design based on biological treatment with research done by both commercial and university-related firms. The bio-oxidation route looked promising, according to Shumaker, and after two years of laboratory work, the company built a nominal 25,000-gpd pilot plant at the Tuscaloosa site.

After nine months' operation, however, the results were less than spectacular. Six separate waste streams were not amenable to biological treatment and would have needed incineration. The company estimated the capital costs of the combined treatment scheme to be in excess of $2 million with direct operating costs of an additional $280,500 annually.

While Reichhold had been investigating biological treatment, the company, with the help of the Calgon Corp., had also been looking at carbon adsorption as a polishing process, "At first look, the operating costs of once-through carbon were prohibitive, although the results achieved were very interesting," Shumaker says.

But with the idea of carbon regeneration and the costs savings that could be realized, Reichhold took a second look—this time to evaluate carbon adsorption as the principal method of treatment.

Batch clarification and adsorption studies were run on grab and composite samples of plant waste water to establish the feasibility of physical/chemical treatment. Once the feasibility was established, dynamic carbon column tests were run to establish design parameters.

The batch clarification tests showed that a combination of neutralization to pH 6.5–8.5 followed by a 2-mg/l. dose of WT-2690, a nonionic water-soluble polymer manufactured by Calgon, would reduce the suspended solids to less than 20 mg/l.

Batch adsorption isotherm studies demonstrated that the organic content of the waste could be reduced to an acceptable level via adsorption.

These tests, together with the column tests, brought about an adsorption system which Reichhold thought would reduce BOD to 1650 lb/day, and COD to 2675 lb/day (about a 90% reduction). Phenolics would be cut to fewer than 27 lb/day and the pH of the final effluent would range from 6.5–8.5.

Total capital costs were pegged at $1.3 million for a plant capable of treating 500,000 gpd, including the cost of a pretreatment system, holding basin, and adsorption system. Direct operating costs—including labor, fuel, power, makeup carbon, and maintenance—were projected to be about $320,000 annually.

Full steam on PCT

On the basis of those projections, Reichhold decided to build a full-scale physical/chemical plant. The process flow looks something like this:

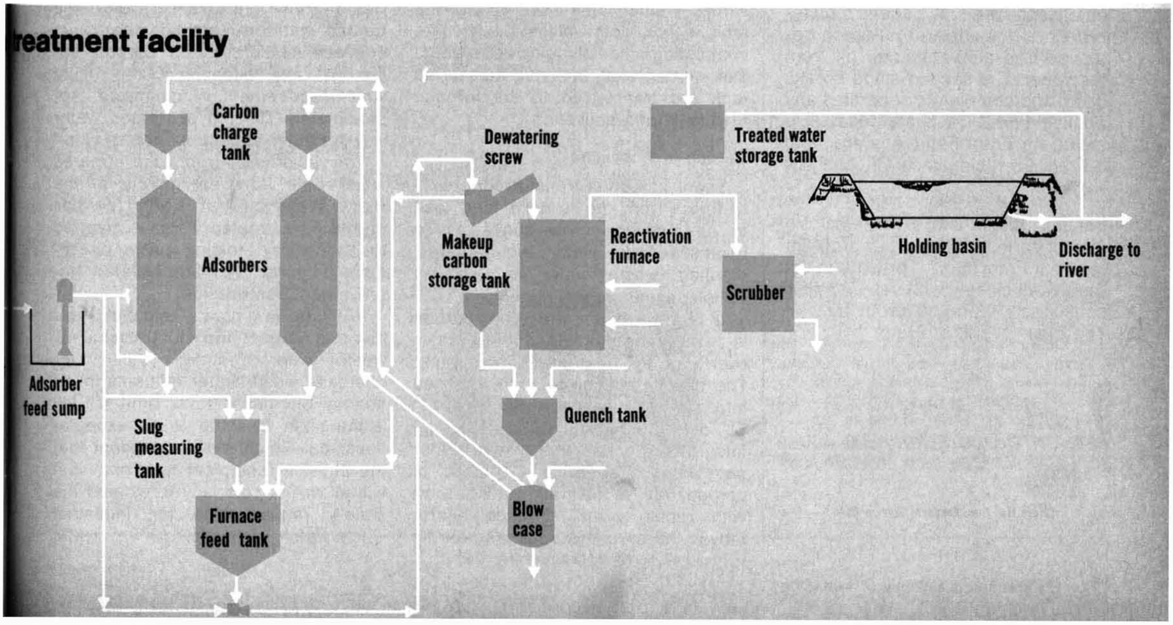
The process waste waters flow to a 1,250,000-gal earthen equalization basin with a residence time of 2.5 days which serves the triple function of equalizing flow, pH, and organic content. Four turbine-type agitators provide complete mixing and prevent solids settling.

Waste water is then pumped to an acid-mixing chamber—concrete basin with a rapid mix turbine-type agitator—where concentrated sulfuric acid is added to maintain the pH in the 6.5–8.5 range. Although the pH of the raw waste water can be as low as 5, a caustic soda feed system is not required since the periodic acid slugs can be handled by equalization.

Waste water flows from the acid-mixing chamber to a flocculation basin. The nonionic polymer is added to the neutralized waste water as it leaves the acid mix chamber and the waste is gently agitated in the flocculator to enhance the formation of large floc particles.

The flocculated waste water then flows to a clarifier—a 40-ft square concrete basin with a circular clarifier mechanism—where essentially all suspended solids and floating material are removed.

reatment facility



Settled solids are periodically withdrawn from the clarifier sump and pumped to a thickener. The supernatant from the thickener is recycled to the equalization basin. The thickened solids are presently hauled to a land disposal site, Shumaker says, although dewatering studies are now under way.

Carbon adsorbers

After pretreatment, the clarified waste water flows to the adsorber feed sump. The waste water enters the bottom of two parallel moving-bed adsorbers through a circular pipe header. Each lined carbon steel adsorber is 12 ft in diameter with a 36-ft sidewall height and a cone-shaped bottom and top. Each adsorber contains 124,000 lb of Calgon's granular activated carbon, Filtrasorb 300. At the design flow of 175 gpm per adsorber, the superficial or empty bed contact time is 173 min.

The waste water flows upward through the carbon beds, and dissolved organics are physically adsorbed. When the carbon at the bottom of the bed becomes exhausted, the spent carbon is removed from the bottom of the bed in batches or slugs. The volume and frequency of slugging is dependent on the rate of carbon exhaustion, according to Calgon, and at the Reichhold plant, each moving bed adsorber is slugged once per shift. (One slug volume is equivalent to approximately 5200 lb of carbon or about 5% of the bed.) During the slugging operation, a valve at the bottom of the adsorber is opened allowing a slurry of spent carbon to flow to the slug-measuring tank. Simultaneously, a valve at the top of the adsorber is opened allowing reactivated carbon to flow from the surge tank to the top of the adsorber. When the slug-measuring tank is full, both valves are closed, completing the slugging operation. The contents of the slug-measuring tank are transferred to the furnace feed tank for reactivation.

Carbon regeneration

Spent carbon is transferred in slurry forms from the furnace feed tank to an inclined screw conveyor. To minimize utility water requirements, clarified waste water is used to transfer spent carbon.

In the conveyor, the spent carbon is dewatered by gravity and the water overflows to the furnace feed tank. The dewatered carbon is discharged into the reactivation furnace, a 13′ 6″ o.d. x 5 hearth furnace with an integral or "zero" hearth afterburner capable of processing 42,000 lb of carbon/day. A central rotating shaft with rabble arms at each hearth moves the carbon across the hearths and through drop holes causing it to pass through the furnace.

The furnace is normally fired with natural gas with LPG used on a standby basis. Supplemental steam is added to the furnace to control the reactivation atmosphere. In the furnace, the damp carbon is dried and heated to 1700–1800°F. The spent carbon is reactivated by controlled oxidation of the impurities in the pores of the carbon granules.

The off-gases are vented to an integral afterburner to ensure complete combustion of the organics and to prevent odors. The afterburner exhaust gases exit to a wet scrubbing system where the hot gases are cooled and any particles are removed. Treated effluent is used for scrubbing.

The reactivated carbon is discharged from the furnace by gravity into a quench tank. There the hot reactivated carbon is cooled and wetted. The quenched carbon drops to a blowcase and is transferred pneumatically to the two adsorber charge tanks. A time sequence programmer automatically controls the transfer of reactivated carbon.

During the transport and reactivation of spent carbon, carbon losses occur which make periodic addition of make-up carbon necessary. An accurate make-up carbon requirement has not been established for this plant to date since it only recently began operation, according to Shumaker, but make-up will probably be 3–5% by weight. Make-up carbon is added from a storage tank.

After carbon treatment, process water is collected in a trough at the top of each adsorber and sent to a 5500-gal FRP surge tank from which a portion of treated water is pumped for various uses throughout the waste treatment plant. When the treated water is used for scrubbing, polymer dilution, virgin carbon unloading, and quenching, the utility water requirement is minimized. Approximately 70 gpm of treated water is reused on a continuous basis.

The overflow from the treated water tank flows by gravity to the Black Warrior River. During periods of low flow, treated water is diverted to a five-day holding basin as required by the Alabama Water Improvement Commission.

With its new plant, Reichhold now has the "largest and most advanced" waste water treatment facility for chemical waste water effluents in Alabama, Shumaker says. Time will tell if the plant lives up to its expectations, but Reichhold is confident that the physical/chemical treatment unit will allow the company to exceed the state's requirements for industrial waste water discharge. HMM

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EPA's CHESS program correlates environmental
quality with public health

Air pollution affects community health

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Research Triangle Park, N.C. 27711

CHESS, an acronym for the Community Health and Environmental Surveillance System, is a national program which relates community health to changing environmental quality. It consists of a series of standardized epidemiologic studies designed to measure simultaneously environmental quality and sensitive health indicators in sets of communities representing exposure gradients to common air pollutants. The program is conducted by the Environmental Protection Agency in cooperation with local public health agencies, universities, and private research institutes. The purpose of the CHESS program is:

- to evaluate existing environmental standards
- to obtain health intelligence for new standards
- to document health benefits of air pollution control

The program began in 1968 with the health appraisal of air quality standards. The CHESS concept developed simultaneously with the growth of a multidisciplinary research team in 1969. The creation of the Environmental Protection Agency in 1970 signaled a more comprehensive and, now, multimedia approach to environmental hazards. CHESS became fully operational for air pollution effects in 1973 and will be operational for multimedia toxic substances by 1975.

Area sets

Early this year the CHESS program was greatly expanded to include 33 neighborhoods in six areas of the U.S.: New York–New Jersey (8), Chattanooga, Tenn. (3), Birmingham–Charlotte (9), St. Louis, Mo. (2), Utah (4), and the Los Angeles Basin (7). These neighborhoods form one of the key elements of the CHESS program, the so-called CHESS area sets—a group of three to seven communities selected to represent an exposure gradient for designated pollutants. Each community within a CHESS set is a middle class residential neighborhood containing three or four elementary schools (500–1000 children per school) and usually a junior and senior high school. The economic characteristics of neighborhoods are carefully matched within the same CHESS set. Current CHESS area sets are shown in Table I.

Health indicators represent another key element in the program. The seven health indicators under surveillance in the program include: • Chronic respiratory disease in adults • acute lower respiratory disease in children • acute upper respiratory disease in families • daily asthma frequency • acute irritation symptoms during air pollution episodes • pulmonary function of school children, and • tissue residues of cumulative pollutants in humans. In addition, daily aggravation of symptoms in subjects with preexisting heart and lung disease is being followed in the New York and Utah CHESS communities.

Studies completed in the 1970–71 school year (the first full year of CHESS operations) were analyzed and will be published in an EPA monograph entitled "Health Consequences of Sulfur Oxides: A Report from the CHESS Program 1970–1971." These studies revealed an entirely new finding that adverse human health effects are consistently associated with exposure to suspended sulfates, more so than to sulfur dioxide or total suspended particulate matter. The results are highly significant in that suspended sulfates are dispersed far more widely throughout the Northeast and at greater distances from urban emission sources than is true for gaseous sulfur dioxide. EPA possesses incomplete information on sources, emissions, transformation, dispersion, and control of atmospheric suspended sulfates.

CHESS studies were also able to demonstrate the benefit of improved air quality with respect to the chronic respiratory disease experience of subjects who moved out of New York City to low-exposure communities. Furthermore, recent improvements in air quality in New York appeared to have a beneficial effect on the lung function of younger children, who no longer showed impaired ventilatory performance when compared with matched children in low-exposure neighborhoods. Similarly, children living in polluted communities for three or more years were found to have more acute respiratory disease episodes than recent immigrants to that community, suggesting that improved air quality would prevent this adverse response. To document the health benefits of control, CHESS will remain in each community while air quality is improved.

Each CHESS set generally includes high, intermediate, and low-exposure communities within which air quality varies from day to day. Health indicators are contrasted over time and space within this framework. Replication of pollutant exposures in several CHESS sets permits development of exposure-effects models in one area and con-

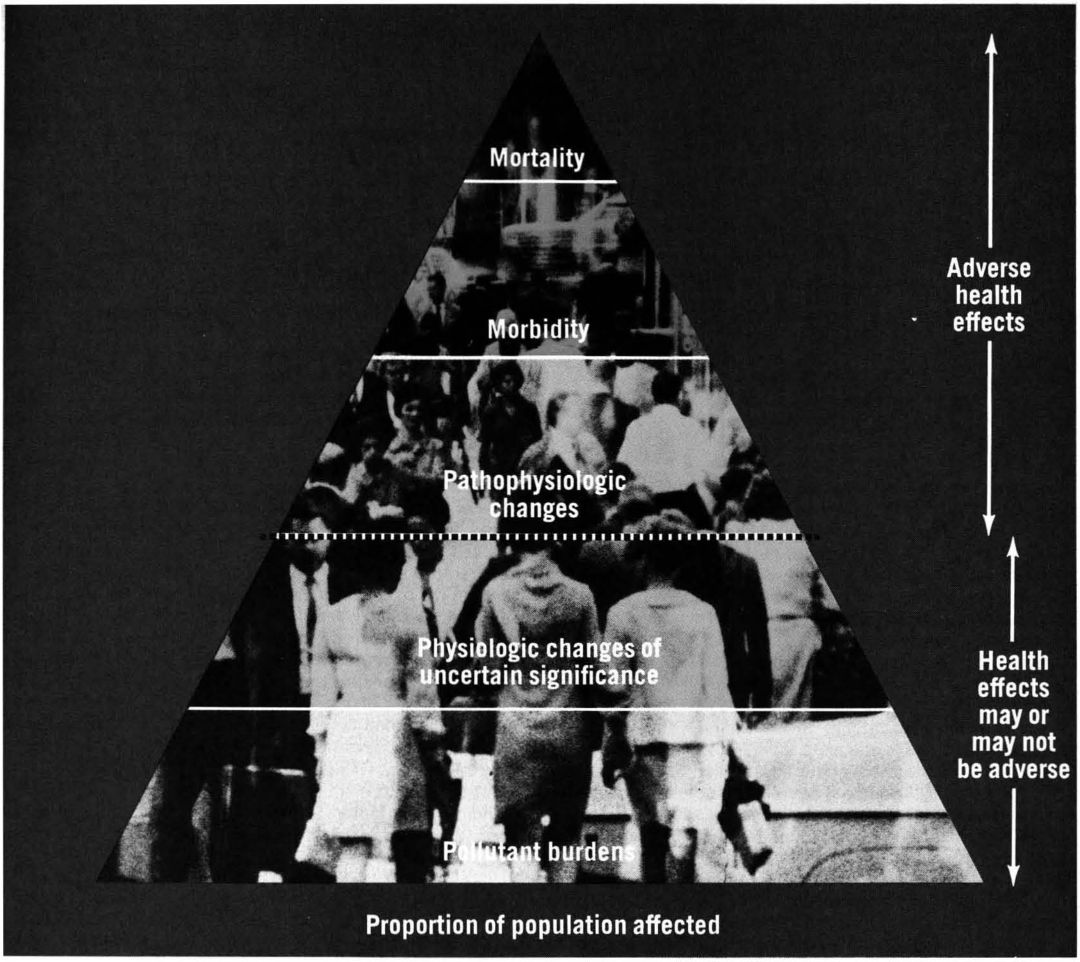

Figure 1. *Biological response to pollutant exposure*

firmation of models in another. CHESS area sets are selected with particular emphasis on highly prevalent ubiquitous pollutants including particulate matter, sulfur oxides, and nitrogen oxides. The possibility of detecting pollutant interactions is enhanced by selecting CHESS sets with principal exposure to SO_2 alone, to particulate matter alone, and to combinations of the two pollutants.

Health indicators

Environmental pollutants can affect the health of individuals over a broad spectrum of biological response (Figure 1). More severe effects such as death and chronic disease will be manifested in relatively small proportions of the population. However, the role of environmental pollutants in the mortality and chronic disease experience of a community is difficult to quantify because so many other determinants of death and disease cannot be adequately measured.

The lower strata in the response spectrum of Figure 1 are subclinical manifestations of pollutant exposure. At a point in time, many more individuals in an exposed community will respond with altered physiology or pollutant burdens (tissue residues of pollutants which accumulate in the body) than will die or develop chronic disease. Furthermore, lower levels of the response spectrum can be more readily quantified and measured objectively. Because responses at lower levels are more rapidly manifested, they may be more useful to demonstrate an immediate health benefit of pollution control.

CHESS health indicators focus on measures of selected acute and chronic diseases, altered physiology, and pollutant burdens. These indicators may be conveniently divided into two categories: health effects attributable to short-term pollutant exposure and effects attributed to long-term exposure. Sample sizes and response frequencies employed for each CHESS health indicator are shown in Table II. Acute health effects are observed by following systematically preenrolled panels of subjects and comparing response frequency against daily variations in pollutant levels. Various statistical analyses are employed to isolate the effects of temperature and season on response frequency. By making simultaneous observations in low-exposure communities, effects of environmental covariates (factors which, along with environmental pollution, codetermine the level of a health indicator in a community) such as temperature can be quantitated, and pollutant-temperature interactions can be detected. These health indicators are related to exposures of 1–96 hr, depending on the nature of the response.

Effects attributable to long-term exposure are identified by contrasting disease prevalence in high- and low-exposure communities. An acute effect, such as excess acute respiratory disease, may be a manifestation of chronically impaired resistance to disease. Persistence of illness

TABLE I

Current CHESS area sets in U.S.

Pollutant gradient	Area	Number of communities	Comments
SO_2	Utah	4	Low particulate matter
Particulate matter	Southeast	6	Low SO_2
SO_2 and particulate matter	New York	7	Other urban pollutants present
SO_2 and particulate matter	Chicago	4	Other urban pollutants present
SO_2 and metals	Idaho–Montana	5	
NO_2	Chattanooga	3	
NO_2 and oxidants	California	7	Other urban pollutants present

excess or of altered physiology in a high-exposure community provides a means to discriminate between effects attributable to short-term and to long-term exposure. Disentangling the effects of dose rate, a large dose in short intervals vs. repeated small doses over long periods, is difficult in community studies and generally requires controlled experimentation.

Many factors contribute to community differences in the distribution of diseases associated with air pollution exposure. Important covariate information obtained in the CHESS program includes age, sex, race, education of parents, occupational dust and fume exposure, cigarette smoking habits, geographical migration, and previous illness experience. Covariates may be kept constant across study groups by careful selection of participants, or covariates may be measured and then through application of statistical procedures can be isolated or appropriately adjusted for.

Environmental monitoring

Air monitoring stations are sited in each CHESS community to provide credible estimates of pollutant exposure for the study population. The large majority of study subjects live within 1.5 miles of the monitoring station. Whenever possible, the sample inlet of the station is placed at head level in an appropriate shelter removed from sources of pollution not representative of communitywide exposure. Topography, land used adjacent to the station, emission sources, and population distribution are considered in selecting CHESS monitoring sites.

Since the inception of the CHESS program in 1969, manual instruments operated seven days each week have monitored 24-hr integrated concentrations of pollutants. Cyclone samplers used to measure respirable particulate matter less than 5 μ in size are being replaced with five-stage cascade impacters fitted on the head of a high-volume sampler. Beginning in January 1972, automated methods were introduced into some CHESS stations, but the entire monitoring program will not be automated until this year. Automated stations will telemeter real-time pollutant measurements to a central processing station, providing data to relate short-term environmental variations to health indicators of acute response.

Reagents and filters used in manual instruments are prepared centrally and periodically checked at designated quality control points before shipment to field stations. Instruments are also calibrated and maintained centrally. Environmental samples obtained in the field are processed at a central laboratory in which systematic checks of procedures are made. Duplicate side-by-side monitors are operated intermittently at selected field stations to determine reproducibility of individual sampling trains. Automated instruments, having on-call telemetric output, permit daily routine instrument performance checks from the central processing point. Computer programs are presently being developed to monitor daily output of automated instruments and to flag deviations from expected performance.

Stationary monitors have inherent drawbacks as estimators of human exposure. Within short-term frames, individuals frequently change between indoor and outdoor environments, from one neighborhood to another, and from residential to occupational exposures. Quiet, acceptable small-scale instruments for personal monitoring have not been developed, though the need has been evident for years. Likewise, quiet indoor air monitors having desirable response characteristics have yet to be marketed. These deficiencies require reliance on stationary monitors to estimate current environmental exposures of communities.

Attempts to relate chronic diseases to long-term exposures are fraught with methodologic difficulties. Chronic disease is likely to result from cumulative exposures of several years to several decades. Current quantitative air monitoring data for a given neighborhood or city usually are available only from the past few years. Attributing area differences in chronic disease prevalence to current pollutant exposures frequently will lead to underestimates of the true exposure associated with illness. Air pollutant concentrations of the 1940's and 1950's, when coal was widely consumed for domestic heating and industrial control measures were less prevalent, tended to be considerably higher than values measured in 1970 or 1971. This is especially true in cities where stationary sources are principal contributors to community air pollution. Therefore, estimates of past exposure are required and have

TABLE II

CHESS health indicators

Exposure	Indicator	Sample size per CHESS community	Frequency of response
Short term (<4 days)	Frequency of asthma attacks	50–75	Daily
	Aggravation of chronic respiratory symptoms	50–75	Daily
	Aggravation of cardiac symptoms	50–75	Daily
	Acute irritation symptoms during episodes	400–1000	3–4 times yearly
	Daily mortality	Variable	Daily
Long term (usually 1+ years)	Pollutant burdens	800–1200	Once in 2 years
	Impairment of lung function	1500–2000	3 times yearly
	Incidence of acute respiratory disease in families	1000	Once every 2 weeks
	Frequency of acute lower respiratory disease in children	1500–3000	Once in 2 years
	Prevalence of chronic respiratory disease	1500–3000	Once in 2 years

Major CHESS efforts in 1973

Document in publishable form a summary of the effects of CO exposure on behavior and physiology that can be used to support the primary ambient air quality standards

Complete a human exposure facility in the Chapel Hill Laboratory in which a program identified as "CLEANS" (clinical laboratory evaluation and assessment of noxious substances) will be conducted. Program will be designed to determine behavioral and physiologic effects of acute exposure to controlled levels of pollution.

Develop a rapid screening procedure for predicting the potential toxicity of chemical substances

Develop a protocol and initiate studies of potential hazards associated with accidental exposure to materials designed for use in closed systems—for example, heat exchangers of the Rankine engine

Develop a basic program designed to determine the effects of noise and odors on human health and well-being

been made in CHESS chronic disease studies. These estimates are based on past emissions in communities dominated by a single point source. Emissions data and meteorologic information are entered into a meteorologic dispersion model, yielding estimates of ambient exposure. These results are calibrated to current ambient air monitoring data.

In multiple source urban areas, adequate past emissions data seldom are available, and dispersion models tend to cope inadequately with the complex variability of urban exposures. In these situations, local suspended particulate matter or dustfall measurements dating back to the early 1950's, when available, proved to be a valuable baseline for extrapolating from current air monitoring data to past exposure. In addition to long-term exposure estimates, some CHESS studies attempt to discriminate between chronic disease prevalence of long-time residents and recent immigrants to a high-exposure area. After discounting the relatively high illness rates of most recent immigrants (residence duration of one year or less), disease prevalence is compared in residents of two to four years duration from high- and low-exposure areas. Excess disease found among recent residents of high-exposure areas may be attributed to more recent exposure. If the effect is cumulative, area differences in disease prevalence will tend to be amplified among long-term residents.

Chronic respiratory disease

Five surveys have investigated the chronic respiratory effects of sulfur oxides, coupled with varying amounts of total suspended particulate matter. These surveys were conducted in the Salt Lake Basin, in smelter communities in Idaho and Montana, in the New York Metropolitan area, and in the Chicago area. In the Salt Lake Basin, a single copper smelter accounts for the great majority of sulfur oxide pollution, but leaves the region relatively free of suspended particulate matter. At the other end of the spectrum, the atmospheres of New York and Chicago contain a complex urban mixture of pollutants, with high levels of both sulfur oxides and particulate matter. The sixth survey, in Chattanooga, Tenn., investigated the effects of exposure to nitrogen dioxide. This city contains a large single source of nitrogen dioxide, a munitions plant, but contains low levels of other air pollutants.

As a result of these studies, there now exists a body of evidence that oxides of sulfur contribute substantially to the aggravation of chronic respiratory disease. The surveys in Utah, Idaho-Montana, New York, and Chicago suggest that sulfur oxide pollution exerts an effect which may rival the effect of cigarette smoking, particularly in areas with high exposures to both sulfur oxides and suspended particulate matter. Examination of excess risk figures suggests that the effects of sulfur oxides and of smoking on chronic bronchitis prevalence are roughly additive. Residence data from New York suggest that moving from a polluted area to a clean one can promote substantial improvement in symptoms. Finally, the New York survey of panels of elderly persons underscores the need for further assessment of suspended sulfates as a potentially dangerous health hazard.

Ventilatory function

One of the sensitive health indicators in the CHESS program is ventilatory performance. Significant decrements in ventilatory performance early in life may be a risk factor for later respiratory disorders. A summary of air pollution effects on ventilatory function of U.S. school children from CHESS studies in Cincinnati, Chattanooga, and New York point out that the pollutants of major interest in these areas were suspended particulate matter, sulfur oxides, and nitrogen oxides.

These three studies confirm results obtained in other countries, including England, Japan, Italy, and Canada. The accumulated evidence demonstrates a consistent relationship between exposure to particulate matter combined with sulfur oxides and impaired ventilatory function in children 5–13 years of age. Impairment was not normally associated with overt clinical manifestations and could be detected only by comparison with tests of children in low-exposure communities matched for age, race, sex, and socioeconomic characteristics. The influence of cigarette smoking and occupation could be eliminated by selection of elementary school children for study. In several reports, including the present Cincinnati data, performance of children in polluted communities improved during seasons of low pollution but did not attain the level of their counterparts in low-exposure neighborhoods.

In Chattanooga, exposure to the prime pollutant nitrogen dioxide was closely related to trinitrotoluene production. High exposures had therefore existed for only two to three years prior to this 1968–1969 study, which may account for the smaller pollutant effect on ventilatory function.

Though the magnitude of the air pollution effect on ventilatory performance was slight (varying from 2 to 17%) in the three studies, the fact that this impairment was imposed at an early age, prior to more severe insults as cigarette smoking and occupational exposures, renders these findings all the more significant in terms of disease prevention. CHESS evidence suggests that this early impairment can be reduced or eliminated by improved air quality.

Pollutant burdens

Studies aimed at linking pollutant burdens to biological response and environmental exposure have yielded interesting preliminary results. Whereas easily collected specimens such as hair and blood have proved utility in estimation of environmental exposure, these tissues cannot, as yet, be considered a good quantitative indicator of body pollutant burdens. Studies of occupationally exposed groups or groups of individuals with diseases have failed to clearly implicate pollutant burdens with either disease production or aggrevation although, in general, blood levels of pollutants do reflect increased exposure.

Studies of multiple tissue sets collected at necropsy are encouraging since these tissues apparently will provide pollutant burden information useful in constructing predictive models and, in addition, provide flashback capabilities. The development of sensitive biochemical response indicators as correlators or quantifiers of pollutant burden effects is under way as well. The aim of these studies is to adapt these systems to field survey use on a broad scale.

Acute respiratory disease

Children suffer the highest incidence of acute respiratory disease, and there is increasing evidence that a history of repeated acute lower respiratory illnesses in childhood may contribute to the development of chronic bronchitis in later life. To prevent chronic disease in adults it is important to identify and control factors which might induce or aggravate acute respiratory illness in children. Laboratory and epidemiologic reports have linked air pollutant exposure to increased frequency and severity of acute respiratory disease in children.

CHESS studies have been carried out to determine the effect of sulfur dioxide and suspended sulfates on acute respiratory disease in children and adults in four areas of the U.S. Studies involving 20,472 children and adults clearly linked excessive acute respiratory disease in those people living in communities heavily polluted with sulfur dioxide and suspended sulfates. Pollution exposure of three years or longer was an important component in contributing to increased risk for acute respiratory disease. Laryngotracheobronchitis, or croup, was the major reason for excess acute lower respiratory problems in children in heavily polluted communities in the Salt Lake Basin and Rocky Mountain communities. The effect of pollution on excess acute respiratory disease was independent of socioeconomic status and cigarette smoking.

Study strategies

CHESS area sets are selected to evaluate existing air quality standards for particulate matter, sulfur oxides, nitrogen oxides, and photochemical oxidants. Because effects of short-term carbon monoxide (CO) exposures are more precisely studied in controlled exposure chambers, a CHESS area set to measure CO effects was not established.

Middle class neighborhoods are chosen because they represent a large proportion of the population, have a more homogeneous family and social class distribution, and reside in neighborhoods whose characteristics change more slowly than in central city neighborhoods. However, because residents of central city areas often experience pollutant exposures higher than those of the surrounding neighborhoods, certain CHESS area sets have deliberately included inner city segments of the population. These residents are exposed to additional stresses of congestion, substandard housing, urban noise, and low income. Disentangling the causal webs of this environment will be difficult, but the potentially large benefit of pollution control warrants the efforts.

Family participants for surveys of acute upper and lower respiratory disease frequency, chronic respiratory prevalence, and irritation symptoms during episodes are recruited from elementary and secondary school enrollments in CHESS neighborhoods. Recent school busing across neighborhoods has complicated this method of recruiting families. Subjects for asthma, cardiac, and chronic respiratory disease panels are obtained from responses to the chronic respiratory disease questionnaire and from patient listings of private physicians. Depending on the health indicator, families and panel members are contacted through single-time prevalence surveys, mailed weekly diaries, bi-weekly telephone calls, or telephone calls during air pollution episodes. Lung function of children is measured at each participating school (volumetric methods are for these surveys). Hair samples obtained from family members are analyzed routinely for concentrations of zinc, cadmium, lead and copper, and selected other trace metals. Maternal fetal tissue sets, including cord blood, maternal blood, maternal hair and placental tissue, and autopsy tissues are obtained from each CHESS neighborhood for pollutant burden studies. Cooperation of local hospitals is solicited for tissue collections.

In the CHESS program, health characteristics are not measured in probability samples of the population for two reasons. First, air quality standards are being established to protect particularly vulnerable segments of the population. Therefore, asthmatics and subjects with existing heart and lung disease are deliberately recruited. Second, these methods for enrolling subjects are far less costly and cumbersome than probability sampling. Selected population groups are matched across each CHESS area set for characteristics which may influence the frequency of the health indicator. The ubiquity of middle class families with school children and of persons with preexisting heart and lung disease allows CHESS officials to be reasonably confident about the applicability of the findings to most communities of this country.

CHESS programs will operate from three to five years in most areas. Measurement of sensitive health indicators during an interval of improving quality is an optimal way to quantitate the health benefits of pollutant controls. Studies may be extended to detect time lags between air quality improvement and anticipated health benefit. Developmental work is now in progress to deploy more sensitive and objective health indicators, particularly physiologic and biochemical responses, of short-term variations in air quality.

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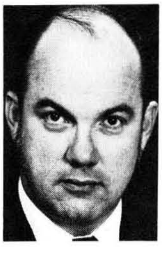

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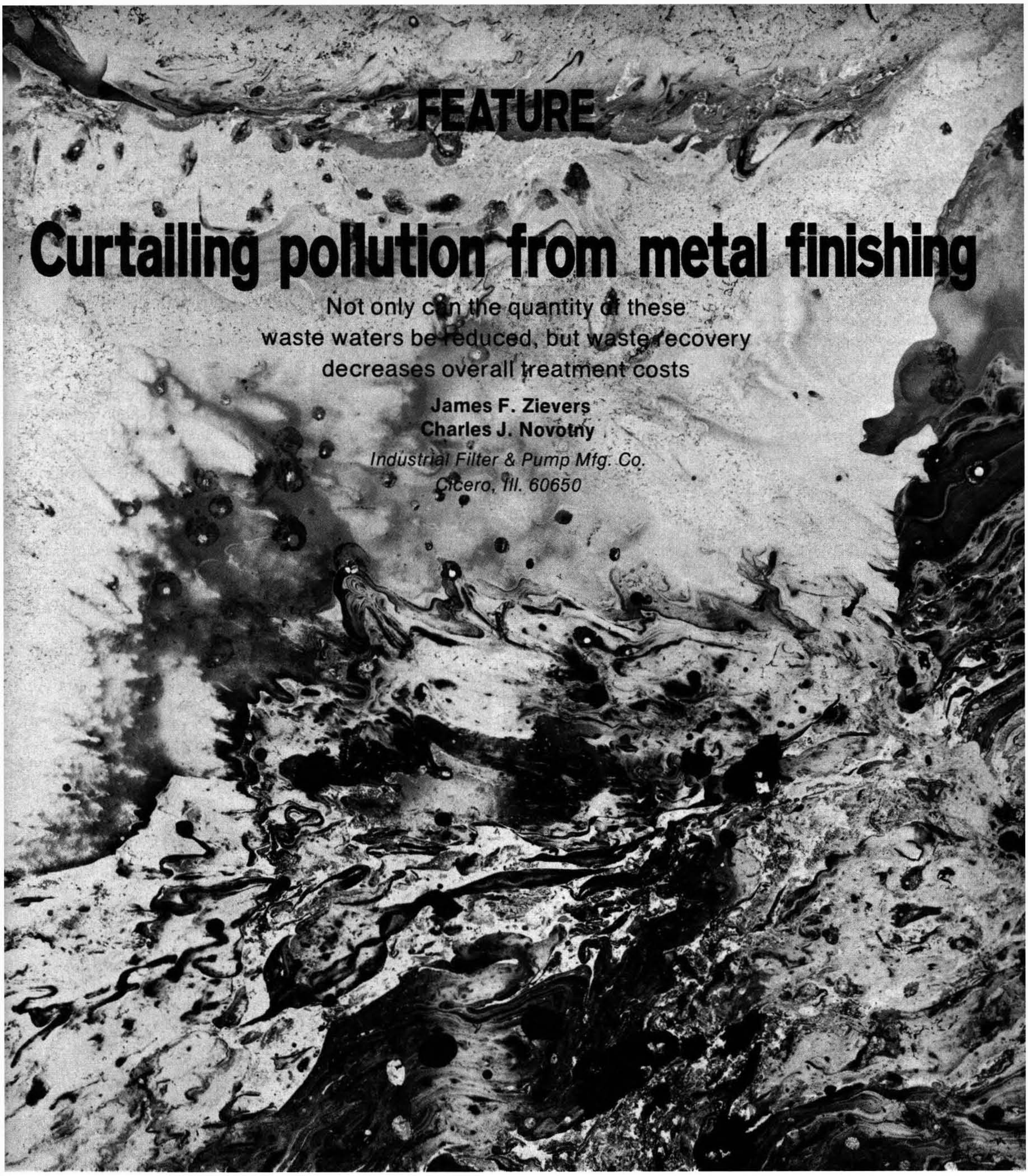

FEATURE

Curtailling pollution from metal finishing

Not only can the quantity of these waste waters be reduced, but waste recovery decreases overall treatment costs

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Seven types of pollution are commonly associated with the normal metal-finishing operation. These wastes include cyanides, hexavalent chromes, pH fluctuations, oil, heavy metals, phenols, and phosphates.

Cyanides and hexavalent chromes must be treated because they are toxic, and this is usually done by alkaline chlorination and low pH sulfonation, respectively. Wide fluctuations in pH need to be corrected since such fluctuations can be considered corrosive and hence destructive. Alkaline or acid pH correction agents usually handle this problem.

Oil is inflammable and dangerous; and by covering the surface of water bodies, it prevents life-giving oxygen from entering the water. Depending on the quantity of oil involved, it may be skimmed or otherwise taken from the water surface, or it may be "broken"—normally at low pH at relatively higher temperatures. The oil fraction is usually recovered, and the aqueous fraction is treated further to required water quality standards.

Heavy metals, usually metallic hydrates, are considered toxic, depending on the quantity, by water pollution control authorities. Sedimentation, clarification, and/or filtration can be used to remove heavy metals from metal-finishing wastes.

Depending on the type of metal-finishing operation, phenols may be present in the effluent. These odoriferous compounds may be treated by adsorption onto activated carbon. If the quantity of phenol in the effluent is great enough, it may be recovered by scrubbing and distillation.

The last major pollutants from metal finishing are phosphates, which the majority of the scientific community believes contributes to eutrophication of rivers and lakes. Phosphates can be removed by a number of methods. When they are in relatively small concentration and consequently appear most difficult to handle, adsorption on activated carbon is an effective method of removal; they can also be precipitated with lime.

Waste plant design

Six procedures in metal-finishing operations can be followed to result in the smallest treatment plant possible handling the least possible quantity of wastes. The first item, "housekeeping," involves personnel discipline and morale. Maintenance of a clean plant will normally guarantee against injurious and obnoxious spills, mixes, and process losses that would otherwise be expensive.

The second routine is segregation which includes identification of all sources of waste that must be treated and segregation of those sources into channels permitting sensible treatment of the various components of the overall waste flow in the most efficient manner. In other words, cyanide-bearing wastes should be separated from chrome-bearing wastes. It further entails handling concentrated dumps (periodic discharges of very strong wastes) so that those dumps can be bled slowly into running rinses for treatment; this removes shock loads, overdesign of dosage equipment, etc.

The next method of preparation is scheduling. If water is to be recovered, all concentrated dumps can be scheduled for treatment for a limited period of time per week, or per unit period of operation, and running rinses can be treated the rest of the time. Since the amount of dissolved salts in running rinses is relatively small, the cost of recovering water will be relatively small. During the period when the dumps are used, the waste can be neutralized and still safely discharged to the receiving water body.

The fourth consideration in waste plant design is reducing effluent volume, which can be commonly accomplished by employing countercurrent rinsing and increasing the number of countercurrent rinses or by using conductivity control on rinse water. Next, reduction of intensity is accomplished by switching the type of plating bath used. For example, shifting from a high cyanide bath to a low cyanide bath reduces the intensity of cyanide in process to $\frac{1}{10}$ of its previous concentration. Mist suppressants are commonly used in conjunction with chrome baths for similar purposes. In some cases, the substitution, for example, of cyanide baths, can lead to difficulty in breaking down chelating agents utilized in the substitute. The sixth technique is termed change of chemistry. For example, the use of copper sulfate baths as a substitute for copper cyanide can eliminate the need for cyanide treatment in some cases.

The importance of waste plant design and, of course, reducing the amount of water entering the plant and the amount of water leaving the plant via the waste system is shown by the average changes in raw water cost and in sewer charges in the U.S. Water is expensive, and plants should be operated to use as little water as possible.

There are 12 commonly used methods for treating metal-finishing wastes. Dilution was more commonly used in past years where, for example, an effluent flow containing 25 ppm of cyanide could be diluted with sufficient water to drop the total cyanide in the effluent to whatever the tolerable limits were. However, with rising water costs and tighter control on allowable limits by regulatory agencies, this technique will probably be used less and less.

The second technique, containment, is lagooning some materials for eventual disposal by evaporation. In other cases, drumming of materials such as solvents or radioactive materials may be used. Drumming will probably remain as a widely used containment technique for many years; lagooning, however, may fall into disuse as tighter restrictions on materials entering the subsoil are enforced and as prices of land available for lagooning continue to rise.

Chemical conversion includes cyanide destruction by alkaline chlorination, chrome reduction by low pH sulfonation, and pH adjustment for conversion of soluble heavy metals to heavy metal hydrates for subsequent disposal by other techniques. These are widely accepted as general treatment techniques and can be made economically feasible by careful selection of the chemical equation to be followed and by use of the most ubiquitous and lowest priced chemicals.

Using combustion as a disposal technique may involve a metal finisher attempting to solve a liquid pollution problem and producing a subsequent air pollution problem. Combustion has been used in the past with oil, solvents, and some contaminated carbons. Evaporation, and/or reverse osmosis are both used for the recovery of fairly concentrated metal baths for reuse.

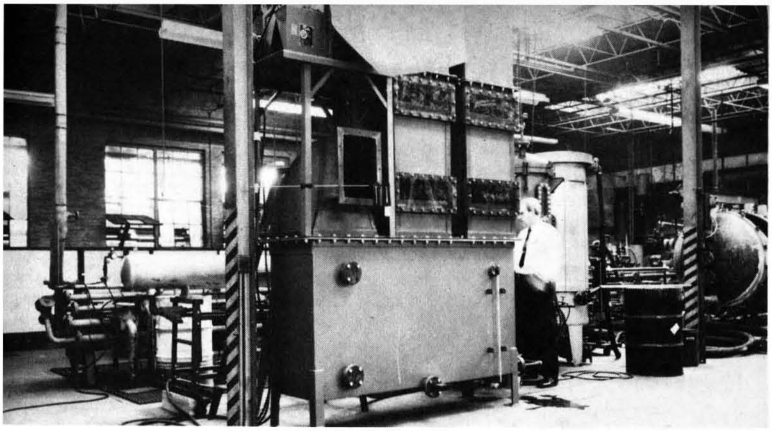
Ion exchange can be used to concentrate wastes to reduce treatment plant size but is more commonly used for metal recovery. Often ion exchange and evaporation will be used in conjunction with each other to recover metal baths for reuse. Ion exchange is also widely used for preparing treated effluents for reuse in the treatment plant itself.

In some cases, extremely difficult acids and some ammonia compounds (weak ammonia liquors from steel plants) are more easily disposed of by pumping them into a deep well drilled into suitable strata in the subsoil. In the U.S., such wells are usually drilled to a depth of 2500–4000 ft. Permission must be obtained from the cognizant government authority prior to deep-well injection, and the effluent is normally filtered to a high degree of

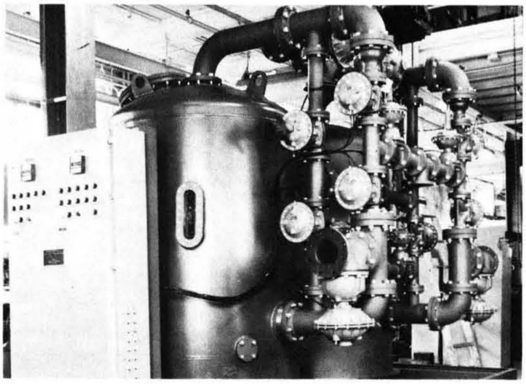
TABLE I

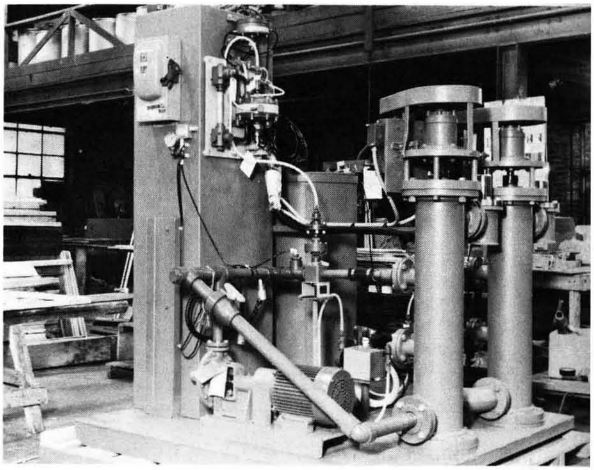
Metal finishing wastes treatment techniques

TREATMENT	COMMENT
Dilution	With rising water costs and stringent limits, probably will be used less and less
Containment	Lagoons for some materials; drums for solvents
Chemical conversion	Cyanide destruction; chrome reduction
Combustion	Oil–solvents–carbon
Evaporation/reverse osmosis	Recovery of fairly concentrated metal baths for reuse
Ion exchange	Capture of metals for recovery; purification of water for reuse
Deep well disposal	Difficult acids, some ammonia compounds
Sedimentation	Natural "fall-out" of hydrates, etc.
Clarification	Promoted "fall-out" of hydrates, etc.
Aeration	Reduction of BOD
Filtration	Removal of suspended solids—practically a "must" for recovery or reuse
Combination	Viz use of fly ash to aid removal of heavy metal hydrates



Waste treatment. *Chromic acid can be profitably recovered from metal finishing wastes by an atmospheric evaporator (above), and high quality rinse water is produced by a two-bed ion exchange unit (below). A packaged two-stage cyanide destruction system (right) prepares wastes, by chemical conversion, for disposal by other techniques*





clarity prior to disposal to prevent plugging the well. Although well disposal is fairly widely practiced, six states still do not allow it.

The eighth treatment technique is sedimentation or the natural precipitation and settling of hydrates and other suspended matter in a relatively quiescent pond—the effluent from which is then fed to the receiving water body. From time to time, the ponds must be dredged and the sludge disposed of by dumping or piling.

Because of the rising cost of land, clarification, rather than sedimentation, is used. Precipitation of hydrates and other suspended matter is promoted in a hydromechanical device to which polymeric flocculants, alum, etc., are added to induce the sedimentation of materials. Underflow from a clarifier will normally contain 1½–3 wt % solids. Overflow will normally contain a liquid with a clarity equivalent to perhaps 15–30 ppm of suspended solids, which is normally satisfactory for discharge to a receiving water body.

Aeration is normally used for reduction of BOD. Filtration is used to remove suspended solids and can be accomplished with pressure- or vacuum-type equipment. Filtration is practically a must when recovery or reuse of treated waters is being considered. The recovered waters must be suitable for rinse purposes; suspended solids cannot be tolerated. When vacuum equipment is used, accumulated solids on the filter are normally discharged at about 80% moisture. Solids from pressure filters are usually about 50% moisture. Effluent clarity will average 0–3 ppm suspended solids.

The last treatment technique, combination, will use two obnoxious materials together to accomplish one mutually compatible end. For example, fly ash from a stack scrubbing operation can be used as a filter aid and precipitation promoter for the filtration of heavy metal hydrates. Each of the two items, the fly ash and the metal hydrates, constitute a problem, and yet when combined each helps the other to solve the problem.

Waste treatment and profit

Can waste treatment be profitable? Probably not overall, but some methods certainly can be less expensive than others, and recovery credits can go a long way toward alleviating treatment cost debits.

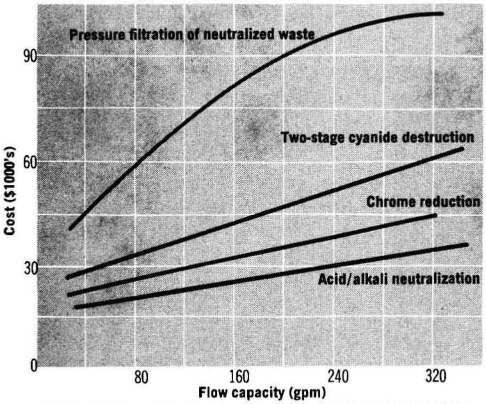
First, a look at costs is in order. Figure 1 illustrates up-to-date initial capital costs (including installation) of various metal-finishing waste treatment plant components. The graph illustrates the economic importance of reducing individual waste flows to the lowest possible volume. Those same initial capital costs have been amortized over 10 years and included with chemical and labor costs to produce the operating cost curves shown in Figure 2. Of special interest in Figure 2 is the cost-reducing effort of change in plating bath chemistry, such as the use of low-cyanide baths. Further reductions in operating costs can be made, for example, by using SO_2-bearing flue gases in treatment of chrome-bearing wastes.

Recovery of acids and/or metals may result in waste treatment producing financial credits. Such recovery usually involves evaporation and may or may not involve ion exchange equipment or reverse osmosis equipment. If we assume evaporation system is properly sized and operated, a metal finisher may expect to recover 95–96% of the valuable product present in his rinse stream. Recovery can comprise an average of 40% of total usage.

Recovery by evaporation is practiced, for example, in conjunction with phosphoric acid used in pickling steel. In recent years, cation purification and evaporation have been widely used profitably to recover chromic acid.

FIGURE 1.

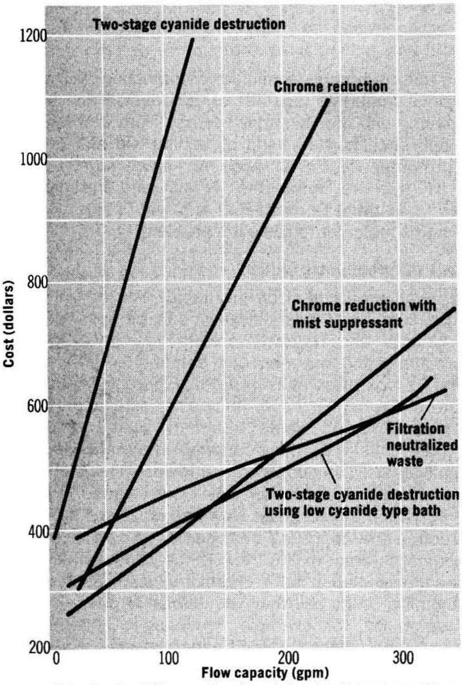
Initial capital costs for treating metal finishing wastes



Note: Based on installation, minimum instrumentation, manual valves, package plants where applicable

FIGURE 2.

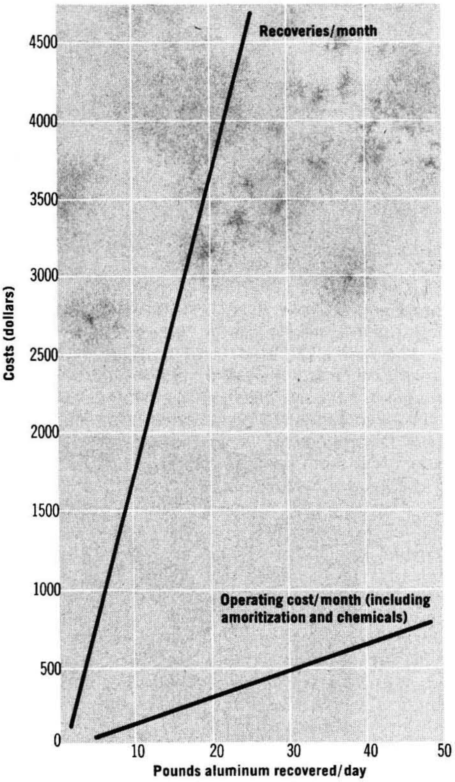
Monthly operating costs to treat metal finishing wastes



Note: Based on 172 hr. operation, depreciation of capital equipment 10 yrs—straight line basis. Contaminant level at 50 ppm for CN and Cr^{+6}

FIGURE 3.

Ion exchange costs relate to aluminum recovered



Countercurrent rinsing can reduce volume of rinse flow which in turn reduces evaporation costs.

Ion exchange can also be used to create a less expensive waste problem. For example, in the new hard-coat anodizing bath (in metal finishing), dissolved aluminum ties up some of the anodizing acid. Part of the bath can be discarded to the waste treatment plant and replaced with new solution to maintain the aluminum concentration at an acceptable level.

An alternate method is to remove dissolved aluminum with a cation exchange system. The waste regenerant goes to the waste plant just as discarded bath would have gone. However, ion exchange allows reuse of the anodizing bath, which is valued at $1.00/gal.

The monthly cost of such an ion exchange system (including amortization and chemicals) is a function of the amount of aluminum which must be removed each day. The value of the recoveries—the value of the bath which would have been discarded without ion exchange—indicates the profits of the system or the reduction in the cost of waste treatment (Figure 3).

Recently a large automobile manufacturer installed two ion exchange systems to produce high-quality water for rinsing purposes and to recover and concentrate nickel sulfate solution which in turn is reused in the nickel plating baths. By utilization of a multiple countercurrent regeneration system, 2.4 lb of nickel/ft^3 of cation resin installed was recovered. In the larger (120 gpm) system, the pay-out time is 2.1 years, and for the smaller (80 gpm) system, pay-out time is 2.4 years which includes cost of capital equipment, installation, and operation.

Where smaller flows are anticipated, reverse osmosis can be used to achieve similar economies.

After all of the alternatives for recovery have been explored and those that are most feasible for each individual finisher have been applied, there will still be a treated effluent flow. If we assume dumps are scheduled for a fixed period each week, the average concentration of dissolved solids in the effluent will be approximately 500 ppm. Water for rinsing purposes (except critical rinses) is satisfactory if the level of dissolved solids approximates 300 ppm. Depending on combined raw water and sewer charges, and further depending on the analysis of the raw water, it will often be feasible to recover effluent waters by ion exchange. Raw water and sewer charges are rising very rapidly and apparently will continue to rise, making water recovery a thing that must be reassessed continually.

A survey of 21 U.S. and European cities made in 1972 revealed that as of January 1972 the average of combined raw water and sewer charges was $0.460 per 1000 gal. Water recovery by ion exchange is feasible if the effluent flow approaches 300 gpm. Other factors can make such recovery feasible sooner. For example, if raw water analysis is such that treatment would be required, recovery could very well be the most attractive alternative.

Some researchers have advocated using ion exchange for water recovery by applying ion exchange directly to mixed running rinses, and have cited operating experience that indicates, for example, that cyanides (not captured by weak base resins) do not reach dangerous levels in the recycled water. Should such a procedure be acceptable to local safety regulations, it would make water recovery economically feasible at flow rates as low as 40 gpm.

Continuous ion exchange equipment is no more costly initially than conventional equipment and is approximately 30% less expensive to operate. With continuous ion exchange equipment, water recovery just may approach profitability.

Additional reading

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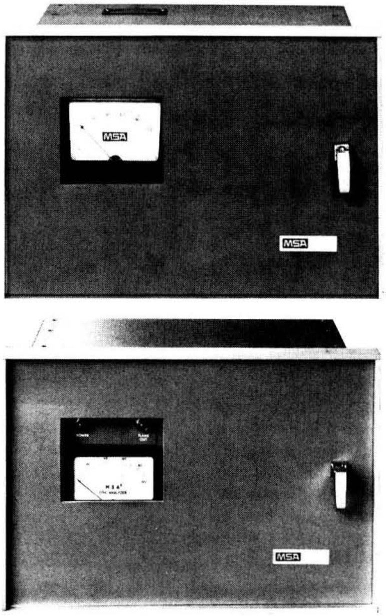
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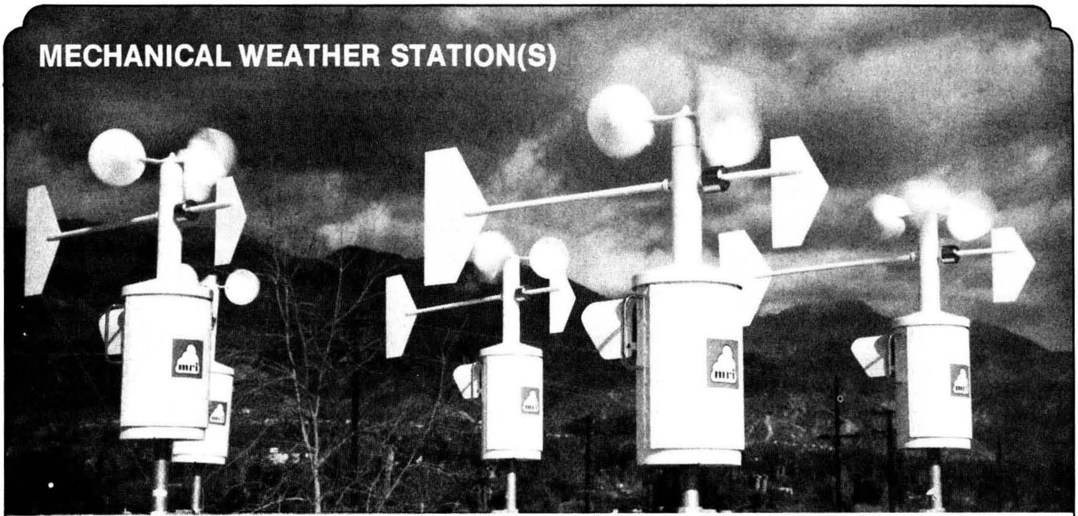
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Conference on Science in the Control of Smog

The conference on Science in the Control of Smog was held at the California Institute of Technology on November 15 and 16, 1971, to review the current status of research on photochemical smog, particularly as it relates to control measures and policy. The meeting was held in honor of Dr. Arie Haagen-Smit on the occasion of his appointment as Professor Emeritus at Caltech. The classic papers of Dr. Haagen-Smit on photochemical smog, including "The Chemistry and Physiology of Los Angeles Smog," *Ind. Eng. Chem.*, 44, 1342 (1952), had been published almost 20 years previously. In these original papers Dr. Haagen-Smit had described a series of laboratory and field experiments which clearly demonstrated the key role which automobile exhaust played in the generation of the peculiar kind of air pollution afflicting the Los Angeles basin. The mechanisms by which the primary pollutants are formed in the automobile are described in the conference papers.

An important result of Haagen-Smit's early work was the elucidation of the main features of the chemical system involved in the generation of photochemical smog. Several different primary chemical pollutants reacted in the atmosphere in the presence of solar radiation to produce many new chemical species at low concentrations. The new chemical species included oxidants, eye irritants, and phytotoxicants and the formation of condensable chemical species contributed to visibility-degrading aerosols. Despite the low concentrations, significant human and plant response was reported.

To measure the atmospheric levels of these pollutants, many new instruments capable of continuous on-line measurement of very low gas concentrations were developed over the years following Haagen-Smit's discoveries. (However, there is still no proved commercial instrument that can measure any of the chemical constituents of particulate pollution on a continuous on-line basis.) Increasingly sophisticated monitoring networks were created of which the one in Los Angeles is among the most complex. With the availability of data, it became possible to set up detailed models relating air quality to emission sources, and some of these are discussed in the papers of this conference. The development and validation of air pollution models for urban basins are vital to the development of rational air pollution control policies.

Despite initial reluctance, by 1970 the automobile industry had finally made a significant commitment in its research and development programs to the control of emissions. This has led to the exploration of the possible use of new types of propulsion systems controlled by computer.

Thus by the 1970's, the field of air pollution had passed into a new phase: Technical concerns had shifted from considerations of gross tonnages of inert gases or dusts to modeling, sensor design, and data analysis and data handling of multiphase, nonequilibrium chemical systems. From limiting emissions to prevent acute exposures as reflected in morbidity or mortality statistics, the new concerns are with behavioral responses to very low pollutant levels or the effects of chronic, low-level exposure over long time periods.

One of the remarkable aspects of Dr. Haagen-Smit's career has been the vigor with which he has pursued on a state and national level the policy implications of his scientific findings. He served as chairman of the President's Task Force on Air Pollution, and is presently chairman of the State of California Air Resources Board.

Several conference papers were invited on the role of the sciences, particularly chemistry, in the development of air pollution control policy. These were among the most stimulating presentations but have not been published in this collection. The insistence of the reviewers on originality and an integrated presentation could not be reconciled with the efforts of the authors to relate science to public policy. Independent review and entirely separate judgments in each case led to a decision not to publish these papers in *ES&T* at this time.

The need remains for such contributions-discussions of the relationship of public policy to technical findings prepared by engineers and scientists well-grounded in the subject matter. I hope our conference will stimulate further efforts of this type.

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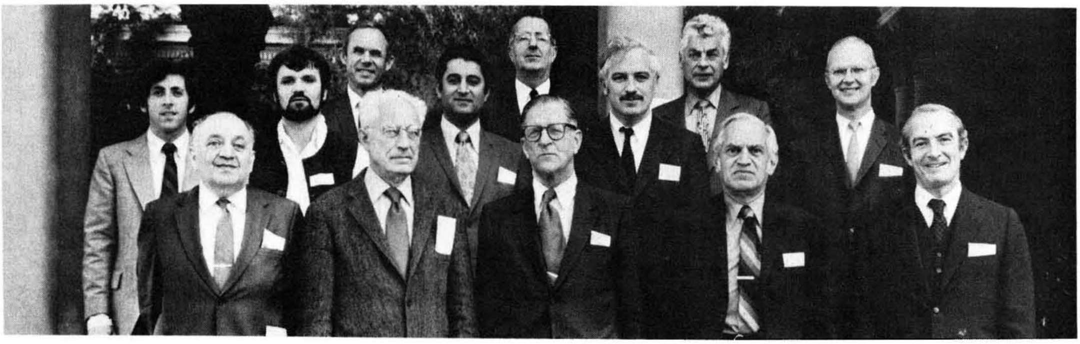

Speakers and session chairmen, conference on Science in the Control of Smog, November 15–16, 1971; front row (from left to right), Francois Frenkiel, F. E. Blacet, A. J. Haagen-Smit, Morris Neiburger, S. K. Friedlander; second row, J. H. Seinfeld, R. B. Husar, Kamran Habibi, J. J. Morgan, J. C. Keck; top row, J. G. Edinger, W. H. Corcoran, Bernard Weinstock

CURRENT RESEARCH

Formation of Hydrocarbons and Oxides of Nitrogen in Automobile Engines

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■ The basic mechanisms responsible for the production of nitrogen oxide and hydrocarbon emissions from automotive spark-ignition engines are reviewed. It is shown how the formation of nitric oxide is rate controlled in the high-temperature burned gases inside the engine cylinder. A mathematical model which predicts nitric oxide emissions for given engine design and operating variables is then described. In contrast, the hydrocarbons are formed when the flame quenches at the cylinder head and piston walls. The magnitude of these quench layers and crevices and the boundary layer aerodynamics by which the hydrocarbon-rich gases exit the cylinder are discussed.

In the paper we have the privilege of presenting at this symposium honoring Professor Haagen-Smit, we will review what has been learned about the basic processes responsible for the production of hydrocarbons and nitrogen oxides in automotive engines. The objective of this work has been to develop the quantitative understanding of these processes necessary for the design and evaluation of techniques for reducing smog at its source. The importance of this objective is easily appreciated when one considers the tremendous capital investment required to make even minor changes in the millions of automobiles produced annually and to monitor their performance once they are on the road. Other aspects of the problem, including the emission of particulates, the atmospheric reactions between hydrocarbons and oxides of nitrogen which produce smog, and the measures necessary to develop control programs are discussed in the subsequent papers at this symposium.

The 100 million motor vehicles on the road in the U.S. today are the source of about 60 million tons of CO, 16 million tons of HC, and 7 million tons of NO_x annually—1200 lb of CO, 320 lb of HC, and 140 lb of NO_x per car. In an uncontrolled vehicle—that is a car sold before any emission controls were required—these emissions came from the engine crankcase, from fuel evaporation in the fuel tank and carburetor, and from the exhaust. The crankcase and evaporative HC emissions are now effectively controlled in all new vehicles. The engine itself is responsible for the remaining source of HC and of CO and NO_x emissions. Though 80 and 70% control of HC and CO exhaust emissions, respectively, has already been achieved with current new vehicles, substantial further reductions in all exhaust emissions will be required within the next five years. The control techniques already employed, and those proposed for the future have been reviewed by Brehob (1971). Here we will concentrate on the physics and chemistry of pollutant formation.

The processes responsible for the production of hydrocarbons and nitogen oxides in the cylinder of a spark-ignition engine are illustrated qualitatively in Figure 1 which shows three important stages in the combustion process. In the first stage the compressed fuel-air mixture is ignited, and a flame front propagates across the chamber. As the flame approaches the walls, it is quenched leaving behind an extremely thin layer of unburned gas typically a few thousandths of an inch thick. Unburned gas is also left in the crevice above the piston ring between the piston and cylinder wall. This unburned gas is the source of the hydrocarbons. At the same time nitric oxide (NO) is formed in the combustion products throughout the cylinder by high-temperature nonequilibrium reactions involving the nitrogen and oxygen in the air. Another important pollutant also formed during the combustion is carbon monoxide (CO), but this is not important in smog formation and will not be discussed in detail. In the second stage the piston recedes depositing the unburned hydrocarbons in the crevice above the piston ring along the sides of the cylinder and rapidly cooling the bulk combustion products by expansion. As a result of the falling temperature, the chemical reactions which would normally remove the NO and CO become extremely slow, "freezing" the concentrations of these pollutants at levels far above those expected for equilibrium at exhaust temperatures. In the final stage the exhaust valve opens, and the polluted combustion products leave the cylinder-entraining parts of the unburned hydrocarbon layers on the walls as they go.

From this qualitative discussion it should be clear that the processes responsible for the production of nitric oxide and unburned hydrocarbons are distinctly different. The former involve primarily combustion kinetics, and the latter flame quenching and boundary layer aerodynamics. It is also known from the pioneering work of Hershey et al.

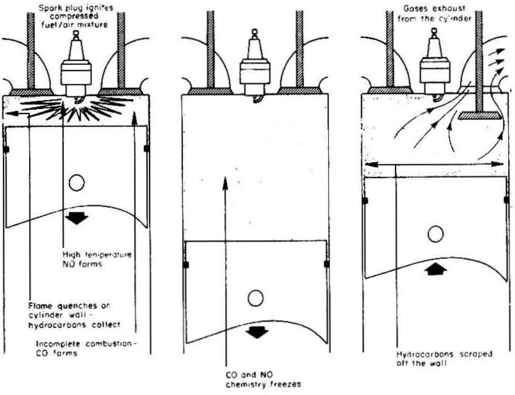

Figure 1. Schematic shows how three major pollutants—unburned hydrocarbons (HC), carbon monoxide (CO), and nitric oxide (NO)—form inside the spark-ignition engine cylinder during combustion process

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[1] To whom correspondence should be addressed.

(1936) that the thermodynamic state of the burned gas in an internal combustion engine is very close to equilibrium and that the trace concentrations of pollutants present represent a minor perturbation of the system. Thus the problem of treating the production of nitric oxide and hydrocarbons may be conveniently divided into three parts: the determination of the temperature, density, and concentrations of major species for burned gas in equilibrium; the investigation of the chemical kinetics of nitric oxide in this environment; and the study of the formation and aerodynamics of the hydrocarbon-containing boundary layers.

Thermodynamics of Internal Combustion

The combustion process in a spark-ignition engine is illustrated in Figure 2. The top curve shows a typical cylinder pressure, p, vs. crank angle; the second curve, x, shows the mass fraction of the charge which has burned. The fuel–air–residual gas mixture is sparked at $\theta = -40°$, and combustion is complete at about $\theta = 30°$. An important consequence of the finite time required to burn the charge is the different temperature–time histories of parts of the mixture which burn at different times during the combustion process. The following model illustrates this process; more exact models are discussed later.

Based on the assumption of equilibrium in the burned gases, Lavoie et al. (1970) have developed a simple model of internal combustion which permits one to calculate the thermodynamic state of the burned and unburned gases from a knowledge of the pressure and volume of the system as a function of time. In addition to assuming equilibrium in the burned gas, the model assumes that: the original charge is homogeneous; the pressure is independent of position; the volume occupied by the gas in a state of partial combustion is negligible; the unburned gas is "frozen" at its original composition and undergoes an isentropic compression; and both burned and unburned gases have constant local specific heats. Under these conditions the mass fraction of the charge which has burned, x, can be calculated from the laws for conservation of mass and energy and the equations of state for the burned and unburned gases.

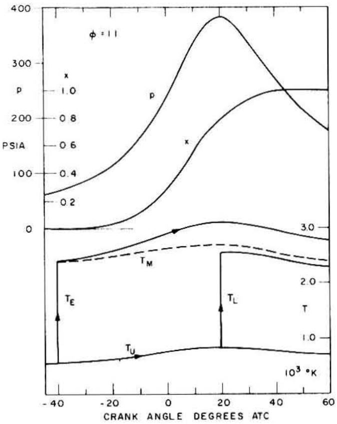

Figure 2. Gas pressure inside cylinder (p), mass fraction burned (x), and temperatures of unburned mixture (T_u) and elements of charge which burned early (T_E) and late (T_L) as a function of crank angle

Dashed line shows the average burned gas temperature (T_M) if it were fully mixed

To determine the temperature distribution in the burned gas, it is necessary to make an assumption about the state of mixing in these gases. In most previous treatments of the problem, it has been assumed that each element of the charge which burns mixes instantaneously with the previously burned gas resulting in a uniform temperature throughout the burned gases in the cylinder.

We do not believe that this "completely mixed" model is a good approximation, however, because it is incompatible with both the observations of a relatively thin turbulent flame front and substantial temperature gradients in the burned gas (Rassweiler and Withrow, 1935; Lavoie, 1970). A more realistic approximation is that there is no mixing during the early part of the combustion process, and that each element of gas which burns is isentropically compressed from its state just behind the flame front as the pressure rises. The unburned mixture is also compressed isentropically. Thus each element of the charge burns at constant but different pressure and enthalpy. Each element is then compressed and expanded isentropically as the rest of the charge burns and the piston recedes.

Typical temperature–time histories for the unmixed model are shown in the lower part of Figure 2 for two elements of gas: one which burned early in the cycle denoted T_E and one which burned later denoted T_L. Also shown are the mean temperature T_M of burned gas and the temperature T_U corresponding to isentropic compression of the unburned gas. A substantial temperature gradient exists, and the gas which burned early has a peak temperature approximately 500°K higher than that which burned late. Due to the extreme temperature sensitivity of chemical reaction rates, such temperature differences can easily produce order of magnitude variations in the concentrations of NO formed in the burned gases, and it is very important to take them into account.

For detailed kinetic calculations of the NO formation process, more accurate information on the state of the burned gases is required than can be obtained from a perfect gas model of the type described. However, the same calculation procedure can be carried out using computer programs which give the properties of the unburned mixture and the equilibrium thermodynamic properties and composition of the burned gases. Such calculations have been carried out (Heywood, et al., 1971; Blumberg and Kummer, 1971), and the magnitude of the temperature gradient across the burned gases is close to that predicted by the perfect gas model.

Although the "unmixed" model appears to be satisfactory for correlating measurements on actual engines where the pressure–time history can be measured, it cannot be used for design studies without the addition of a "burning law" from which pressure–time histories can be calculated. To date no satisfactory "burning law" based on fundamental principles has been developed. This gap in our knowledge is currently being bridged by the use of semiempirical "burning laws" of the type

$$x(\theta) = (1/2)[1 - \cos \pi[(\theta - \theta_o)/\Delta\theta]] \quad (1)$$

where θ_o is the apparent ignition angle which may include a substantial "ignition delay" and $\Delta\theta$ is an apparent burning angle of the order of 40–50 crank angle degrees. With $x(\theta)$ known, $p(\theta)$ can be calculated from conservation of mass and energy as described previously. There is little doubt, however, that more accurate burning laws are needed, and the deviation of these is an important area for future research.

Kinetics of NO Formation

The chemistry of NO formation in gas phase mixtures of O, N, C, and H has been extensively studied in shock tubes, stirred reactors, and flames, and rate constants for all the important reactions have been determined (see Baulch et al., 1969 for a critical review). With this work as a basis, kinetic models of NO formation in automotive engines have been proposed by Newhall and Starkman (1967), Eyzat and Guibet (1968), and Lavoie et al. (1970). Of these models, that of Lavoie et al. is most complete and includes the other two as special cases. The most important reactions to include are:

$$N + NO \rightleftharpoons N_2 + O + 75{,}000 \quad (2.1)$$

$$N + O_2 \rightleftharpoons NO + O + 31{,}800 \quad (2.2)$$

$$N + OH \rightleftharpoons NO + H + 49{,}400 \quad (2.3)$$

The exothermic rate constants are given in Table I. The exothermicities and activation energies are in cal/g-mol, and the rate constants are in cm^3/sec.

If we assume that the concentrations of O, O_2, OH, H, and N_2 are in local equilibrium in the burned gases, the Reactions 2.1 to 2.3 may be combined to give two first-order nonlinear differential equations for the concentrations of NO and N. Although numerical integration of this pair of equations is possible, it can easily be shown that the characteristic relaxation time for N is several orders of magnitude shorter than that for NO. It is thus an excellent approximation to assume a steady-state value for N. The set may then be reduced to a single equation for the NO formation rate:

$$\frac{d\{NO\}}{dt} = \left(\frac{2M_{NO}}{\rho}\right)(1 - \alpha^2)\left(\frac{R_1}{1 + \alpha K}\right) \quad (3)$$

where $\{NO\}$ is the mass fraction of NO, M_{NO} is the molecular weight of NO, ρ is the gas density, $\alpha = [NO]/[NO]_e$ is the concentration of NO divided by its equilibrium value, $K = R_1/(R_2 + R_3)$, and R_i is the "one-way" equilibrium rate of the ith reaction—e.g., $R_1 = k_1[NO]_e[N]_e$. This reaction scheme corresponds to the well-known Zel'dovich mechanism extended to include the reaction of N with OH.

If Reaction 2.3 is omitted, K in Equation 3 is then R_1/R_2. Typical values of R_1, R_1/R_2, and $R_1/(R_2 + R_3)$ for lean, stoichiometric, and rich mixtures are given in Table II. Since α can exceed unity under spark-ignition engine conditions, the addition of Reaction 2.3 to the Zel'dovich mechanism would be expected to affect the calculated NO concentrations especially for rich mixtures. For example, for $\phi = 1.2$, the omission of Reaction 2.3 increases the calculated exhaust NO concentration by about 50% at typical engine-operating conditions.

If we use temperature, density, and species concentrations given by the full equilibrium thermodynamic model outlined in the previous section, Equation 3 may be integrated numerically to obtain the mass fraction of NO as a function of time for any element of burned gas. Although this procedure is not applicable in the flame front where the radical concentrations are far from equilibrium, there is both experimental and theoretical evidence that NO formation in this region is negligible compared to that in the postflame gas at gas pressures and temperatures typical of spark-ignition operation.

A comparison of the rate-limited and equilibrium NO mass fractions as a function of crank angle degrees is shown in Figure 3 for elements of gas which burn at −30° and 15°C. In both cases, the rate-controlled solutions rise from the residual concentration at a finite rate, cross the equilibrium solution, and "freeze" at levels well above the equilibrium values for exhaust conditions. Note that in the element of gas which burned early, the rate-controlled solution approaches equilibrium during the high-temperature part of the cycle but "freezes" at levels significantly below the peak. In the element which burned late, the rate-limited solution never reaches the peak equilibrium level. This is a result of the very much slower reaction rates associated with the lower temperature of the gas which burns late in the cycle.

Experimental studies of the time and space dependence of NO formation in internal combustion processes have been carried out under a wide variety of conditions and have verified virtually all the predictions of the "unmixed" model of NO formation. Using the γ-band absorption technique, Newhall and Shahed (1971) have measured the NO production as a function of time behind hydrogen/air flames in a cylindrical bomb. Their results are compared with the predictions of the "unmixed" model in Figure 4, and it can be seen that the agreement is excellent. Note that the NO concentration rises smoothly from zero indicating there is negligible production in the flame front.

The effect of the temperature gradient on NO production in single-cylinder reciprocating piston engines burn-

Table I. Exothermic Rate Constants for Reactions 2.1 to 2.3

Reaction	Rate constant[a]
2.1	$5.2 \times 10^{-11} \exp(-334/RT)$
2.2	$1.1 \times 10^{-14}\, T \exp(-6250/RT)$
2.3	7×10^{-11}

[a] Units cm^3 sec^{-1}. Activation energies in cal/g-mol.

Table II. Typical Values of R_1, R_1/R_2, and $R_1/(R_2 + R_3)$[a]

Equivalence ratio	R_1[b]	R_1/R_2	$R_1/(R_2 + R_3)$
0.8	5.8×10^{-5}	1.2	0.33
1.0	2.8×10^{-5}	2.5	0.26
1.2	7.6×10^{-6}	9.1	0.14

[a] At 10-atm pressure and 2600°K.
[b] Units g-mol cm^{-3} sec^{-1}.

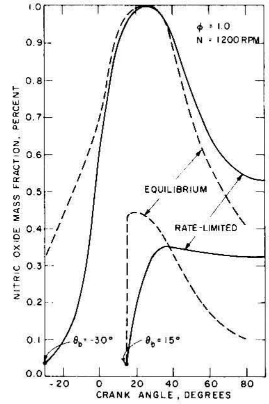

Figure 3. Calculated NO concentrations as functions of crank angle in two elements which burn at different times (−30° and 15°)

Dashed lines are NO mass fraction if NO were in equilibrium; solid lines are rate-limited NO concentrations

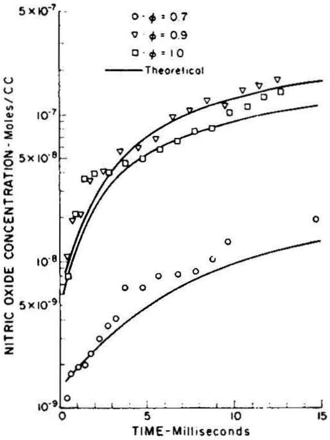

Figure 4. Measured and calculated rate-limited NO concentrations behind flame in high pressure cylindrical bomb experiments by Newhall and Shahed (1971) with lean and stoichiometric hydrogen-air mixtures. An "unmixed" model was used for the calculations—i.e., each element of mixture retained its identity after combustion

ing hydrocarbon/air mixtures has been demonstrated by Alperstein and Bradow (1967) and Starkman et al. (1969) using gas-sampling techniques, and by Lavoie (1970) using the chemiluminescent radiation from the reaction NO + O → NO_2 + hv. The measurements of Lavoie are compared with the predictions of the "unmixed" model in Figure 5 which shows the NO mole fraction at two distances from the spark plug as a function of crank angle. The stars indicate the estimated NO concentration due to mixing of the residual gas with the fresh charge. NO levels observed at window W_2 closest to the spark were substantially higher than those observed at window W_3. The effect of the residual gas was not included in calculating the kinetic solutions, and the NO concentration ahead of the flame front was assumed to be zero. This has little effect on the frozen NO concentrations, and the agreement between theory and experiment is satisfactory.

The unmixed model may also be used to calculate the average NO mass fraction in the exhaust of automotive engines. This requires an evaluation of the integral

$$\{\overline{NO}\} = \int_0^1 \{NO\}_f dx \qquad (4)$$

where $\{NO\}_f$ is the final frozen NO mass fraction in the element of charge which burned when the total mass fraction burned was x. The predictions of the model have been compared with the results of numerous experimental investigations by Blumberg and Kummer (1971). In general, they report good agreement between the calculated and measured exhaust NO concentrations over a wide range of engine-operating conditions.

An example of our own comparisons between measured and calculated exhaust NO concentrations in single-cylinder CFR experiments is shown in Figure 6. Measured pressure-time curves were used to generate burned gas temperatures and species composition using the "unmixed" thermodynamic model. Equations 3 and 4 were then used to obtain exhaust NO concentrations. The agreement is within the experimental error and uncertainties in the calculation procedure over a wide range of fuel-air ratios.

Blumberg and Kummer have also shown that the "unmixed" model may be used as an effective design tool to evaluate various practical methods of reducing exhaust NO emissions. This technique is illustrated in Figure 7 which shows the effect of recycling various fractions of the exhaust on the NO emissions. It can be seen that, for a given total mass of gas, NO can be more effectively reduced by recirculating exhaust gas than by adding excess air. This is due in part to the higher heat capacity of the exhaust gas which makes it more effective than air in reducing the peak burned gas temperatures, and in part to the oxygen in the air which favors the formation of NO.

Origin of Unburned Hydrocarbons

The variation of engine HC emissions with air-fuel ratio provides a starting point for this discussion. Emissions are

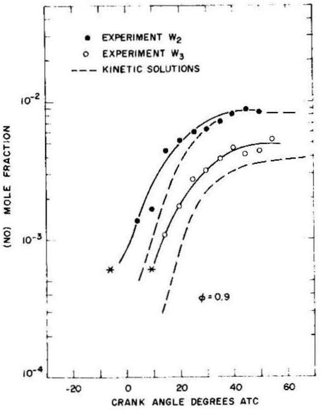

Figure 5. Measured and calculated NO concentrations in single-cylinder CFR engine experiments of Lavoie (1970). NO concentrations were measured by monitoring radiation from burned gases through quartz windows in cylinder head. Flame front reaches window W_2 earlier (−5°) than window W_3 (10°), and a higher final NO concentration is measured and predicted at W_2

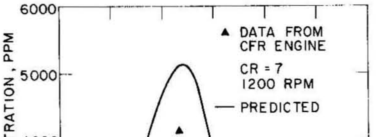

Figure 6. Comparison of measured exhaust NO concentrations in one of our single-cylinder CFR engines, with predictions made using measured pressure–time curves, the "unmixed" thermodynamic model, and rate-limited NO formation calculations. Compression ratio 7.0, engine speed 1200 rpm, spark advance 30° BTC, wide-open throttle

higher for both fuel-rich and fuel-lean mixtures with minimum emissions occurring at an air-fuel ratio of about 18:1. The rise in emissions as the mixture becomes very lean is due to engine misfire. The flame does not propagate across the charge fast enough to complete combustion before the expansion process cools the gases and quenches the flame reactions. Under normal engine operation, combustion is essentially complete in the bulk of the gas. It is the quench layers and crevices at the cylinder walls, as outlined at the beginning, which are the source of the unburned hydrocarbon.

Figure 8 shows schematically how these hydrocarbon-rich regions are formed. Daniel (1957) was the first to demonstrate the existence of quench layers with photographs showing a decrease in flame luminosity close to the wall. The flame propagates up to the wall, but heat transfer from the unburned mixture adjacent to the cool cylinder wall and piston face quenches the flame reactions before the last few thousandths of an inch of mixture is fully burned. Hydrocarbon compounds formed by heating, but not completely burning the fuel, and the gasoline hydrocarbon components are left in these layers. Over 200 organic compounds have been identified by gas chromatographic analysis of the exhaust.

The thickness of the quench layer q_d depends on the pressure p and temperature T_u of the unburned mixture at the time quenching occurs and on the fuel-air ratio. Measurements of quench distances on plane walls have been correlated with these variables as

$$q_d = q_r(p_r/p)^{\alpha}(T_r/T_u)^{\beta} \tag{5}$$

where subscript r denotes a reference condition. Examples of values of q_r, α, and β estimated by Daniel (1970) are given in Table III. It is seen that q_r is least for rich mixtures as expected since flame speeds are greatest. Typical values of q_d measured by Daniel (1957) in an engine at about stoichiometric fuel-air ratios increase from 0.003 in. at full throttle to 0.015 in. at idle. Since the flame reaches different parts of the cylinder wall at different times, quench distances are not uniform over the cylinder head and piston face.

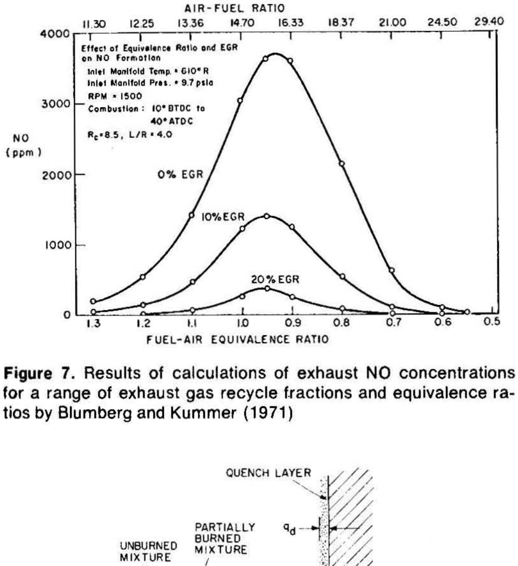

Figure 7. Results of calculations of exhaust NO concentrations for a range of exhaust gas recycle fractions and equivalence ratios by Blumberg and Kummer (1971)

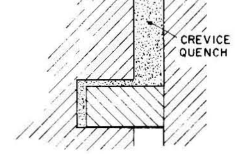

Figure 8. Schematic section of part of the piston and cylinder wall showing quench layers and the piston crown–first ring–cylinder wall quench volume

A further source of unburned hydrocarbons are crevices in the combustion chamber which are too narrow for the flame to enter. The most important crevice is the volume between the piston and cylinder wall above the first piston ring shown in Figure 8. The flame is quenched by wall cooling at the crevice entrance. Other quench crevices around the valves and between piston face and cylinder head have now been largely eliminated.

The mass of HC formed in quench crevices, m_{qc}, is given by

$$m_{qc} = V_{qc}F\ \rho_u(p, T_u)/(1 + F) \tag{6}$$

where V_{qc} is the quench crevice volume, F is the fuel:air ratio, and ρ_u is the fuel-air mixture density at the pressure and temperature at which flame quenching at crevice entrance occurs. The relative importance of the piston crown-cylinder wall crevice is indicated by results of Wentworth (1969); a reduction in this crevice volume by 80% reduced exhaust HC by 40%.

The aerodynamics of these dense hydrocarbon-rich quench gas layers adjacent to the wall during the expansion and exhaust strokes will determine what fraction of the total HC formed during each cycle will be exhausted. In addition, some of the unburned HC which mixes with the bulk burned gas will be oxidized, the amount varying with fuel-air ratio and gas temperature. One would therefore expect the HC concentration in the gas leaving the exhaust valve to be nonuniform.

Daniel and Wentworth (1964) were the first to show such nonuniformities exist; Figure 9 shows HC concentrations they measured in the engine exhaust port with a rapid-acting sampling valve. High concentrations were measured at the end of the exhaust stroke; the early part of the exhaust stroke cannot be resolved, however, because the fresh exhaust mixes with gas left in the exhaust port from the exhaust process in the previous cycle. To link exhaust HC measurements such as these with the quench layers and crevices which form while the piston is close to top dead center, the flow inside the cylinder and out of the exhaust during the expansion and exhaust strokes must be understood.

Table III. Typical Parameter Values in Quench Distance Correlation[a]

Air–fuel ratio	r_r, 10^{-3} in	α	β
20:1	5.8	0.55	0.89
14.7:1	3.1	0.52	0.56
12.6:1	2.7	0.66	0.71

[a] $q_d = q_r(p_r/p)^{\alpha}(T_r/T)^{\beta}$. Values given are for p_r = 287 psia, T_r = 540°R (from Daniel, 1970).

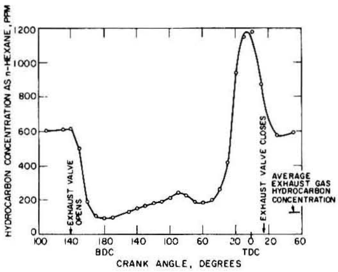

Figure 9. Hydrocarbon concentrations measured by Daniel and Wentworth (1964) with a rapid-acting sampling valve in the exhaust port during the exhaust stroke in a single-cylinder engine

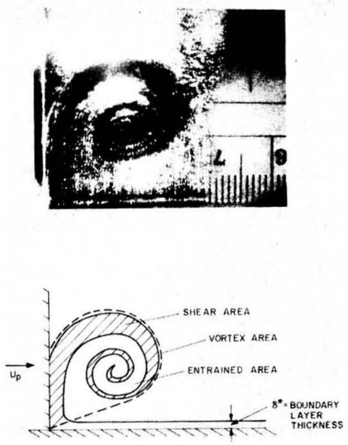

Figure 10. Photograph and schematic of vortex formed as piston (vertical surface on left) scrapes the shear layer (appears dark) off the cylinder wall in hydraulic analog experiments of Tabaczynski et al. (1970)

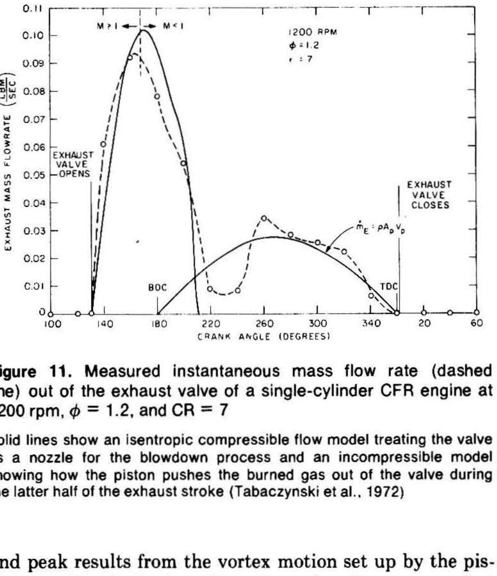

Figure 11. Measured instantaneous mass flow rate (dashed line) out of the exhaust valve of a single-cylinder CFR engine at 1200 rpm, $\phi = 1.2$, and CR = 7

Solid lines show an isentropic compressible flow model treating the valve as a nozzle for the blowdown process and an incompressible model showing how the piston pushes the burned gas out of the valve during the latter half of the exhaust stroke (Tabaczynski et al., 1972)

Tabaczynski et al. (1972) have shown what happens to the gas in the piston crown cylinder wall crevice. As the piston moves down the expansion stroke, this gas expands out of the crevice and is laid along the cylinder wall. As the piston moves up during the exhaust stroke, the boundary layer on the cylinder wall (which contains these hydrocarbons) is scraped off the wall and rolled into a vortex. Figure 10 shows a photograph taken of a hydraulic analog of this flow. The schematic underneath indicates the geometry; the piston is the vertical surface at the left, and it scrapes the boundary layer shear flow which appears dark in the photograph, into a vortex. Tabaczynski et al. (1970) have shown that the area of this vortex divided by the square of the stroke correlates with the Reynolds number.

Tabaczynski et al. (1972) also made measurements of the mass flow rate out of the exhaust valve and the hydrocarbon concentration in the gas in the exhaust port as functions of time. They were able, therefore, to calculate the HC mass flow rate as a function of time and provide additional data to support these aerodynamic models of how the unburned hydrocarbons exit the cylinder.

Figure 11 shows the instantaneous mass flow rate out of the exhaust valve. During the first part of the blowdown process, the flow is choked; as the cylinder pressure falls, the mass flow rate decreases until the flow due to piston motion becomes important. The earlier solid line represents an isentropic compressible flow analysis treating the valve as a nozzle; the second solid line assumes the burned gases are incompressible and are pushed out of the valve by the piston. Both models are good approximations to the measured flow in the regions where they should apply.

Measured HC concentrations in the exhaust port and HC mass flow rates out of the valve are given in Figure 12. A purge was used to clear the exhaust port at the end of each exhaust stroke; the HC concentration at the beginning of the exhaust stroke could then be resolved. The HC mass flow rate curve is the HC concentration curve times the exhaust mass flow rate in Figure 11; the HC mass emission during the last 60 degrees of the exhaust stroke was measured directly. The HC concentration at the end of the stroke is much higher than at the beginning, and the shape of the curve is estimated.

These measurements show that the unburned hydrocarbons exit the cylinder in two distinct peaks: one at the beginning of the exhaust stroke—during the blowdown process, and one at the end of the stroke. About half the total mass emissions come from each peak. The first peak is assumed to result from entrainment of the cylinder head quench layer during the blowdown process. The second peak results from the vortex motion set up by the piston scraping the hydrocarbons from the piston crown–first ring quench crevice off the cylinder wall.

Considerable evidence supports this latter phenomenon. Wentworth's (1969) data showed that an 80% reduction in this quench crevice volume gave a 40% reduction in total HC emissions, implying that about half the total HC came from the quench crevice. Tabaczynski et al. (1972) showed that the vortex in their CFR engine experiments reached the valve when the piston was about 2 in. from the cylinder head; since the clearance height is 0.75 in., a substantial portion of the vortex would be expected to exit the cylinder. If all the HC in the piston crown–first crevice is entrained in the vortex, the mass of HC would be 1.4×10^{-6} lb. The mass leaving the cylinder during the latter part of the exhaust stroke was 1.2×10^{-6} lb so 2×10^{-7} lb of the vortex HC was left inside. The clearance volume of the CFR engine is 6.3 in.^{3}, giving a residual HC concentration after valve close of about 800 ppm from the

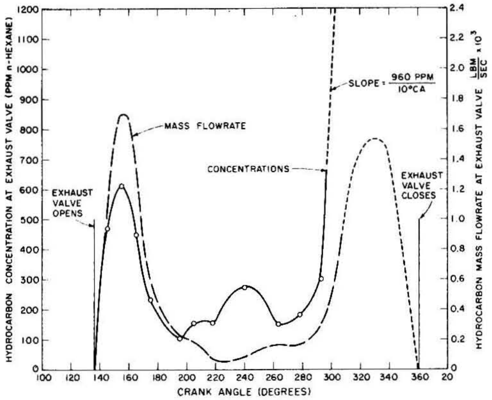

Figure 12. Variation of hydrocarbon concentration and hydrocarbon mass flow rate with crank angle at the exhaust valve of a single-cylinder CFR engine at 1200 rpm, $\phi = 1.2$, CR = 7.0 (Tabaczynski et al., 1972)

vortex. When allowance is made for the piston face quench layer, also expected to remain inside the cylinder, this is close to the value of 1085 ppm measured by Daniel and Wentworth (1964) in a similar engine at similar conditions.

Daniel (1970) has attempted to quantify many of the processes described above to explain why variations in engine-operating conditions affect HC emissions. He estimated quench layer and crevice quench HC, the oxidation of HC inside the cylinder after flame propagation was complete, the fraction of the HC in the cylinder exhausted, and the fraction oxidized in the exhaust system. The overall model was empirically fitted to data obtained from a number of single-cylinder engine experiments. Explanations of the effects of changes in air-fuel ratio, speed, compression ratio, and ignition timing were obtained.

Table IV summarizes the results for rich, close-to-stoichiometric and lean engine operation. The second column gives the exhaust HC concentration—highest for rich and lowest for lean mixtures. The ratio of quench layer HC to crevice HC is lowest for rich mixtures (because quench layers are thinnest and fuel fraction in the crevices greatest), and the proportions reverse at very lean air-fuel ratios. Little oxidation of the HC occurs subsequent to flame quenching for rich mixtures, but substantial oxidation occurs for lean mixtures. As a consequence, the HC emissions are lowest at lean air-fuel ratios until misfire occurs.

A summary of the mechanisms responsible for HC emissions is given in Figure 13. Quench layers are formed on the cylinder head, walls, and piston face as shown in (*a*). The crevice between piston crown and cylinder wall above the first ring is filled with fuel-air mixture at about the peak pressure and temperature; this mixture does not burn because the flame is quenched at the crevice entrance. As the piston moves down, the crevices of HC expand and are laid along the wall (*b*). When the exhaust valve opens, the head quench layer is entrained in the exhaust blowdown flow and exits the cylinder early in the exhaust stroke. The piston motion up the cylinder scrapes the boundary layer containing the crevice HC off the wall into a vortex; a large part of this vortex leaves the exhaust at the end of the exhaust stroke. As the unburned and partially burned fuel-air mixture is entrained in the bulk burned gases, some of it is oxidized, the amount depending on temperature and oxygen partial pressure.

Conclusions

From this discussion it is clear that the basic mechanisms responsible for exhaust NO_x and HC emissions in reciprocating spark-ignition engines are now understood. For NO_x emissions, quantitative models give good agreement with experimental data and are already being used as design aids for lower emissions. For HC emissions, the important processes have been demonstrated, and a more complete overall quantitative model is the appropriate next stage. Though it now appears that catalysts may be required to reduce exhaust emissions to the levels required in the 1970 Clean Air Amendments, the importance of understanding the origin of the basic engine emissions will not diminish. For any reasonable expectation of meeting these requirements, the emissions from engine itself must still be held as low as is compatible with adequate engine performance. A quantitative understanding of the basic processes responsible for the production of these emissions can greatly assist in this task.

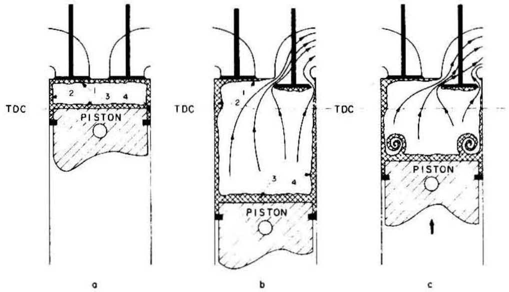

Figure 13. Schematic summarizing processes important in hydrocarbon emissions

(*a*) Formation of quench layers 1, 2, 3 and crevice quench 4 as flame is extinguished at cool walls. Not to scale, quench layers are about 0.003 in. thick

(*b*) Gas in quench volume between piston crown and cylinder wall above the first ring, 4, expands as cylinder pressure falls and is laid along cylinder walls. When exhaust valve opens, head quench layers 1 and 2 exit cylinder

(*c*) Roll-up of hydrocarbon rich cylinder wall boundary layer into a vortex as piston moves up cylinder during exhaust stroke

Table IV. Origin of Hydrocarbon Emissions: Rich and Lean Engine Operation[a]

Air-fuel ratio	Exhaust HC, ppm	% HC from Quench	% HC from Crevice	% HC reacted in cylinder	% Unreacted HC entering exhaust	% HC reacting in exhaust	% HC entering atm
12.6	680	39	61	12	55	3	47
15.7	425	44	56	38	55	10	31
20.1	320	59	41	38	55	26	26

[a] From Daniel (1970).

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Characterization of Particulate Matter in Vehicle Exhaust

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■ The particulate matter emitted from present-day cars is a complex mixture of inorganic salts, soot and carbonaceous material. Measurement and characterization of such particles require elaborate sampling systems and sophisticated analytical techniques. This paper is a review of the major contributions in this area. A number of systems suitable for sampling and characterization of the exhaust particles are described. Also included is a wide selection of data from a number of workers that, in the author's opinion, best represent the state of the art.

Although the subject of vehicle emissions has received much attention during the past 15 years, there is little information on the mechanism of particle formation during engine combustion and on the character of the particles in vehicle exhaust. The main reason for this lack of information is the complexity of the physical and chemical reactions that govern particle formation and their subsequent deposition and regeneration in the exhaust system of cars. Consequently, in this area, a coherent theory can follow only in the wake of experiments, and development of proper sampling procedures and analytical techniques for characterization of exhaust particles is of great importance. Individual improvements in the techniques, no matter how small, can play a significant role in improving our understanding of the phenomenon of particulate emissions from cars.

The particulate matter emitted from present-day cars is a complex mixture of lead salts, iron as rust, base metals, soot, carbonaceous material, and tars. Measurement and characterization of these particles require elaborate sampling procedures and sophisticated analytical methods. Many factors, in particular the mode of vehicle operation, the age and mileage of the car and the type of fuel, can affect the composition and the total particulate emission rate.

Some of the particulate matter found in the exhaust is generated in the engine combustion chamber and nucleated and agglomerated in the vehicle exhaust system before it is emitted from the tail pipe. On the other hand, some of the particulate material deposits on the various surfaces of the exhaust system. At some later time, this deposited material flakes off and becomes re-entrained in the exhaust gas prior to emission from the tail pipe. Thus, during vehicle operation various types of physical and chemical processes affect the exhaust particles continuously and, as the result, the overall particulate emission process for a car is quite complex and difficult to define.

Under certain driving conditions, lead salts account for the major portion of the exhaust particles. In view of this, and for reasons relating to toxic properties of lead, most of the major studies on the exhaust particles have concentrated on characterization of the lead salts. Information on lead emission rates, chemical composition of lead-bearing particles, their size and air suspendability, and their effect on ambient air quality were considered of great importance and have been studied. This interest is reflected in the bulk of information on lead particles presented in this paper. Studies of the total particulate matter in vehicle exhaust are relatively new. The relationship of lead salts to the total particulate matter in vehicle exhaust has been considered only recently.

Early workers in the area of exhaust particles concentrated on characterization of the lead particle. Hirschler et al. (1957) carried out a comprehensive study in which the entire exhaust stream was first diluted with filtered air and then passed through an electrostatic precipitator for particle collection. The efficiency of the electrostatic precipitator was measured to be 90-95% by sampling of the effluent stream for lead concentration. The material in this effluent stream was measured and taken into account in all test runs. Hirschler coated the surfaces of the electrostatic precipitator with a polyvinyl acetate plastic, and released the particles collected during a run by dissolving the plastic coating with a solvent, thus making his measurements on a suspension of the lead particles. Using the solvent dispersion technique, the organic fraction associated with the exhaust particles was dissolved, thus only the inorganic fraction was measured with this procedure. To determine the size distribution of the exhaust particles, the suspension was concentrated into two size fractions, $<5\ \mu$ and $>5\ \mu$ by settling and centrifugation. The samples from the separated fine particles were then resuspended in a toluene–ethanol mixture for photomicrographic size counts. Particles of $<0.2\ \mu$ in diameter were sized and measured using the electron microscope.

Hirschler's lead emission data for two cars operating on chassis dynamometers are summarized in Table I. The results highlight four important factors:

Lead emission rate from cars is dependent on the mode of operation. The higher the speed or the load, the greater the rate of lead emission.

A large amount of lead burned is retained in the engine, the oil, and the exhaust system of the car during normal driving.

This retained material is partly re-entrained in the exhaust gas during high speed, high load conditions. This results in lead emission rates ten- to twenty-fold greater than the lead burned during this type of operation.

There is a general increase in lead emission rate with mileage accumulation. Increases in fuel lead concentration also increased the rate of lead emission.

In terms of particle size, Hirschler reported lead particles ranging from 0.01 μ to several millimeters in diameter. He concluded that one half to three quarters of the lead exhausted under city driving conditions is associated with particles of 5 μ and smaller diameter, with the remainder as coarser particles. The ratio of fine to coarse particles ($>5\ \mu$) decreases under high speed and high load conditions, which are associated with greater total lead emissions. Only 5% of the lead exhausted was associated with particles of less than 1 μ in diameter. Hirschler found that the concentration of lead in gasoline had little effect on the size of the exhausted lead, but addition of sulfur and phosphorus produced slightly greater amounts of inorganic particulate matter in the 3–5 μ size range.

Hirschler's lead emission measurements still stand as one of the most comprehensive sets of data in this area. The size information, however, has been questioned in view of the collection technique—i.e., total collection and subsequent dispersion and fractionation of the particles. Such operations can lead to agglomeration of small particles leading to inaccurate size data.

Mueller et al. (1964) attempted to overcome these problems by sampling and sizing the exhaust particles in an aerosol form. Test vehicles were operated under steady-state conditions (25, 45, and 60 mph), and samples of the exhaust were collected isokinetically by inserting a sampling probe into the vehicle tail pipe. The sampled aerosol was then diluted approximately fivefold with filtered dried air and the mixture passed through a rectangular sampling chamber. The exhaust particles in various size fractions were measured by sampling from the above chamber downstream of a perforated baffle acting as a flow distributor. The Goetz aerosol spectrometer, the Andersen sampler and a two-stage dust sampler were used for sample collection. After weight gain measurements, the collected samples were analyzed for lead content.

Table I. Hirschler's Data on Vehicle Lead Emissions

	% of burned lead emitted	
Type of service	Single exhaust, 1954 car	Dual exhaust, 1953 car
City driving after extended suburban service	20–24	20–25
City driving after extended city-type service	50–60	30–40
Full throttle acceleration to 60 mph	870–1230	1990
Constant speed 60 mph road load	110–460	67–250

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Based on tests with three 1961–62 test cars, Mueller concluded that under steady-state driving conditions, 60–80% by weight of the exhaust particles were less than 2-μ equivalent diameter, and almost 70% of these fine particles were less than 0.3 μ in diameter. The fine particle concentration in the exhaust and their lead content were not affected by variations in car speed or the type of vehicle. The concentration of these fine particles in the exhaust was estimated at 32,000 μ per M^3 and the average lead content of these particles was 13,000 μg per M^3—i.e., 40% by weight.

Mueller adapted several new techniques to the measurement of exhaust particles. However, the particulate sampling system used for this study was criticized on three points:

Probe sampling of the particulate matter in vehicle tail pipe is subject to errors due to nonuniformity of particle distribution in the tail pipe and presence of some large particles, 300–3000 μ in diameter.

There was high loss of material in the sampling system prior to the measurement stage.

The driving patterns used were not representative since only cruise conditions were investigated.

The potential error in probe sampling at the tail pipe of a car was studied by Ter Haar et al. (1971) in a series of runs with leaded and unleaded fuel. The total particulate mass emission rates as measured by a tail pipe probe were compared with values obtained on dilution (8:1) of the whole exhaust stream in a 2400-ft^3 bag and sampling of the air-suspended particulate matter in the bag. Using the 7-Mode Federal Test Procedure (Federal Register No. 108, 1968b) in a continuous hot cycle test, tail pipe probe sampling at constant flow rate underestimated tail pipe particulate emission approximately fivefold for the leaded fuel and between twenty- and fifty-fold with the unleaded fuel. Factors contributing to the discrepancy include nonuniformity of particulate profile in the tail pipe, nonproportionality of the sample and inaccurate sampling of the larger particles.

Particulate Lead in Vehicle Exhaust—Emission Rate Measurements

To measure the vehicle exhaust lead emission rates rapidly and conveniently, Habibi (1970) developed a total exhaust filter which will withstand exhaust gas temperatures and is mounted directly on the tail pipe of the car. The filter unit shown in Figure 1 is a cylindrical drum, 18 in. in diameter, 24 in. long, and packed with a high efficiency fiber glass medium. The exhaust gas flows directly into the cylinder, then passes outward through the filter media supported externally by a stainless steel grid. The unit is sealed by internal springs located at the top and bottom pans and also by a stainless steel strip over the seam. The pressure drop across the filter is low—less than 2 in. of water at 70 mph cruise. The pressure drop increases with the accumulation of material on the filter but is less than 6 in. of water after 500 miles of continuous hot-cycle operation. Thus, the use of the filter does not affect the vehicle operation.

After each test, the unit is disassembled, and the lead on the filter media is extracted in boiling hydrochloric acid. The small amount of lead deposited on the inlet pipe and the internal parts of the holder is extracted with Versene. The efficiency of this filter for exhaust lead removal has been investigated in a number of experiments and reported previously (Habibi, 1970). Under normal driving conditions, the unit is 99% efficient for lead removal.

To characterize the quantity of lead particles emitted with the exhaust, vehicles have been tested under steady-state and cyclic modes of operation. In one study (Habibi, 1970), a standard vehicle with automatic transmission was used and steady-state road load operation at 20, 45, and 70 mph was investigated. The tests (Figure 2) ranged from 200–400 miles in duration and were run on a fuel containing 3 grams of lead per gallon as Motor Mix. The results in terms of percent of the burned lead emitted from the vehicle show that an increase in the road speed was associated with an increase in the fraction of the lead burned emitted with the vehicle exhaust. Further, at any one speed there is a significant variation in the amount of lead emitted from run to run due to a continuous buildup on, and subsequent re-entrainment of lead from, the walls of the exhaust system. These findings are in agreement with data by Hirschler et al. (1957), Hirschler and Gilbert (1964), and Ter Haar et al. (1971).

To obtain lead emission rates under motorist cyclic-driving conditions, a two-car test program was conducted using the Federal mileage accumulation cycle (Federal Register No. 2, 1968a) on chassis dynamometers. The vehicles were popular 1969, 350-CID models of different make and were run on a fuel containing 2.5 grams of lead per gallon. The lead emission rate from these cars was measured continuously for 50,000 miles using the total exhaust filters mounted on the vehicle tail pipe. The results are shown in Figure 3. With a new exhaust system, the initial lead emission rates are somewhat lower than the "equilibrated" condition as deposit buildup in the engine and the exhaust system takes place. After approximately 3000–5000 miles, a base point emission value is reached. As mileage is accumulated beyond this point, there is wide fluctuation in the rate of lead emission, again indicating a lead buildup and flake-off phenomenon in the exhaust system of the car. Although the data in Figure 3 enable the calculation of an overall average lead emission rate for the specific car and test cycle, it is evident that data from short duration tests are subject to wide variations.

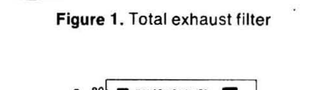

Figure 1. Total exhaust filter

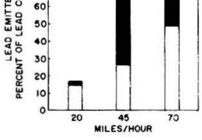

Figure 2. Steady-state operation at road load

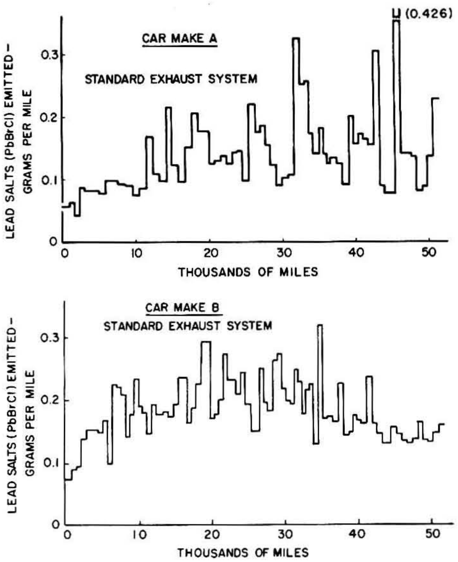

Figure 3. Lead particulate emission rate

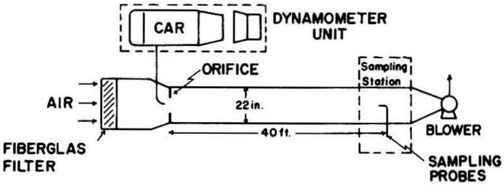

Figure 4. Proportional sampling system for exhaust particulate

Proportional Sampling System for Exhaust Particulate Matter

To enable detailed characterization of the exhaust particles, Habibi (1970) developed a proportional sampling system to obtain representative samples of the exhaust particulate material. Details of this sampling system are shown in Figure 4. The test vehicle is operated on a programmed chassis dynamometer, and the operation of the vehicle and dynamometer is controlled from information stored on magnetic tapes recorded under actual driving conditions on the road. Thus, city, suburban, expressway, or any other required type of driving can be directly and accurately simulated on the dynamometer. The system is also equipped with quick cooldown facilities that enable vehicle cold starts with the appropriate amount of choke operation. This is achieved by recirculating chilled water through the radiator and the engine block and blowing cold air onto the carburetor choke spring and exhaust manifolds. Cooling the exhaust system of the car is obtained by suitably positioned blowers.

The total exhaust stream from the vehicle is lead into a large duct and diluted with a stream of filtered ambient air (23:1 dilution at 45 mph road load). This approach is very similar to actual road driving in that the exhaust is immediately diluted with a fairly large proportion of turbulent air.

The duct diameter is 22 in., giving a maximum gas velocity of 490 ft/min at the flat section of the velocity profile at the sampling station where partculate samples are collected isokinetically. The overall mixing length is 40 ft and was chosen after experiments indicated that thorough mixing of the exhaust particles and ambient air streams is achieved in this length. This length is also necessary to enable gravitational settling of some very large particles (200–3000 μ) present in vehicle exhaust. The removal of these particles prior to the sampling station is essential since they cannot be mixed and distributed uniformly at the cross section of the tunnel's sampling station, nor can they be sampled accurately using a probe for sample removal.

To maintain the low duct gas velocity and yet promote mixing in a reasonable length, a large-hole (8 in.) orifice plate was used at the point where the exhaust is introduced into the tunnel (Figure 4). The orifice proved to be very effective in achieving the required mixing and in obtaining a flat velocity profile at the sampling station. It also virtually eliminated the flow disturbances that otherwise would have been caused by the fluctuating exhaust flow under normal motorist driving conditions. The variable dilution principle was used to obtain a proportional sample of the exhaust particles under cyclic operation. The mixture, consisting of the total exhaust and the ambient air, was drawn through the duct and past the sampling point at a constant volume flow by the blower located at the downstream end of the tunnel. The system is quite similar in principle to that developed for mass emission analysis of gaseous exhaust components by Broering et al. (1967).

As mentioned earlier, there is gravitational settling of the very large particles present in vehicle exhaust along the tunnel base. There is also some turbulent deposition of particles on the remaining surfaces of the tunnel, although the quantity of such deposits is very small. The amount of the material deposited in the tunnel is determined after each run or series of identical runs. The size of these particles has also been determined by suitably positioned microscopic slides and microscopic size counts.

One area of interest which has received considerable attention is the particle size of the lead-containing particulate matter present in automotive exhaust. The instruments selected for this work were impactor units. These instruments are simple to operate, widely used, and have been calibrated with success. The main problem reported in their application appears to be re-entrainment of particles impacted on the various stages. This is not a serious problem with exhaust lead aerosols for two reasons. First, owing to the very sensitive analytical procedures available for lead, accurate measurement of the quantity of lead per stage can be made at stage loadings well below that at which re-entrainment begins to be a problem. Second, the particles appear to adhere firmly to the impactor plates and tests with or without an "adhesive" coating of the impactor plates show no significant difference in the results.

Two impactor units were used for size measurements simultaneously (Figure 5). The Andersen Sampler (Andersen, 1966) covers the size range of ½–9 μ equivalent diameter and operates at a sample flow of 1 cfm. This instrument appears to be reasonably well suited, although the wide size distribution of the exhaust particles limits the amount of lead sample retained on the various stages of the unit. The second instrument selected was the Monsanto Impactor (Brink, 1958). This unit can size particles as small as 0.3 μ equivalent diameter at a flow rate of only 0.14 cfm. Using the two units simultaneously, an acceptable portion of the sampled lead is retained in the size-measuring instruments.

Characterization of Particulate Lead

Effect of Mileage Accumulation. As mileage is accumulated on vehicles, the amount and size of the lead particles emitted from the vehicle change. This is understandable since deposition and re-entrainment processes occurring in the vehicle exhaust system probably never reach equilibrium conditions but are constantly changing. To obtain a better understanding of the gross effects which might be taking place, a test was carried out in which the amount and size of the lead particles emitted were monitored for 28,000 miles.

A 1966 model vehicle equipped with a 327-CID engine was operated on a fuel containing 3 grams of lead per gallon as Motor Mix. The vehicle was driven on a programmed chassis dynamometer using the Federal mileage accumulation schedule (Federal Rerister No. 2, 1968a). At times during the mileage accumulation, the vehicle was also operated under steady-state constant-speed conditions for special test programs. Exhaust lead particle size measurements were made at four nominal test mileages during the mileage accumulation schedule. Andersen and Monsanto impactors were used for particle size measurements as described in the previous section. The details of vehicle operation and lead particulate emission rates for the size determination runs are shown in Table II. The average test duration was approximately 200 miles.

Table II. Lead Particle Emission Rates During Federal Mileage Accumulation Schedule

Average mileage	Lead salt emissions, g/mile	
	Average	Range
5,000	0.16	0.14–0.19
16,000	0.15	0.13–0.15
21,000	0.13	0.12–0.15
28,000	0.18	0.15–0.20

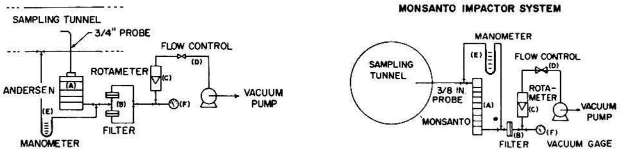

Figure 5. Schematic diagram of impactor-type size measuring equipment

The results show that size runs were carried out under conditions of relatively constant lead emission rate averaging about 48% of the lead burned. There is some increase in the percent lead burned which was emitted during the final phase of the study, when the lead emission rate increased to an average of 57% of the lead burned with values ranging from 47 to 65%.

While lead particle emission rates did not vary appreciably, particle size distribution showed major shifts, as shown in Table III. The increase in mileage resulted in an increase in the percent of emitted lead in the coarse particle size fraction. There was also a reduction in the percent of lead emitted associated with particles of <0.3 μ equivalent diameter.

In Table IV, data are presented in terms of grams per mile. The results indicate a reduction in the air suspendibility of exhaust lead particulate with mileage accumulation. The absolute quantity of the coarse particles emitted from the car increased and at the same time there was a reduction in the absolute amount of fine material emitted to the environment.

The increase in size of the exhaust lead with mileage was confirmed in a recent study by Ter Haar et al. (1971). These workers sampled the exhaust particulate in two size fractions using a two-stage collection unit mounted on the tail pipe of the vehicle and housed in the trunk of the car. The exhaust was first passed through a cyclone to remove the coarse particles and then through a large filter for fine particle collection. The 50% cut-size for the cyclone ranged from 5 μ to 30 ft^3/min down to 0.6 μ at 60 ft^3/min. The pressure drop of the filter section was low at 0.1 in. H_2O at 60 mph cruise. Actual road tests were carried out by driving the equipped car on a road course approximating the Federal mileage accumulation cycle for 12,000 miles. The cyclone can and the filter were changed a number of times during the test. The results showed a marked increase in the percent of lead burned, emitted as coarse particles with mileage. The percent of burned lead emitted as fine particles also increased but to a much smaller degree, as did the lead emission rate from the car. These results would indicate an increase in the mass median equivalent diameter with mileage.

The increase in the amount of large particles with mileage is probably related to the exhaust system deposits. As deposition continues to build up, the thickness of the deposited material increases so that when flaking occurs, the flaked particles are larger than would be the case when the exhaust system is new. The reduction in the amount of fine particles, if any, may be related to changes in turbulent deposition processes.

Table III. Lead Particle Size Distribution (Federal Mileage Accumulation Schedule)

Av mileage	MMED,[a] μ		Percent of emitted lead		
	Andersen	Monsanto	>9 μ	<1.0 μ	<0.3 μ
5,000	1.1	2.1	27	45	30
16,000	3.6	3.8	39	36	25
21,000	4.7	5.7	44	36	26
28,000	>15	>15	57	19	11

[a] Mass median equivalent diameter.

Table IV. Lead Particle Emissions as Function of Size and Mileage (Federal Mileage Accumulation Schedule)

Av mileage	Lead salt emissions, g/mile		
	>9 μ	<1.0 μ	<0.3 μ
5,000	0.04	0.07	0.05
16,000	0.06	0.05	0.04
21,000	0.06	0.05	0.03
28,000	0.10	0.03	0.02

Table V. Lead Particle Emission Rates (Simulated Consumer Test Conditions)

Test miles	Lead salt emissions, g/mile
86	0.36
89	0.35
69	0.35
74	0.31
77	0.33
Av 79	0.34

Table VI. Lead Particle Size Distribution (Simulated Consumer Test Conditions)

Mileage	MMED		Percent of emitted lead		
	Andersen	Monsanto	>9 μ	<1.0 μ	<0.3 μ
32,600	>15	>15	60	22	13
32,700	>15	>15	58	25	16
32,800	15	>15	54	27	16
32,900	>15	>15	57	27	17
Av	>15	>15	57	25	16

Size Distribution of Lead Particles Emitted by Average Car on the Road. To characterize the lead particles under typical motorist driving conditions, a test program was carried out using a 1967 popular make production car. The initial 15,000 miles was accumulated under actual consumer operation on the road. After completion of the 15,000 miles on the road, an additional 17,000 miles was accumulated on programmed chassis dynamometers using the Federal mileage accumulation procedure and a simulated consumer driving schedule including cold starts designed to match the previous consumer driving patterns.

Five tests were carried out on the above car at 32,000 miles for the purpose of making lead particle size measurements. Lead emission rates observed during these runs are shown in Table V.

As shown, there is a substantial increase in lead emission compared with that observed under continuous hot cycle operation, Table II. At 28,000 miles the 327-CID test car with a continuous hot-cycle dynamometer mileage accumulation, history showed a lead particulate emission rate of 0.18 g/mile or 57% of lead burned. In the above tests, an 89% emission rate was observed and this value was confirmed with total exhaust filtration results obtained before and after the size runs. Similar lead emission rates were observed with this car at 20,000 miles.

Twenty-five percent of the lead burned and subsequently emitted from the vehicle under consumer driving conditions was associated with particles less than 1 μ in size as shown in Table VI. Fifty-seven percent of the emitted lead was associated particles >9 μ equivalent diameter.

The MMED (mass median equivalent diameter) values in Table VI are too large for accurate measurement with our present impactors. The details of the size distribution data are shown in Figure 6. The steep slope of this plot indicates a polydispersed aerosol of wide size distribution and is typical for the lead-containing particles in the exhaust of cars.

The above size data are in agreement with measurements by Ter Haar et al. (1971) using the cyclone-filter approach. The exhaust lead was collected in two size fractions designated as coarse and fine and data were gathered on 26 cars operating under a range of driving conditions. The results indicated that for the average car, 55% of the exhausted lead is associated with particles >5 μ equivalent diameter, which is in reasonable agreement with the value of 57% as >9 μ shown in Table VI and Figure 6.

Chemical Composition of Particulate Matter Emitted from Cars. A number of runs were carried out to determine the composition of particulate matter emitted from the previously described consumer test car operating on the consumer-type driving cycle. Samples were collected using the proportional sampling system and by filtration of the exhaust at the tail pipe. The fuel for this study was a commercial base fuel containing 2.7–3 grams of lead per gallon as Motor Mix. Elemental analysis, X-ray diffraction, and X-ray fluorescence were employed in analyzing samples. Eight main conclusions were as follows:

Composition of emitted exhaust lead particles is related to particle size.

Very large particles of greater than 200 μ have a composition similar to exhaust system deposits, confirming that they are re-entrained or flaked material. These particles contain approximately 60–65% lead salts, 30–35% Fe_2O_3, and 2–3% soot and carbonaceous material. The major lead salt is PbBrCl with large amounts of PbO (15–17%) occurring as the 2PbO·PbBrCl double salt. Lead sulfate and lead phosphate account for 5–6% of these deposits (low sulfur and low phosphorus fuel).

PbBrCl is the major lead salt in particles of 2–10 μ equivalent diameter with $2PbBrCl \cdot NH_4Cl$ present as a minor constituent.

Submicron lead salts are primarily $2PbBrCl \cdot NH_4Cl$.

Lead-halogen molar ratios in particles of less than 10 μ equivalent diameter indicate that much more halogen is associated with these solids than the amount expected from X-ray identification of $2PbBrCl \cdot NH_4Cl$. This is particularly true for particles in the 0.5–2 μ size range.

There is considerably more soot and carbonaceous material associated with small particles than with coarse re-entrained deposit from the exhaust system.

Particulate matter emitted under consumer-type conditions is rich in carbonaceous-type material. There is substantially less such material emitted under continuous hot operation.

Only small quantities of $2PbBrCl \cdot NH_4Cl$ were found in samples collected at the tail pipe from the hot exhaust gas. Its formation, therefore, mainly takes place during cooling and mixing of exhaust with ambient air.

The above data are in agreement with the X-ray analysis of exhaust lead by Hirschler et al. (1957) and Hirschler and Gilbert (1964), who reported that exhaust lead is primarily a mixture of PbClBr, α and $\beta NH_4Cl \cdot 2PbClBr$, and $2NH_4Cl \cdot PbBrCl$. When phosphorus was present in the fuel, approximately one fifth of the exhausted lead was $3Pb_3(PO_4)_2 \cdot PbClBr$.

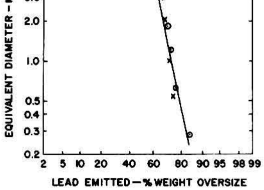

Figure 6. Size distribution of exhaust lead for an average car

Characterization of Total Particulate Matter in Vehicle Exhaust

Although there is a considerable amount of information available on the nature of the lead in vehicle exhaust, the amount of effort spent on characterization of the total particulate matter has been small. A number of factors make the study of the total particulate very complex and further emphasize the importance of vehicle operation and the sampling procedure. For example, it has been observed (Habibi et al., 1970) that during the first few miles of vehicle operation after a cold, choked start, the amount of particulate matter emitted from the tail pipe is considerably greater than the amount observed during the subsequent hot-cycle operation. Thus, the driving cycle becomes most critical, not only in terms of the amount of cyclic operation, but also in terms of the number of cold starts and the average trip length. Further, it has been observed that cooling of exhaust gas results in an appreciable increase in the amount of particulate matter. Thus, at tail pipe gas temperatures some potentially organic particulate matter is still in a vapor form. Such particles are formed on exhaust dilution and cooling in the atmosphere. Consequently, the degree of exhaust dilution and exhaust cooling in the sampling system for total particulate matter becomes very important.

Early studies of the total particulate emission from cars were made using the total exhaust filter described earlier. The total filterable particulate emission was measured on two popular model cars equipped with 283-CID engines. These cars were privately owned and operated. Car A had 64,000 miles of normal road operation on commercial leaded gasoline, while Car B had 40,000 miles of normal road operation on a commercially available unleaded fuel. Air-fuel mixture ratios were measured on the two cars and found to be essentially equivalent. The oil consumption history of these cars was also investigated and agreed closely at about 1 qt/1000 mi, including that used at oil change.

In preparation for a run, the total exhaust filter was conditioned and weighed. After the run, the unit was again conditioned overnight and the weight gain determined. While the above procedure is subject to limitations due to high exhaust temperatures, it is reasonably useful in yielding information on factors that affect total particulate emissions. A simulated consumer-type mileage accumulation schedule was used for these tests. Between each trip, the engine and the exhaust systen of the car were artificially cooled to make cold starts possible.

Three types of driving conditions, differing in the amount of cold start, choked action, were employed in this study. These ranged from complete choke action on every start, representing cold winter conditions, to no choke action on every start representing frequent trip operation under summer conditions. To simulate the average motorist's driving habits, a combination of one-third starts with full choke action and two-thirds starts with no choke action were used (Conte, 1968). Tests ranged from 25–200 miles.

Results obtained with the unleaded fuel are shown in Figure 7. Total particulate emission rate was very low with no choke operation but increased to over 0.4 gpm when the car was choked on each start after an average trip length of 5 miles. At the typical motorist driving condition of one out of every three starts on full choke opera-

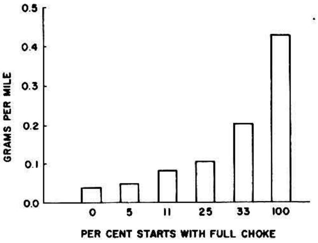

Figure 7. Total particulate emissions with unleaded fuel

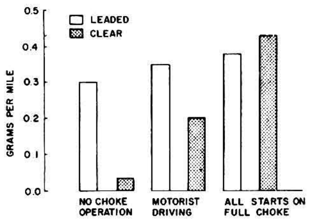

Figure 8. Total particulate emissions with leaded and unleaded fuels

tion, the total particulate emission rate ranged from 0.15–0.24 gpm. The particulate matter on the filter media was black, sooty, and carbonaceous.

The total particulate emission rates of the car with leaded fule are compared with the unleaded fuel data in Figure 8. The total particulate emission levels with leaded fuel appear less sensitive to the degree of choking. Thus, with no choke operation (or steady-state hot-cycle operation) there was a large difference in the particulate emissions observed with the two fuels. Although the leaded fuel particulate emission was still higher than that of unleaded fuel under motorist driving conditions, the values were more comparable. With all starts on full choke operation (winter condition) the leaded fuel and unleaded fuel particulate emissions were approximately the same.

In general, the above findings have been confirmed by subsequent work using different sampling procedures. Ter Haar et al. (1971) operated test cars on a chassis dynamometer using the 7-Mode Federal emission test cycle (Federal Register No. 108, 1968b). The total exhaust from the car was diluted approximately 8:1 in a large 2400 ft^3, black polyethylene bag. Samples of the air suspended particulate matter from the black bag were collected for quantitative measurement and chemical analysis.

In one study, Ter Haar determined the total particulate emissions from a number of new cars using unleaded Indolene. The total air-suspended particulate material in the black bag and the carbon content of these particles was measured as shown in Table VII. The fuel was then switched to Indolene 30 and the suspended particulate emission measured under the same test conditions. In another study, 16 privately owned cars with exhaust systems conditioned on leaded fuel were compared with a number of well-conditioned consumer cars that had been operated on unleaded fuel only. The results with the high mileage cars are shown in Table VIII.

Ter Haar's data indicate that, although cars vary in their total particulate emissions, cold-cycle operation produces two and, in some specific runs, up to eight times more air-suspendable particulate than hot-cycle operation. The carbon content of the air-suspendable particulate matter for deposit-stabilized cars averaged about 35% of the total particulate matter for leaded fuel and 70% for unleaded fuel.

Ninomiya et al. (1970) used a measurement system in which one half of the exhaust gas from the test cars was diluted to a total volume of 180 cfm with filtered ambient air. The diluted exhaust was then filtered through an 8 × 10-in. Acropor filter for particle collection. The weight gain of the filter provided a value for total particulate emissions. Measurements showed that under some conditions, and in particular with unleaded fuel, the efficiency of the Acropor filter was low because of the high filtration velocity. However, a correction factor was obtained for leaded and for unleaded fuels. Using two 1969, 302-CID test cars, one with 4000 miles of leaded fuel operation and the other with 6000 miles of unleaded fuel usage, the particulate emission rates were measured and compared for each successive Federal 7-Mode Cycle (Federal Register No. 108, 1968b). The corrected mass emission rates are shown in Figure 9. The data confirm previous observations that greater vehicle particulate emissions are obtained under cold start conditions. The data also show a greater reduction in the amount of particulate emission with unleaded fuels as the car warms up to conditions representing continuous hot-cycle operation. If we take an average motorist trip length of about 7 FTP cycles, Ninomiya's data are in general agreement with the preceding data on total particulate emission rates.

The type of particulate matter obtained with leaded

Table VII. Suspended Particulate Emissions

(New cars, 0–1000 miles)

Federal cycles	No. detn	Particulates, g/mile Total	Pb	Carbon	Pb, %	C, %
		Leaded Fuel Runs—Indolene 30				
4 Cold	6	0.204	0.026	0.111	12.7	54.4
4 Hot	15	0.117	0.019	0.040	16.2	34.2
Weighted[a]	6	0.152	0.020	0.071	13.2	46.7
		Unleaded Fuel Runs—Unleaded Indolene				
4 Cold	3	0.223				
4 Hot	22	0.107				
Weighted[a]	3	0.165				

[a] Weighted 35% cold and 65% hot.
Data from Ter Haar et al. (1971). Reprinted with permission.

Table VIII. Suspended Particulate Emissions from Unleaded Fuel Cars

(Stabilized deposits, 30,000–50,000 miles)

Federal cycles	No. detn	Particulates, g/mile Total	Carbon	Carbon, %
4 Cold	5	0.316	0.242	76.5
4 Hot	5	0.134	0.074	55.2
Weighted[a]	5	0.197	0.133	67.5

[a] Weighted 35% cold and 65% hot.

Suspended Particulate Emission and Composition from Leaded Fuel Cars[a]

(Stabilized deposits, 30,000–100,000 miles)

Federal cycles	No. detn	Particulates, g/mile Total	Pb	Carbon	Pb, %	C, %
4 Cold	16	0.512	0.085	0.184	16.4	35.9
4 Hot	17	0.240	0.044	0.076	18.3	31.7
Weighted[b]	16	0.339	0.059	0.115	17.4	33.9

[a] Data from Ter Haar et al. (1971). Reprinted with permission.
[b] Weighted 35% cold and 65% hot.

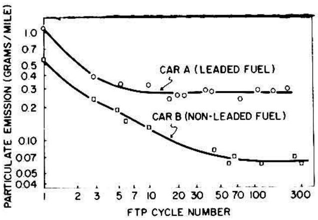

Figure 9. Corrected particulate mass emission vs. driving cycle number, Ninomiya (1970). Reprinted with permission of author

and unleaded fuel appears to be quite different on visual observation. The unleaded fuel particulate is a black, sooty material and is finer and lighter than the particulate matter collected with leaded fuel operation. Consequently, it is of greater volume per unit mass than material collected with leaded fuel operation. To illustrate this, the mass emission values shown in Figure 8 were converted to volume using the density of combustion chamber deposits accumulated with leaded and unleaded fuels. The calculated volumes are shown in Figure 10. In terms of atmospheric effects of exhaust particulate material, visibility and soiling are two of the undesirable characteristics to be considered. Since both these factors are related to the actual size or volume of the particles, Figure 10 indicated that a study of the visibility and soiling characteristics of the exhaust particles was of importance.

Influence of Exhaust Particulate Matter on Visibility and Soiling

Experimental Techniques. When we consider the atmospheric effects of exhaust particulate, only the air-suspendable size fraction becomes of direct interest. The particulate sampling system of Habibi (1970) is well suited for such a study, since the material that is air suspended at the sampling station after 5 sec of transit flow in the tunnel will approximate the air suspendable particulate matter in the atmosphere. The coarse material that settles in the tunnel will also settle rapidly along the roadside. Using this system, Pierrard and Crane (1971) conducted a program in which the mass, the light-scattering coefficient, and the soiling index of the air-suspendable exhaust particles were measured.

The vehicles were operated on a chassis dynamometer using the 1972 Federal Mass Emission Cycle (Federal Register No. 219, 1970) known as the LA-4 cycle. This cycle with a cold start every 7½ miles is considered a reasonable representation of typical consumer driving. Each test consisted of one LA-4 cycle after 16 hr of soak. The duration of the soak period proved to be important in terms of particulate emissions and was kept constant. Other factors that remained constant during all visibility and soiling experiments were: exhaust dilution (average for LA-4 driving cycle was 35:1), the dilution air temperature (50–55°F), the boiling range of the test fuels, and their Reid vapor pressures.

The mass of the air-suspendable particles was measured by filtration using a 0.45 μ Millipore filter. To measure the light scattering coefficient, a Meteorology Research, Inc. integrating nephelometer was used and the average increase in the light scattering coefficient (Δb_{scat}) for each LA-4 cycle was measured. The sample for the nephelometer was heated 15°F prior to entering the nephelometer flash tube to maintain the maximum relative humidity to less than 65% during the test cycle. The soiling index of the air-suspendable particles was determined using a Precision Scientific spot tape sample. The soiling index was calculated from the reduction of white light transmission through the spot after each LA-4 cycle according to ASTM Method D 1704 (1970).

Test Program. To determine the effect of the exhaust particles on light scattering and soiling, a 2^3 factorial design experiment with a center point was carried out. The variables were the fuel lead dosage, the aromatic content, and the fact that phosphorus and sulfur were treated as a single variable. The concentration range of the above variables in the test fuels is shown in Table IX.

Each of the three test cars used was operated on one specific lead dosage throughout the conditioning phase and the test phase of this program. This was necessary owing to the vehicle lead retention characteristics described previously. The conditioning phase involved 10,000 miles of cyclic operation on the chassis dynamometer with the specific lead dosage. On changing the concentration of other variables in the fuel during the test phase, each car was conditioned for 100 miles of cyclic operation ending with the LA-4 cycle prior to actual test runs. At each test condition at least three runs were carried out.

To ensure a close match and satisfactory operation of the three test cars, the air/fuel ratio was measured on each car under idle and seven steady-state conditions. The exhaust hydrocarbon and carbon monoxide concentrations were also measured using the LA-4 cycle. The results from all cars were in good agreement.

Test Results. For the nine fuels tested, the mass of the air-suspendable particulate matter emitted from the cars is shown in Figure 11. Each value is the average of at least three LA-4 cycles. The results show that at low aromatic concentrations, the addition of 2.5 grams of lead per gallon to the fuel causes an increase in the "air suspendable" particulate mass emission rate. At high aromatic concentrations this trend is reversed, with the leaded fuels producing less particulate matter. The average of the four unleaded fuels is the same as the average of the four leaded fuels (0.18 gpm), and agrees well with the center point, suggesting that the net lead effect on mass emission of air-suspendable particles is insignificant.

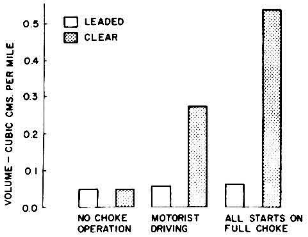

Figure 10. Volume of particulate emissions—leaded and unleaded fuels

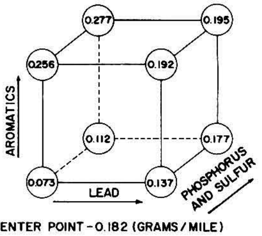

Figure 11. Particulate mass emission rate—grams per mile
Center point: 0.182 grams per mile

Table IX. Fuel Composition for Visibility and Soiling Test

Variable	Low	Midpoint	High
Aromatics, vol %	24	36	55
Lead, g/gal as Motor Mix	0	1.25	2.5
Combined effect of:			
Phosphorus, mg/l.	8	16	25
Sulfur, wt %	0.004	0.02	0.036

Figure 11 shows a consistent trend toward higher mass emissions on increasing the aromatic content of the fuel. Although the effect is very pronounced for the unleaded fuels, the average mass emissions for all high aromatic fuels was significantly higher (84%) than the average of the low aromatic fuels.

In all tests, the mass emissions from the higher phosphorus and sulfur fuels were above those obtained with the low phosphorus and sulfur fuels. However, the average increase in mass emissions due to these compounds was low, amounting to a 15% increase.

The effect of fuel composition on air-suspendable particulate mass emissions is summarized in Figure 12, where the average of all the data at high and low concentration of each variable is compared with the center point car. Figure 12 shows that the fuel aromatic content has the largest effect on the amount of air-suspendable particulate matter emitted with the exhaust. The sulfur and phosphorus combination also produces an increase but to a lesser degree. The overall lead effect is significant.

These findings agree with the work of Ter Haar et al. (1971) on low mileage 1970 cars. In that study, unleaded fuels produced 0.165 g/mile of air-suspended particulate matter while leaded fuels produced 0.152 g/mile (see Table IX) as measured by the large black bag technique. In another study, a low-mileage (5000) 1970 car was operated on the Federal 7-Mode Cycle and the air-suspended carbon concentration in the bag was measured using fuels of different aromatic content. Ter Haar found that the suspended carbon concentration, and hence vehicle emission, doubled when the fuel aromatic content was increased from 10–40%.

The effects of changes in fuel composition on the light-scattering coefficient are shown in Figure 13. With each fuel the addition of lead shows a reduction in the light-scattering coefficient of the exhaust particles. Thus, the average Δb_{scat} value for all leaded fuels is substantially lower than the value for the unleaded fuels. In contrast, an increase in the aromatic content of the fuel increased the light-scattering coefficient of exhaust particles in all tests. The increase is pronounced with the unleaded fuels. Although to a lesser extent, the addition of sulfur and phosphorus also increased the light-scattering coefficient of exhaust particles. The light-scattering data are summarized in Figure 14 where the average value of all data at the high and low level of each variable are compared with the center point fuel. All three test variables had a significant effect on the light-scattering coefficient of the exhaust particles. The aromatic and lead effects are highly significant.

The above light-scattering results are consistent with the work of Ter Haar and Stephens (1971), who used the integrating nephelometer to measure the light scattering due to air suspended exhaust particles. The exhaust from test cars was diluted with filtered preconditioned air approximately 10:1 in a 3600-ft^3 black bag. The light-scattering coefficient of the suspended exhaust particles, the total particulate loading in the bags, the lead concentration, and the carbon content of the particles was measured at different time intervals. No change in the mass loading of the bag was observed in the first 160 min, indicating little particulate settling or diffusional loss to the bag surface during that time. Using leaded fuels, nonleaded fuels, cold- and hot-cycle runs of the Federal 7-Mode Cycle (Federal Register No. 108, 1968b) and a number of test cars covering the 1966–70 production models, the authors came to the following conclusions:

The results from approximately 100 different exhaust samples show a good correlation between light scattering and the concentration of lead and carbon in the black bag. The correlation was expressed as:

$$b_{scat} \times 10^{-4} = 23.8 + 1.48\, C_{Pb} + 3.36\, C_C$$

where C_{Pb} is the lead concentration in μ g/ft^3 and

C_C is carbon concentration in μg/ft^3

Thus the carbonaceous particulate matter produced more than twice the scatter of lead particulate matter. Since elemental carbon, for example, would absorb light readily and would scatter to only a slight degree, it was concluded that the carbon must be in the form of carbonaceous materials, such as oil droplets, high-molecular-weight organic droplets or high-molecular-weight solid particles.

The light scattering immediately after the exhaust entered the bag was between 10–70 units of $b_{scat} \times 10^{-4}$.

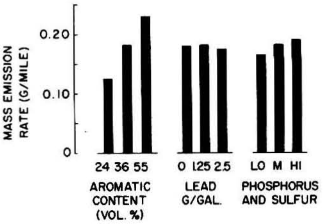

Figure 12. Mass emission rates of air-suspendable particles

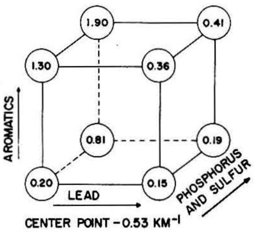

Figure 13. Light-scattering coefficient of exhaust particles (km^{-1})

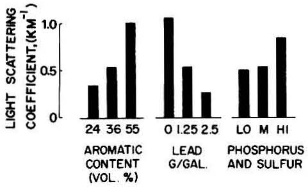

Figure 14. Light-scattering coefficient of diluted exhaust

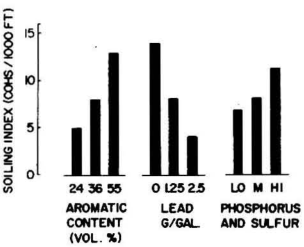

Figure 15. Soiling index of diluted exhaust

This is consistent with Crane's data in view of differences in exhaust dilution.

There was a substantial increase in the light-scattering coefficient of the suspended particles with time during the first 120 min in the bag. This was attributed to the increase in the size of the aerosol with time due to agglomeration, thus increasing the number of particles in the light-scattering range.

The effect of fuel composition on the soiling index of exhaust particles is shown in Figure 15. The results are very similar to the changes in light scattering and indicate a significant effect with all three test variables. An increase in lead concentration appreciably reduced exhaust particulate soiling. Increases in the aromatic content significantly increased soiling, as did increases in the sulfur and phosphorus content but to a lesser degree.

The above mass emissions, light scattering, and soiling data indicate a decrease in the amount of carbonaceous particulate in vehicle exhaust on addition of lead to gasoline. One possible explanation is the catalytic oxidation of the carbonaceous material by lead. This observation may be related to earlier work on the carbon-burning qualities of lead salts reported in studies of surface ignition and preignition from the combustion chamber deposits (Melby et al. 1953; Sabina et al. 1953). A number of workers have found that combustion chamber deposits of soot and carbonaceous material were oxidized with the addition of lead to the gasoline. The same mechanism may explain the reduction in emission of carbonaceous particulate material with leaded fuels.

To examine the above observation further, Crane used the unleaded car in the above fuel composition study and measured the light scattering of the air-suspendable exhaust particles with the high aromatic and high sulfur and phosphorus unleaded fuel. Confirming his previously measured high values for the light-scattering coefficient, he added 2.5 grams of lead per gallon as Motor Mix to the same test fuel and measured the light scattering of the exhaust particulate with mileage accumulation. The Federal mileage accumulation cycle was used and test runs were carried out on the LA-4 cycle at 200, 1000, 2000, 3000, and 4000 miles. The results showed no change in the light scattering of the exhaust particles for the first 2000 miles. Then a rapid decrease in the light-scattering coefficient of the exhaust particles was observed, and the data after 3000 and 4000 miles of the leaded fuel operation are consistent with the high aromatic and high-sulfur and phosphorus leaded fuel results in Figure 13. These findings indicate that the role of lead in reducing carbonaceous particulate in vehicle exhaust is a surface phenomenon. A change in the emission of carbonaceous matter as indicated by changes in the light-scattering coefficient is observed only after a minimum amount of lead surface deposition is established. The 3000 miles of conditioning necessary to produce the above change corresponds to the minimum conditioning required for measurement of vehicle lead emission rates as discussed previously—see Figure 3.

Controlled Atmosphere Studies

To relate the measured characteristics of the exhaust particulate matter to the atmosphere, a theoretical or an empirical approach can be used. For example, on the basis of the size distribution of the exhaust particles, it is possible to estimate the air suspendability of the various sized fractions, or on the basis of chemical composition of such particles, postulate possible chemical changes that may take place on exposure in the atmosphere. Empirical correlation can also be developed by making measurements in the atmosphere and at the vehicle tail pipe and establishing relationships under specific atmospheric and topographic conditions. For example, one can measure the size distribution of the exhaust lead particles under city driving and measure the size distribution of the lead found in the city air. By determining or estimating atmospheric dilution of the exhaust, it is possible to correlate the air suspendability of exhaust lead in the various size fractions. To provide the most realistic correlation between exhaust particulate emissions and atmospheric effects, experiments in "controlled atmospheres" are necessary. Ideally, a controlled atmosphere is a large chamber in which realistic exhaust dilution can be achieved with realistic surface to volume ratios and realistic background particulate loading. If vehicles are operated in this atmosphere under motorist driving conditions, the aerosol properties observed can provide reasonable correlations on the effect of exhaust particles in the atmosphere.

Utilizing an unused turnpike tunnel (Sideling Hill, Pa.), Pierrard and Crane (1971) conducted a controlled atmosphere experiment using two fleets of cars to measure the soiling and visibility degradation due to exhaust particles. Each fleet was comprised of four vehicles of 1969–71 production models. Three of the four cars in one fleet were operated on premium grade leaded fuel of normal aromatic content. Three of the four cars on the other fleet were operated on commercial unleaded gasoline of high aromatic content. The fourth car in each fleet was operated on a fuel of normal aromatic content, one leaded and one unleaded. The leaded and unleaded fueled cars were matched in terms of make, model, mileage, air/fuel ratio, and hydrocarbon and CO emissions.

Test Site. The highway tunnel used is a two-lane roadway of concrete, 6200 ft long. The tunnel has an approximate rectangular cross section with a volume of 2.4 million ft^3. Because of the large available working volume, exhaust dilution levels which approximate those occurring in the atmosphere could be attained. There are no industrial or vehicular particulate sources in this area. Thus, the remote location provided clean, ambient air for flushing the tunnel between runs. The air temperature was constant throughout these tests at 55°F.

Test Methods. The 6200-ft tunnel length permitted two unique features in these field tests. First, a full 7-Mode Federal test cycle could be driven in one pass using 4445 of the 6200 ft. Second, a long optical path length was available, enabling light transmission measurements with good accuracy at relatively low pollution levels. The transmissometer source was an incandescent bulb. The detector was a multiplier phototube microphotometer (Aminco). Source and detector were located on opposite sides of the road, 2615 ft apart (Figure 16).

Before each test, the tunnel was flushed with ambient air. During this operation, the carbon monoxide concen-

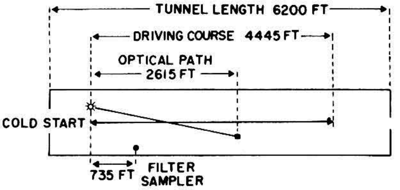

Figure 16. Schematic plan of the Pennsylvania Turnpike tunnel test arrangement

tration and light-scattering coefficient were monitored using a long-path NDIR CO analyzer and an integrating nephelometer. When the measured values corresponded to those of the outside ambient air, the fans were stopped, and the tunnel was sealed off from the outside atmosphere by means of the gasketed portal doors. The initial value of light transmission was calculated from the measured baseline absolute value of light-scattering coefficient, and the transmissometer optical path length using Beer's law. It was assumed that initial extinction was due solely to scattering.

To simulate motorist driving, each car was started cold and driven a distance of about 5.5 miles back and forth in the tunnel according to the 7-Mode Federal test cycle. This resulted in a total of about 22 miles of driving for each test fleet and produced exhaust pollutant concentrations comparable to those in heavy traffic. Figure 16 shows the driving course and light transmission path layout in the highway tunnel.

Samples for determining the soiling potential were collected by a filter sampling station located 735 ft east of the starting point, at curbside (Figure 16). The air was sampled during the entire test which averaged 1 hr for the four test cars in each fleet. Soiling of used filters was determined by measurement of filter reflectance as compared to a MgO standard at 550 nm using a reflectance spectrophotometer.

Although the tannel overhead lights were operable, they were not used during these tests for two reasons: (a) the transmissometer measurements had to be made in the absence of extraneous light, and (b) it was desired to minimize chances of photochemical reactions, as interest was centered on the primary particulate matter.

Test Results. The soiling characteristics of the airborne particles in the tunnel air with leaded and unleaded fuels are illustrated by Figure 17. The results of comparative fleet tests are shown in Figure 18 for soiling and Figure 19 for degradation of atmospheric light transmission. Light transmission degradation as shown is the difference between initial light transmission, which was usually greater than 90%, and its final value after each of the four test cars of a fleet had been driven. Soiling as shown is the difference between initial filter reflectance at 500 nm (average 96.5%) and final filter reflectance after sampling during operation of the test car fleet.

In every case, the unleaded fleet caused more degradation of light transmission than did the leaded fleet. Blackening of white filters by the two fleets exhibited the same trend as degradation of light transmission. On the average, soiling observed for the unleaded fleet was 57% more than for the leaded fleet. These results are in general agreement with and confirm Crane's observations on samples of exhaust particles using the particulate sampling system.

At the conclusion of certain of the driving tests, Pierrard obtained a continuous horizontal profile of light-scattering coefficient of the airborne particles by mounting a nephelometer on a car and sampling the air in front of the vehicle isokinetically along the whole tunnel length. Average values of the light-scattering coefficient over the transmissometer path were derived from the continuous profile data by graphical integration. In this way, Pierrard was able to calculate the light absorption of exhaust particles by assuming that the extinction coefficient is the sum of the aerosol scatter and absorption coefficients only.

Pierrard concluded that most of the excess atmospheric optical degradation caused by the unleaded fleet was the result of increased light absorption as shown in Table X. The increase of extinction coefficient shown is the difference between final extinction coefficient computed by Beer's law and initial extinction coefficient, assumed equal to initial scattering coefficient. Increase of scattering coefficient is the difference between the final average scattering coefficient (over the same path viewed by the transmissometer) computed from the nephelometer traverse record and the initial scattering coefficient. Increase of absorption coefficient is the difference between the increases of extinction and scattering coefficients.

Figure 20 summarizes the mean optical properties in the highway tunnel experiments. The increase of light ab-

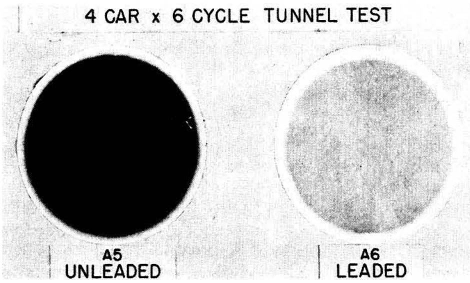

Figure 17. Photograph of filters from air sampled during one turnpike tunnel test

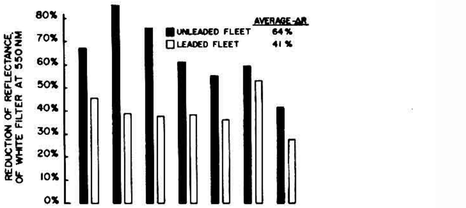

Figure 18. Soiling by airborne particles in turnpike tunnel tests

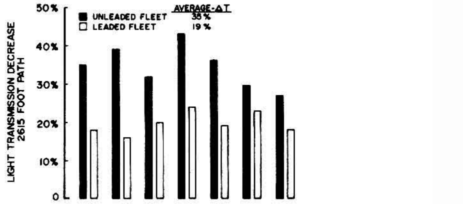

Figure 19. Light transmission reduction in turnpike tunnel tests

Table X. Effect of Fuel Type on Aerosol Optical Properties

Fuel type and test date	Initial scattering coefficient, km^{-1}	Increase in light attenuation component coefficients during test, km^{-1}		
		Extinction	Scattering	Absorption
		Leaded		
5/1	0.22	0.34	0.30	0.04
5/4	0.08	0.37	0.26	0.11
5/5	0.12	0.29	>0.24	<0.05
6/11	0.11	0.28	0.16	0.12
Mean	0.12	0.30	0.24–0.25	0.07–0.08
		Unleaded		
5/1	0.20	0.59	0.36	0.23
5/4	0.08	0.77	>0.41	<0.36
5/5	0.12	0.62	0.24	0.38
6/11	0.27	0.51	0.19	0.32
Mean	0.13	0.59	0.30–0.39	0.23–0.32

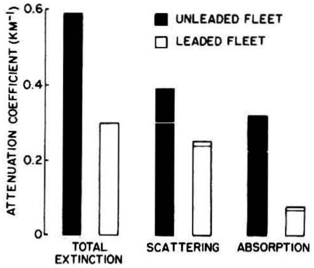

Figure 20. Turnpike tunnel fleet test—mean aerosol optical properties

sorption coefficient averaged approximately three to four times greater after unleaded fleet operation than after leaded fleet operation. This is consistent with the observed greater degree of blackening of filters used to collect samples of particles from the air during unleaded fleet runs.

Summary

Recent developments in the area of exhaust particulate sampling and characterization have contributed significantly to our understanding of the phenomenon of particulate emissions from cars. Techniques have been developed that enable representative sampling of the exhaust particles under meaningful driving conditions. Further, procedures for detailed characterization of exhaust particles have been defined.

Although on the basis of mass the contribution of vehicle particulate emissions to the total atmospheric particulate loading is small, their effect on ambient air quality may be more significant.

To obtain data on atmospheric effects of the exhaust particles, simple mass emission measurements or measurements of mass and size are no longer adequate. Techniques for more realistic assessment of the vehicle contribution are available.

As the present trend toward general availability of unleaded gasoline continues, the particulate emissions from cars equipped with advance emission control systems should be investigated. If such systems do not reduce or eliminate the carbonaceous particulate in vehicle exhaust, then the mechanism of the formation of such particles in engine combustion should be studied and their formation should be controlled.

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Chemical Element Balances and Identification of Air Pollution Sources

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■ Air pollution sources of given types, whether natural or man-made, emit a characteristic set of chemical elements in approximately fixed proportions. If the sources in a polluted region are known, the contributions from each source can be estimated by measuring elemental concentrations at a given point and solving a set of simultaneous linear algebraic equations. The method has been applied to the particulate matter measured in the air of Pasadena over an 11-hr period and averaged over particle size. For the period in question, about 15% of the particulate matter resulted from primary natural sources and 25% from primary man-made sources. About 40% of the total results from atmospheric reactions with one quarter produced by the conversion of gas phase hydrocarbons to particulate form. The estimate for this figure is based on a carbon balance. Altogether, about 70% of the total partculate burden has been accounted for with water probably making up a significant portion of the missing 30%. Improvements and extensions of the method are discussed.

Several dozen chemical elements have been identified in the atmospheres of urban and industrial basins such as Los Angeles. Many of these elements including sodium, chlorine, silicon, and aluminum are associated with the natural background aerosol, but certain exotic species including lead, zinc, and barium are for the most part due to man's activities. In the Los Angeles basin, for example, over 20 tons per day of lead are emitted by the combustion of leaded gasoline (Lemke, 1971). Much of this material eventually leaves the basin, swept along by the prevailing westerly winds; a significant fraction is probably removed by precipitation along the western slopes of the Rockies but experimental evidence has not yet been marshaled to test this speculation.

Interest in the amounts, origin, and fate of certain elemental species has quickened in recent years for several reasons: Trace metals such as mercury, barium, and lead are known to have implications for public health and ecology. Other elemental species such as iodine may, in compound form, serve as condensation nuclei and lead to the artificial stimulation of rain (Schaefer, 1966).

Hidy and Friedlander (1971) and Miller et al. (1972) have used balances on certain elements to estimate the contributions of various sources to particulate pollution in Pasadena. Winchester and Nifong (1971) have used a similar approach for the Chicago area. The sources considered in the Pasadena study included sea salt, soil dust, automobile emissions, and fly ash. In this paper, the method of chemical element balances is further developed and extended to new sources, including cement and tire dusts. The method of calculation has been modified so that sets of equations for the various chemical species, some redundant, can be solved for the source contributions. To estimate the contributions from the secondary conversion of organic vapors, an approximate carbon balance has been carried out for the first time.

Emission inventories for particulate matter, usually reported on a tonnage basis, are by themselves of limited value in relating the characteristics of atmospheric particulate pollution to sources. The fraction of the larger particles remaining airborne after emission is difficult to estimate. A substantial portion of the total atmospheric burden of particulate matter in cities such as Los Angeles results from the conversion of gaseous pollutants to particulate matter. Natural background concentrations of soil dust and sea salt in polluted regions are usually not known. However, as shown in this paper, emission inventories can provide a useful starting point and furnish supplemental information in the process of linking atmospheric concentrations to sources.

Each urban and industrial basin has its own characteristic set of sources and meteorological regime. It was first shown by Haagen-Smit (1952) that the LA basin air pollution is dominated by automobile emissions activated by solar radiation. This is now recognized as one of two characteristic types of urban air pollution; the second is that of the cities of the northeast and of Europe whose pollution is dominated by the combustion products of coal and oil. Thus, results of general value can be obtained from a few case studies such as the one described here.

Elemental concentrations by themselves are not sufficient to define the state of a polluted atmosphere or its effects on public health, weather modification, and so on. The molecular state as well as the phase in which the substance is present may be of determining importance; crystalline states can also be important as in the case of asbestos. This paper is concerned primarily with elemental balances from an input-output point of view and not with the effects of the various agents. In certain cases, however, particularly carbon, sulfur, and nitrogen, it is necessary to have some information on the combined state in order to know whether an element is present in the gas or particulate phase.

Characterizing Polluted Atmospheres

The gaseous portion of a pollution mixture can be characterized by the set of concentrations, C_i, where the subscript i refers to each separately identifiable chemical species present in the gas. The particulate component can be characterized by defining an aerosol size-composition probability density function (pdf), $g\ (v, n_1, n_2, \ldots, n_{k-1})$ (Friedlander, 1970). The size-composition pdf is defined as follows: Let dN be the number of particles per unit volume of gas with chemical compositions in the range n_1 to $n_1 + dn_1$, n_2 to $n_2 + dn_2$, and so on. Then

$$dN = N_\infty\, g(v, n_1, n_2 \ldots n_{k-1})\, dv\, dn_1\, dn_2 \ldots dn_{k-1} \tag{1}$$

The function, g, takes into account the variation in chemical composition among particles of the same size as a result of mixing or of nonuniformities in the generation process. This method of characterizing particulate pollution is incomplete because configurational effects, such as surface layers, are not taken into account. However, it is sufficiently complete for bookkeeping purposes, that is, for keeping track of the elemental or molecular species present, and has been used by Friedlander (1970) in the derivation of dynamic equations for an aerosol distributed with respect to chemical composition.

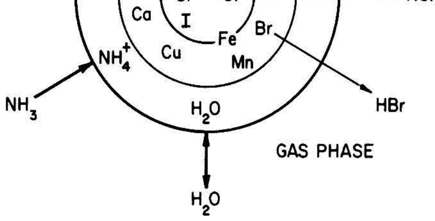
Routine monitoring of the function, g, is not yet possible. To do so would require measurements of the chemical composition of individual particles. Various moments of g are obtained by measurements with each of the wide variety of aerosol instruments available (Friedlander, 1971). For example, concentrations over discrete particle size ranges can be measured by using a cascade impactor in conjunction with neutron activation analysis (Dams et al., 1971).

Concentrations obtained with the cascade impactor are time-averaged, usually over a period of hours to obtain a sample large enough for analysis. Averaging over all particles in a given size range leads to a loss of chemical information on the particles, but the types of data obtained are still quite useful in estimating lung deposition and health effects.

Partition Between Gas and Particulate Phases

Most of the species important to an element balance are in the particulate phase. Those found in both phases but primarily in the gas include carbon, sulfur, chlorine, and nitrogen. In general, thermodynamic equilibrium does not exist between the species present in the gas and particulate phases except, perhaps, for a few substances such as water and HCl. In the case of carbon, sulfur, and nitrogen, gas phase material in the form of reactive hydrocarbons, sulfur oxides, and nitrogen oxides, respectively, are partially converted to particulate form as air passes through a polluted basin. The reaction mechanisms are not well understood, particularly for the carbon compounds, and it is not certain whether the reactions take place homogeneously or heterogeneously. Predicting how the various species are distributed between gas and particulate phases from theory or even from the results of controlled experiments is at present beyond our capabilities. However, some estimates of the overall conversion can be made from average data for the Los Angeles atmosphere, for which the ratios $S_p/S_g \approx 14\%$ and $N_p/N_g \approx 1\%$, where the subscripts p and g refer to particle and gas phases and only oxidized forms of sulfur and nitrogen are considered (EPA, 1971, and Lemke, 1971).

Figure 1 shows schematically how the elements are usually distributed between the gas and particulate phases; directions of transfer of the various species as a result of chemical and physical conversion processes are also indicated. Assorted elements from the natural background joined by metallic elements from primary man-made sources serve as a relatively stable particulate base on which is superimposed matter which is produced (or lost) as a result of atmospheric conversion processes.



CHEMICAL ELEMENTS IN POLLUTED ATMOSPHERES

Figure 1. The inner ring encloses elements present in the natural background (soil dust and marine aerosol), the second ring primary particulate matter introduced by man, and the outermost ring secondary material formed in the atmosphere

Theory of Source-Receptor Chemical Element Balance

A basic assumption of the approach adopted in this paper and the previous related studies is that each *type* of source (automobile, power plant, ocean, and so on) emits a characteristic series of elements. The concentrations of this set of elements can be looked upon as the frequency of appearance of the alphabet of which each emission is composed.

For those elements in the particulate phase, the distribution with respect to size can provide important information on the source of each species. In the first approximation adopted in this paper as well as in previous papers, the chemical composition is averaged over the size spectrum. An important next step in the application of the method will be to take the particle size distribution into account.

The various types of sources can be regarded as separate entities, each producing its own characteristic emission. Let the elemental composition of the particulate matter (or gas) as measured at a given receptor site be denoted by x_i where $i = 1, 2, \ldots n$ denotes the individual elements and where the concentrations may refer either to the particulate or to the gas phase. If m_j is the mass of material originating from source j per unit mass of receptor matter, the following relationship holds:

$$x_i = \sum_j z_{ij} m_j \tag{2a}$$

with

$$\sum_j m_j = 1 \tag{2b}$$

The set of receptor concentrations, x_i, can be regarded as a vector, while z_{ij} represents the source concentration matrix.

The source strength vector, m_j, the quantity which is usually sought, is closely related to the dispersion function or transition probability calculated from atmospheric diffusion theory. The relationship is most clearly illustrated in the case of the single source. The solution of the diffusion equation without chemical reaction leads to an expression for the concentration field as a function of location with respect to the source. When properly normalized, this concentration represents the component of the source strength vector associated with the particular source under consideration. When many sources of the same type are present, as is usually the case in an urban basin, it is generally not possible to separate one from another since their chemical element alphabet will be the same. Hence the approach cannot be considered a substitute for air trajectory analyses or diffusion modeling.

Difficulties in Applying Theory

The formulation of the problem through Equation 1 is exact, so long as it is properly interpreted, since it is simply a material balance on each chemical element. However, its application to practical problems is complicated by a number of intervening factors: The transfer of material from one phase to the other (usually gas to particle) in the atmosphere as a result of various chemical and physical processes. Physical processes include vapor condensation or evaporation. Chemical reactions involved in phase change are very complex and are currently an area of active research. An example is the conversion of SO_2 to sulfate ion which, in some cases, appears to take place as a result of the absorption of SO_2 by the water of particulate matter containing metal ions such as manganese, copper, or iron. Another example is the absorption of NO_2 by droplets containing sea salt with the subsequent formation of NO_3^- and release of Cl^- according to a reaction with the overall form:

$$NaCl + H_2O + 2NO_2 \longrightarrow NaNO_3 + HNO_2 + HCl(\uparrow) \quad (2)$$

Hydrocarbon conversion processes are a particularly important case and are discussed in more detail in the section on the carbon balance. The difficulty in preparing a chemical element balance on either phase arises in estimating the average conversion for each type of source. For each source of a given type, the history of temperature and solar radiation varies depending on location relative to receptor site.

The source concentration matrix, z_{ij}, refers to the concentration of each element in a quantity of material from a given source *measured at a receptor site.* As a good approximation in some cases, it is possible to use the elemental concentrations at the source itself. Difficulties arise as a result of fractionation at the source which may lead to significant differences in composition between the source itself and the material which actually becomes airborne. This is the case for seawater and to a lesser extent for wind-raised dust. The evidence is reviewed in the paper by Miller et al. (1972). Sedimentation may lead to complex changes in chemical composition if the chemical composition with respect to particle size varies.

Pollution Sources in Los Angeles Basin

The preparation of a source-receptor chemical element balance requires the construction of a source concentration matrix for the region. The matrix can be constructed by identifying major sources and determining their compositions together with the appropriate partition coefficients. The goal of the calculation will usually be to determine the source strength vector.

The major sources of pollution in the Los Angeles basin can be identified with the aid of a source inventory of the type published by the LA Air Pollution Control District (Lemke, 1971) together with information on the natural background. It is convenient to divide these sources into natural and man-made categories; in the case of particulate matter, they can be further divided into primary, referring to material introduced as particulate matter into the atmosphere, and secondary, referring to material formed in the atmosphere. Each of these categories can be further divided into specific types of sources as shown on the left-hand side of Table V.

Information on the chemical compositions of various sources is available and has been collected or measured by Miller et al. (1972). The data are summarized in Table I which can be considered the source concentration matrix for the Los Angeles basin. Data for tire dust (Rogers, 1948) and cement dust (Wood and Rockwood, 1962) are also shown, assuming the dusts have the same composition as the parent material. This table has several uncertain aspects: A major one is the relationship of the composition of the sea salt aerosol to the composition of seawater. The compositions listed in the table for sea salt aerosol are those for seawater.

Another cause for uncertainty is the variability in the concentrations of the elemental substances emitted from any given group of sources. For example, the fuel oil fly ash composition given in Table I is for a sample obtained from the Pasadena power plant. During the time that atmospheric measurements were made in Pasadena, this power plant was operating on natural gas. The power plant fly ash composition was assumed to be similar to that of other fly ash resulting from the burning of fuel oil in the basin.

In the case of the data for soil dust, measurements made at seven different sites near the Keck Laboratory at Caltech in Pasadena and in the foothills of the San Gabri-

Table I. Source Concentrations of Particulate Matter

	Percentages					
	Sea salt	Soil dust	Auto exhaust	Fuel oil fly ash	Portland cement	Tire dust
C as carbon	—[a]	—	—	u[b]	—	29.3
C compounds	—	—	40.3[c]	u	—	58[d]
Na	30.6	2.5	u	5	0.4	u
Mg	3.7	1.4	u	0.06	0.48	u
Al	—	8.2	u	0.8	2.4	u
Si	—	20	u	1	10.7	u
S	2.6	—	u	u	—	u
Cl	55.0	—	6.8	—	—	u
K	1.1	1.5	u	0.2	0.53	u
Ca	1.16	1.5	u	1.3	46.0	u
Ti	—	0.4	u	0.06	0.144	u
V	—	0.006	u	7	—	u
Cr	—	—	u	0.1	—	u
Mn	—	0.11	u	0.06	—	u
Fe	—	3.2	0.4	6	1.09	u
Co	—	0.002	u	0.2	—	u
Ni	—	0.004	u	2	—	u
Cu	—	0.008	u	0.2	—	u
Zn	—	<0.01	0.14	0.02	—	1.5
Br	0.19	—	7.9	—	—	u
I	1.4×10^{-4}	—	u	—	—	
Ba	—	0.06	u	0.1	—	u
Pb	—	0.02	40.0	0.07	—	u

[a] Negligible.
[b] Unknown.
[c] As a tarry substance assumed 90% C.
[d] Mostly as a copolymer of styrene and butadiene.

el mountains have shown results close to the average values reported for the earth's crust (Miller et al., 1972).

Determination of Source Strengths

The concentrations of 18 chemical elements in the Pasadena atmosphere were measured in a series of experiments carried out at the Keck Laboratory in September and October 1969. Air from a point about 50 ft above street level and 22 ft above the roof of the laboratory was sampled through a 2.5-in. pipe and passed through a four-stage Lundgren impactor in the basement of the laboratory. The details of the experimental system are described by Hidy and Friedlander (1971). Trace metals were determined for the most part by neutron activation analysis and atomic absorption, sulfur and nitrogen by photoelectron spectroscopy, and carbon (CO_2) by a thermal conductivity cell. Details of the analysis are described by Novakov et al. (1972) and Mueller et al. (1972). Additional data were provided by Mueller (1972). Table II shows the results of the measurements averaged over an 11-hr period on September 3, 1969.

To determine the source strength vector, the following method has been adopted: It is assumed that the five sources (excluding tire dust) shown in Table I control the concentrations of the seven elements Na, Al, Pb, Ca, V, Mg, and K. In solving the set of seven equations for five unknowns, two of the equations should be redundant. Because of experimental and other factors, however, somewhat different values of m_j are obtained for each set of five equations selected. Hence, values of m_j were calculated by a method of least squares in which the sum of the squares of the percentage deviations of the calculated value from the measured value was minimized. Table III shows the results of the calculation for the contribution of the five sources to the concentrations of the seven substances, together with the measured values. The greatest deviation occurs in the case of magnesium which is lower than the measured concentration by a factor of about four.

Table II. Percentages of Several Elements in Pasadena Particulate Matter[a]

(Average 0900–2000, Sept. 3, 1969)

Element	%	Element	%
C	19	V	0.01
N	>0.1	Mn	0.03
Na	1.02	Fe	3.16
Mg	1.1	Cu	0.03
Al	0.80	Zn	0.18
S	>5	Br	0.6
Cl	0.07	I	0.006
K	0.32	Ba	0.04
Ca	0.99	Pb	3.3

[a] Novakov et al., 1972; Mueller et al., 1972; Mueller, 1972.

The concentrations of other elements were then calculated from m_j and z_{ij} and the results are shown in Table IV where they are compared with measured values. In the case of the metals, the calculated concentrations are generally lower than the measured, probably because of the contributions of metallurgical sources. In the case of the halides, the Table IV shows that most of the chloride ion is lost to the gas phase, probably by Equation 2. Bromide ion is conserved while iodine is significantly enriched, although no explanation for this result can be offered at this time.

Discussion of Source Strengths

Values of m_j calculated in this way are shown in Table V. The figures for diesel and aircraft exhaust and industrial emissions were obtained by scaling up the figures of Lemke (1971) based on automobile exhaust. The tire dust contribution was estimated by assuming that the mass ratio of tire dust to automobile exhaust was 10%. Reliable figures are not available but based on experiments in his laboratory, Pierson (1972) suggests that this ratio is a few percent.

The combination of sea salt, soil dust and conversion products of natural organic vapors constitutes the natural background of particulate matter. The primary background consists of 1.3 $\mu g/m^3$ of sea salt (corrected for chloride loss) and 11.4 $\mu g/m^3$ of soil dust. This total of 12.7 is consistent with concentrations measured in regions far from industrial centers. Both the soil dust and sea salt particles are relatively large; most of the mass of this portion of the particulate burden is probably associated with particles larger than 1 μ in diameter.

Primary man-made sources account for about 25% of the total. By direct exhaust emissions, tire dust and, perhaps, roadway abrasion, the automobile constitutes the major single source on a weight basis of primary particulate emissions in Los Angeles.

Secondary particulate matter from man-made sources amounts to perhaps 40% of the total; the method of estimating the hydrocarbon contribution is discussed in the section which follows. The nitrate figure is much smaller than the value of about 5% usually reported, but the reason for the discrepancy is not known. This portion of the particulate matter is dynamic in its behavior and its mechanism of formation and growth is not well understood. The results to this time indicate that the conversion process is driven by chemical reactions involving sulfur oxides and reactive hydrocarbons such as cyclic olefins. Together with condensed water, this material plays a major role in the reduction of visibility in the LA basin.

In weighing the samples, it is customary to equilibrate them at a relative humidity of 50% which leads to a significant amount of water associated with the particulate matter. The amount varies depending on the hygroscopic-

Table III. Contributions of Various Sources to Concentrations of Tracers

Pasadena, 9/3/69

Element	Percentages						
	Sea salt	Soil	Auto exhaust	Fuel oil fly ash	Cement dust	Σ	Measured
Na	0.85	0.28	—	0.0066	0.0069	1.15	1.02
Mg	0.102	0.16	—	7.8×10^{-5}	0.0082	0.27	1.1
Al	—	0.93	—	0.0011	0.041	0.98	0.8
K	0.030	0.17	—	0.00027	0.0091	0.21	0.32
Ca	0.032	0.17	—	0.0017	0.79	0.99	0.99
V	—	0.00068	—	0.00931	—	0.01	0.01
Pb	—	0.0023	3.3	9.3×10^{-5}	—	3.3	3.3

Table IV. Contributions of Various Sources to Concentrations of Nontracers

Pasadena, 9/3/69

	Percentages						
Element	Sea salt	Soil	Auto exhaust	Fuel oil fly ash	Cement	Σ	Measured
Mn	—	0.013	—	0.0010	—	0.014	0.03
Cu	—	0.00091	—	0.00027	—	0.0012	0.03
Fe	—	0.364	0.0330	0.00799	0.0204	0.42	3.16
Cl	1.52	—	0.561	—	—	2.08	0.07
Br	0.0053	—	0.65	—	—	0.66	0.6
I	3.9×10^{-6}	—	—	—	—	3.9×10^{-6}	0.006
Ti	—	0.046	—	8.0×10^{-5}	0.0025	0.048	
Cr	—	—	—	1.3×10^{-4}	—	1.3×10^{-4}	
Co	—	2.3×10^{-4}	—	2.7×10^{-4}	—	4.9×10^{-4}	
Ni	—	4.6×10^{-4}	—	2.7×10^{-3}	—	0.0031	

ity or chemical nature of the material, but probably accounts for a significant portion of the 30% of the particulate matter not accounted for in Table V.

Table V. Source Contributions to Pasadena Aerosol, 9/3/69

	Percentages
Natural background	
Primary	
Sea salt	1.3
Soil dust	11.4
Secondary	
Organic vapors from plants Ammonia Hydrogen sulfide	unknown
Man-made	
Primary	
Automobile exhaust	8.2
Tire dust	0.8
Cement dust (roads and construction)	1.7
Fuel oil fly ash	0.1
Diesel exhaust	1.8
Aircraft exhaust	2.7
Industrial emissions	7.3
Secondary	
Sulfur dioxide → sulfite	>10
Nitrogen oxides → nitrate	~0.1
Organic vapors → particulate	26.7
	>72.3

Carbon Balance

Most of the carbon-containing compounds in the Los Angeles atmosphere are present in the gas phase. The carbon-containing portion of the aerosol, however, represents a significant fraction of the particulate phase, about 19% in the case reported here. With associated hydrogen, oxygen, and nitrogen, the organic constituents represent a major portion of the LA smog aerosol on a weight basis as will be shown below.

The principal primary sources of carbon containing compounds in the Pasadena aerosol are believed to be automobile exhaust, tire dust, diesel exhaust, and aircraft emissions. The principal secondary source is the conversion in the atmosphere, probably as a result of photochemical reactions and of reactive olefins in automobile exhaust. Conversion of organic vapors produced by vegetation probably takes place as well but to a smaller extent.

The details of the hydrocarbon conversion process are not understood at this time. Haagen-Smit noted in his early work (1952) that ring compounds with a double bond are especially active in forming aerosol when mixed with nitrogen dioxide and irradiated. The opening of the ring and the formation of polar groups, such as the carboxylic acid group, lead to nonvolatile products. For example, the dicarboxylic acid, glutaric acid, has a melting point of 97.5°C, while the corresponding cyclic olefin, cyclopentene, is a volatile liquid (bp 44°C). Cyclopentene is present in gasoline to the extent of about 0.15% (Sanders and Maynard, 1968) and has also been found in the atmosphere at concentrations of 0.0044 ppm (Stephens and Burleson, 1969), corresponding to a mass concentration of 24 $\mu g/m^3$ of glutaric acid. Other olefins also form aerosol when mixed with nitrogen dioxide and irradiated if sulfur dioxide is also present. These systems are reviewed by Leighton (1961).

Several possible mechanisms may control the conversion from gas to particulate phase. These include reaction in the gas phase followed by homogeneous nucleation or by condensation on foreign nuclei. Alternatively, reactive species may diffuse to existing particles where reactions may take place on the surface or in the particles. Goetz and Stevenson (1957) offer experimental evidence for reaction in the gas phase followed by condensation on foreign nuclei. This would lead to the conservation of the total number of particles in the system.

A certain amount in known about the organic products of these reactions. Renzetti and Doyle (1959) report that the particulate matter formed by the irradiation of automobile exhaust consisted mostly of carbon, hydrogen, and oxygen with traces of nitrogen and give as the composition on a weight percent basis 34% C, 5.3% H, 1.8% N, and 59% O (by difference). Measurements have also been made of the chemical nature of some of the products. Cholak et al. (1955) reported that more than one third of the benzene soluble fraction consists of organic acids and other water soluble compounds.

A breakdown of the origins of the carbon-containing portion of the aerosol has been carried out as shown in Table VI. Both diesel exhaust (in the absence of barium containing smoke suppressants) and aircraft emissions (McDonald, 1962) are mostly carbon. The carbon in the tarry portion of automobile exhaust was assumed to compose 90% of the tar for lack of more quantitative information. When we used this assumption and other assumptions explained in the table, the carbon in the material formed from hydrocarbons in the atmosphere was calculated by difference to make up 9.1% of the particulate matter. If we assumed the latter number comprised 34% of the organic matter formed in the atmosphere (Renzetti and Doyle, 1959), a contribution of 26.7% to the total particulate burden is estimated. This figure, which should be

Table VI. Carbon Balance

Pasadena Aerosol, 9/3/69

Source	C, % as carbon	C, % in compounds	Remarks
Automobile exhaust	—	3.3	Carbon assumed to be 90% of tar
Tire dust	0.2	0.5	Airborne fraction assumed to be 10% of auto exhaust
Diesel exhaust	1.8	—	Scaled up from Lemke 1971
Aircraft emissions	2.7	—	Scaled up from Lemke 1971
Industrial emissions	1.4		Carbon assumed to be 19% of total (average in atmospheric particulate)
Atmospheric conversion		9.1	By difference—hence a maximum
Total	19		

considered a maximum, is of the order reported for the benzene soluble portion of the LA particulate matter.

Need for Further Studies

Many problems remain in working out this approach and in evaluating the first results of its application:

From an experimental point of view, the need remains for an instrument capable of continuous, real-time measurements of the key components of the particulate matter including lead, sodium, vanadium, zinc, barium, and others. There is no commercially proved device currently available for continuously monitoring the elemental components of the atmospheric particulate, although X-ray fluoresence techniques seem promising in this respect (Goulding and Jaklevic, 1971).

Little information is available on the conversion rates from gas to particles for key elemental species including carbon, sulfur, and nitrogen. These reactions are of major importance from the point of view of visibility and, perhaps, public health. The few data on the partition coefficient between the gas and particle phases must be extended and their accuracy improved. Are the halogens in equilibrium between the two phases?

The next step in the application of the method should be to carry out the balance on a particle size basis. This will provide additional information of the sources of many of the elements. One goal should be to reconstruct the measured atmospheric spectrum with respect to size and chemical composition from the characteristics of the known source.

The question of the fate of the elements originating from the various sources remains to be answered. Where do the 20–30 tons/day of lead, 1 ton/day of zinc, 3 tons/day of particulate bromide, and so on appear in the environment after production and atmospheric dispersion? How much deposits in the basin and how much escapes to be removed by precipitation farther east and then deposited in the soil and carried into the natural water system?

Acknowledgment

Some of the calculations were carried out by Steven L. Heisler whose help is appreciated.

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Growth Mechanisms and Size Spectra of Photochemical Aerosols

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■ A series of photochemical aerosol aging experiments were performed in which the complete time-dependent size spectra (diameter range $0.004 < D_p < 0.35$ μm) were measured using a Whitby Aerosol Analyzer. Based on these data, the role of various physical mechanisms—i.e., nucleation, coagulation, and condensation in the photochemical aerosol formation—is identified. In an initially particle-free system, the aerosol passes through the following stages of evolution: nucleation-condensation (simultaneously), nucleation-condensation-coagulation, and condensation and coagulation. If suitable foreign nuclei are present, in sufficient quantity, the gas-to-particle conversion occurs preferentially on the existing nuclei—i.e., the nucleation is heterogeneous. Available laboratory and atmospheric data indicate that whether homogeneous or heterogeneous nucleation occurs in the atmosphere depends on the relative amount of surface area provided by foreign nuclei. There is evidence that in Los Angeles smog, the nucleation occurs heterogeneously, while in sparsely populated areas the nucleation is homogeneous.

Since the pioneering work of Haagen-Smit on the chemistry and physiology of Los Angeles smog (Haagen-Smit, 1952), considerable attention has been devoted to the understanding of photochemical processes occurring in urban atmospheres. It has been firmly established that decreased visibility, crop damage, eye irritation, objectionable odor, and rubber deterioration are associated with photochemical processes occurring in contaminated urban atmospheres. Also, it has been shown that at least one of the obnoxious smog effects, namely visibility reduction, is caused by the photochemically produced aerosols.

Most of the past research on photochemical smog was directed toward understanding the relevant gaseous chemical mechanisms and reaction rates. Following Haagen-Smit's original approach, this research has been performed in smog chambers designed so that both the chemical and physical parameters, relevant in smog formation, could be varied in a flexible manner. The result of the extensive smog research during the past 20 years is a fair understanding of the major gaseous photochemical reactions occurring in urban atmospheres.

Since these smog simulation experiments in chambers often produce aerosols from the gas-to-particle conversion, it has been concluded that such conversion occurs in the atmosphere. It was also known that both real smog aerosols and those produced in smog chambers were submicron in size. Because visibility reduction is one of the more obnoxious effects of smog, various light-scattering techniques have been popular for measuring aerosols formed in smog chambers. However, because of the experimental difficulty in measuring the unstable submicron smog aerosols, there have been few size distribution measurements accurate enough to permit a quantitative comparison of the size distribution of atmospheric smog aerosols with *simulated* smog chamber aerosols until the recent development of such in situ aerosol size distribution instruments as the optical particle counter and the electric mobility analyzer.

These instruments were first applied to the measurement of smog aerosols in 1969 when the urgent need for more information of the smog aerosol in the Los Angeles basin prompted a group of investigators to perform a series of multidisciplinary experiments. These have subsequently become known as the "1969 Pasadena Smog Aerosol Experiment" (Whitby et al., 1972). Much of our present understanding on the behavior of smog aerosol has been gained from, or stimulated by, the 1969 Pasadena Smog Project.

The purpose of this paper is to present the results of some recent experiments in which the size distribution and concentrations of aerosols formed in a smog chamber were measured and to relate these results to information gained from the 1969 Pasadena smog experiments. From this comparison it is concluded that the size distribution of the aerosol in an initially particle-free smog chamber and in that during smog formation in the real atmosphere, is quite different. The physical reasons for these differences are discussed.

Experimental Apparatus and Procedures

Most of the size distribution data in the size range from 40 Å to 0.6 μm were obtained by a modified commercial Whitby Aerosol Analyzer (Whitby and Clark, 1966; Husar, 1971; Whitby et al., 1972).

The photochemical aging vessel was a 90-m^3 polyethylene balloon. The particulate free air was supplied by a low-speed radial fan, pressing the air through a glass fiber absolute filter. The total nucleus concentration in the balloon was measured by a General Electric condensation nuclei counter. For certain runs, the average particle diameter was estimated by the diffusion battery method as described by Husar (1971).

Formation Mechanisms and Kinetics of Particle Growth

A problem of major interest for the control of smog is that of identifying the formation mechanism and predicting the rate of growth of photochemical aerosols. With the available information as a basis, it may be stated that in the photochemical gas-particle conversion, both chemical and physical mechanisms play dominant roles. Chemical reactions are responsible for the production of species convertible from gas phase to particulate (liquid or solid) phase. The photochemical processes involved are extremely complex, and the exact chemical mechanisms and reaction rates are as yet not established (Leighton, 1961; Altshuller and Buffalini, 1971). On the other hand, the physical processes such as nucleation, condensation, absorption, adsorption, and coagulation are primarily responsible for determining such physical properties as number concentration, size distribution, optical properties, and transport properties of the formed aerosols.

From the point of view of aerosol growth kinetics, the two central questions of interest are: What is the mode of conversion: homogeneous or heterogeneous nucleation? In

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homogeneous nucleation, particles (or nuclei) are formed in the vapor phase by molecular clustering without the aid or intervention of foreign nuclei. The term heterogeneous nucleation refers to the situation where foreign particles or gas ions (clusters of molecules) are present in the vapor and act as nuclei for the subsequently growing particles.

Is the particle growth rate controlled by a surface-catalyzed chemical reaction which proceeds at the particle-atmosphere interface or is the diffusion rate of the vapor phase toward the particle surface the conversion rate-controlling parameter?

In the study of complex systems, such as the photochemical aerosol formation, it is convenient, and frequently essential, to start with a tentative mechanism of the process under consideration. This mechanism is to be modified or abandoned as dictated by the experimental evidence. In regard to the photochemical aerosol formation in the Los Angeles atmosphere, the following mechanism is proposed:

The driving force for the gas-particle conversion is provided by a gaseous photochemical reaction or chain of reactions. The gaseous reaction(s) produces a supply of molecular species (or radicals) which, upon collision with each other, agglomerate and form molecular clusters—i.e., they homogeneously nucleate. If suitable aerosol particles or ions are present, the monomers or radicals deposit preferentially on the existing surfaces and thus the nucleation is heterogeneous. The growth rate of the newly formed particles is determined by the concentration gradient—i.e., the diffusion rate of the condensable species to the particle surface. If the concentration of the droplets is sufficiently high, the droplets may interact by coagulation.

In the following sections, we shall elaborate the various points of the above proposed conversion process. The supporting evidence will be drawn primarily from experimental observations. The lack of an adequate theoretical model to describe the physics of the gas-particle conversion process will limit the theoretical consideration to qualitative discussions.

Photochemical Aerosol Formation in Initially Particle-Free System—Homogeneous Nucleation

Let us first consider a simple experiment performed in Pasadena in 1969. A large 5-m^3 polyethylene balloon was inflated with smoggy ambient air, from which the particulate matter was removed by a series of high-efficiency filters. The transparent balloon, exposed to solar radiation with the total number of particles within the balloon larger than about 25 Å in diameter, was continuously monitored by a General Electric Condensation Nuclei counter. Approximately 3 min after the inflation of the balloon was completed, it was observed that the total nucleus count rose sharply from essentially zero to a maximum of $10^5/10^7$ particles per cm^3. The initial sharp rise was followed by a slow decay of the total nucleus concentration. This phenomenon has been observed by various investigators (Bricard et al., 1968; Goetz and Pueschel, 1967) and at various urban locations. Since in these experiments foreign nuclei and gaseous ions were present only in very low concentrations (<100/cm^3), it may be concluded that the particle formation proceeded by molecular clustering of the condensable species—i.e., by homogeneous nucleation.

A comparison of the Pasadena photochemical nucleation experiments with similar data (Figure 1) obtained by Bricard et al. (1968) using Paris air, reveals that in both urban areas the aerosol formation proceeds in a qualitatively similar manner. From Figure 1, it can be seen, however, that in the Pasadena experiments both the nuclei production rate as well as the attained maximum concentrations were significantly higher than those measured in Paris. On a light smoggy day in Pasadena, the maximum concentration was about 10^5 nuclei/cm^3 while during heavy smog, the plateau was at about a level of 10^7 particles/cm^3.

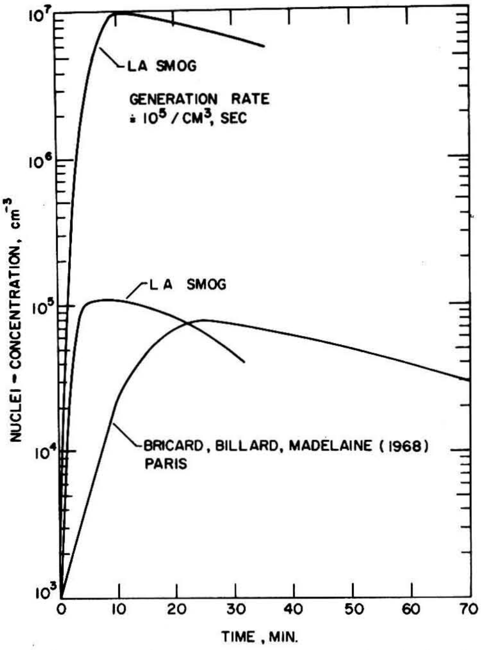

Figure 1. Change of total number concentration in irradiated, initially particle-free container. Initial concentration rise is due to nucleation and the subsequent decay to coagulation

Although these experiments provided information on the nucleation rates, they reveal no details about the particle size–time evolution of the photochemically formed aerosols. Results of other investigators (Bricard, et al., 1968; Goetz and Pueschel, 1967) have shown that the photochemically formed nuclei tend to grow in size after formation. Unfortunately, the diffusion battery method and the total light scattering measurement used by these investigators could not provide sufficiently accurate data to conclude what mechanism is responsible for growth.

Complete size distributions of aging photochemical aerosols were only recently obtained at the University of Minnesota Particle Technology Laboratory. Photochemical aerosols were produced spontaneously in a 90-m^3 polyethylene bag initially filled with particle-free laboratory air and irradiated by diffuse solar radiation penetrating the wide, north-facing window of the laboratory. Parameters other than the aerosol size distribution were not measured. The complete aerosol size spectrum in 20-min intervals was measured by the Whitby Aerosol Analyzer (WAA) (Whitby et al., 1972).

The measurement of complete size spectra has permitted us to calculate the volume and surface moments of the spectra as well as the total number concentration. The evaluation of the development with time of the aerosol volume (or mass) fraction, surface area, and total number could be used tentatively to identify the physical mechanisms which control the aerosol growth starting from the time shortly after formation.

Although these were uncontrolled experiments in that the chemical reactants were unknown and the conversion rate of gases to particles was quite low (less than 1 $\mu g/m^3$ hr), the sequence of physical events appears to be the same as in the photochemical nucleation experiments performed by others.

In total, four runs were made, but for sake of brevity, only the runs with the highest and lowest conversion rates are presented here. If we assume a particle density of unity, the conversion rates correspond to 0.047 $\mu g/m^3$ hr and 1 $\mu g/m^3$ hr, respectively. The two runs not discussed here are qualitatively similar to those presented here.

The formation of photochemical nuclei in the irradiated balloon was first detected by the nuclei counter, after about 15 min of irradiation, but the size of the nuclei was below the measuring limit (0.004 μm) of the WAA. For Run 1, six size distributions were measured starting at t = 40 min after the inflation of the balloon.

Four of the measured size distributions are plotted in Figure 2. As indicated by the dashed line in Figure 2, a fraction of the size distribution at t = 40 min was below the measuring limit of the WAA. From the consecutive size distributions, it can be seen that the photochemical nuclei grow in size as shown by the disappearance of particles at the lower end of the size spectrum and by the emergence of new particles at the upper end. The size spectra at different times are rather similar in shape and may be approximated by a log-normal distribution with standard deviation of σ_g = 1.35 and characteristic diameter, continuously increasing from about 0.005 μm at t = 40 min to 0.01 μm at t = 140 min. The flow regime of particles shown in Figure 2 corresponds to the free molecular flow—i.e., the particles essentially behave as giant molecules obeying the laws of gas kinetics.

Further characteristics of photochemical aerosols may be observed in Figure 3. This figure shows the total number concentration $N(\text{cm}^{-3})$—i.e., the zeroth moment of the number distribution, the total aerosol surface area $S(\mu m^2/cm^3)$ which is proportional to the second moment, and the total aerosol volume fraction $V(\mu m^3/cm^3)$ proportional to the third moment of the size distribution as calculated from the size distributions.

The changes in the total number concentration are in accordance with findings of other investigators—i.e., a strong initial increase, followed by a slow decay. The explanation for the initial increase of the total number concentration is well established. It is attributed to the self-nucleation of the photochemically formed vapors. The nucleation continues over an extended period of time—on the order of an hour. When the aerosol concentration reaches a sufficiently high value, the particles begin to interact by coagulation. The maximum concentration is attained when the production rate Q (particles/sec) is equal to the coagulation rate, $K_p \cdot N^2$ where $K_p(\text{cm}^3/\text{sec})$ is the average coagulation constant of the polydisperse system. With further growth, the aerosol surface area approaches a value which is sufficient to accommodate the condensable vapors. As a result, the condensable vapor concentration decreases and the nucleation rate diminishes. The decay of the number concentration, say for $t > 80$ min in Figure 3, is then entirely due to coagulation. The coagulation coefficient which fits the decay curve best for $t > 80$ min is $K_p = 5.1 \times 10^{-10}$ cm³/sec. Within experimental error, this value is the same as the K_p for pure Brownian coagulation of aerosols of the same size range (Husar, 1971).

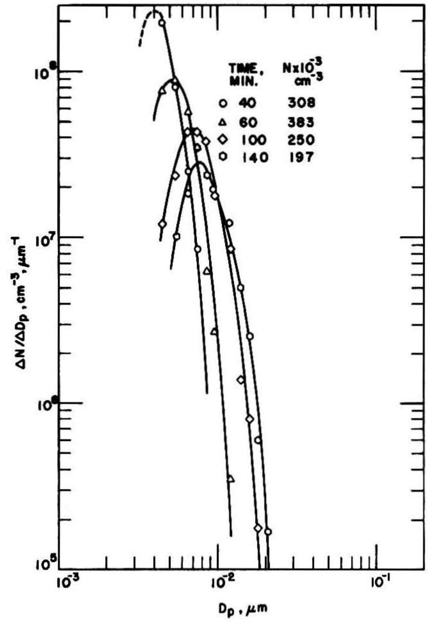

Figure 2. Size distributions of aging free-molecular photochemical aerosols, Run 1, at different times. Aerosol growth is due to simultaneous coagulation and condensation

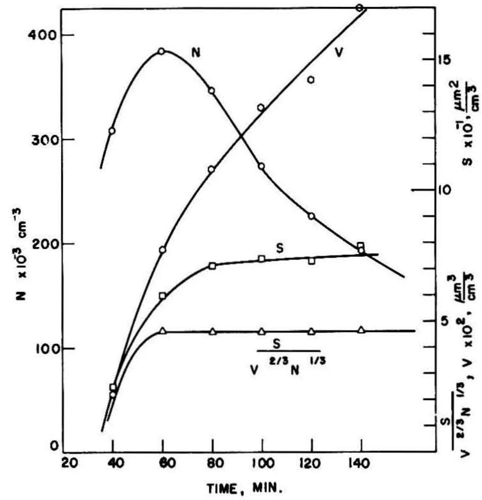

Figure 3. Evolution of several aerosol parameters during photochemical aging for Run 1

N, total number concentration, *S*, total surface area; *V*, total aerosol volume fraction and the parameter $S/V^{2/3}N^{1/3}$. Decay of N for $t \geq 80$ min is governed by coagulation and increase of V by condensation

Significant differences between the evolution of photochemical aerosols and aerosols undergoing Brownian coagulation may be observed by comparing higher moments of the number distribution, such as the total aerosol surface area and the total volume fraction. While for pure Brownian coagulation—i.e., absence of aerosol sources—the total volume fraction is conserved; in the case of photochemical aerosol formation, the volume fraction was increased continuously with time in spite of the decrease of the total number concentration.

It is proposed that the increase of the aerosol volume concentration with time is determined by diffusional de-

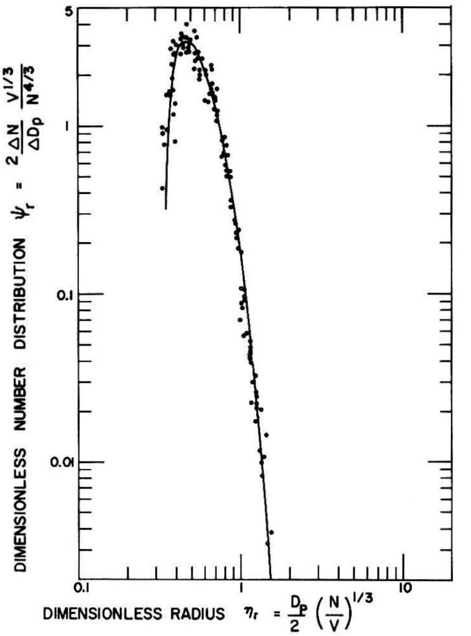

Figure 4. Nondimensionalized size distributions for coagulating and condensing free molecular aerosols

Within experimental scatter, data indicate existence of a universal dimensionless spectrum. Solid line is best fit for experimental data

position of the condensable vapor (or vapors), the vapor itself being the product of gaseous photochemical reactions.

During the aerosol growth, coagulation tends to reduce, while condensation increases, the total aerosol surface area. The result is that for a given run, the total aerosol surface area tends to approach a nearly constant value—i.e., equilibrium value.

The dimensionless parameters $S/V^{2/3}N^{1/3}$, introduced by Pich et al. (1970) in a somewhat different context, may be used as a measure for the spread of a size distribution. The total surface area, S, can be expressed as $S = \bar{D}_{ps}{}^2N$ where $\bar{D}_{ps}$ is the average surface diameter, and similarly, $V = (\pi/6)\bar{D}_{pv}{}^3N$ where $\bar{D}_{pv}$ is the average volume diameter. From these two definitions, the above dimensionless parameter may be redefined as:

$$\frac{S}{V^{2/3}N^{1/3}} = 6^{2/3}\cdot\pi^{-1/3}\left(\frac{\bar{D}_{ps}}{\bar{D}_{pv}}\right)^2 \qquad (1)$$

The dimensionless parameter, $S/V^{2/3}N^{1/3}$, is maximum (4.85) for a monodisperse system—i.e., $\bar{D}_{ps} = \bar{D}_{pv}$. With increasing polydispersity, the ratios of the two average diameters tend to decrease. For Run 1, the value of the dimensionless parameter is nearly constant at about 4.45. This implies that the width of consecutive size spectra is constant.

It has been noted previously that during the decay the successive size distributions are similar in shape. In terms of the rigorous similarity theory introduced first by Friedlander (1960), similarity of spectra means that when properly normalized, all size distributions should fall onto a universal curve. The shape of the universal size distribution may depend upon the average particle size and on the particular transfer process under consideration, for such items as coagulation and condensation, but it is time-independent.

The size distributions shown in Figure 2 may be nondimensionalized by the total number N, and by a characteristic radius, $(V/N)^{1/3}$, which is proportional to the volume mean radius. The dimensionless coordinates are defined as

$$\eta_r = \frac{D_p}{2}\left(\frac{N}{V}\right)^{1/3}; \psi_r = \frac{2\Delta N V^{1/3}}{\Delta D_p N^{4/3}} \qquad (2)$$

for the diameter and for the number spectrum, respectively. The normalized data for Run 1 are presented in Figure 4 along with eight successive spectra from a run not discussed here. The normalized data for free molecular ($D_p < 0.01$ μm) coagulating-condensing aerosols shown in Figure 4 provide strong evidence for the existence of a universal or self-preserving spectrum. The scatter of data around the best fit curve (solid line) is within the experimental error with no detectable systematic drift of the data points.

We shall next consider the results of Run 2, with average growth rate of 1 μg/m^3 hr—i.e., about twenty times higher than that of Run 1. Three size distributions corresponding to t = 50, 145, and 225 min are shown in Figure 5. The corresponding evolution of N, S, V and the parameter $S/V^{2/3}N^{1/3}$ are given in Figure 6. Qualitatively, the results of Run 2 and Run 1 are rather similar; the subsequent size distributions are similar in shape corresponding to σg = 1.5; the total volume fraction, V, increases with time, and the total surface area changes only slightly during the evolution ($S \cong 200$ μm^2/cm^3). Furthermore, the normalized size distributions shown in Figure 7 indicate that the three spectra are nearly self-preserving. It should be noted, however, that the normalized spectra, ψ_r, for Run 2—i.e., transition regime aerosols, $0.01 < D_p < 0.1$ μm—have shapes different from those for free molecular aerosols shown in Figure 4, the latter being considerably narrower. At present, no explanation is offered for the broadening of the self-preserving distributions with in-

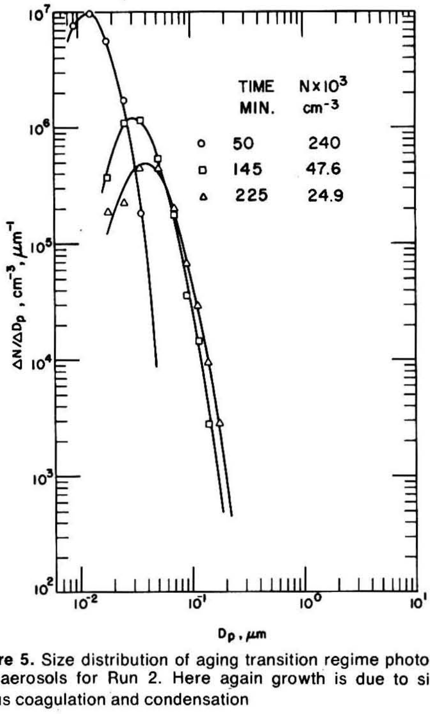

Figure 5. Size distribution of aging transition regime photochemical aerosols for Run 2. Here again growth is due to simultaneous coagulation and condensation

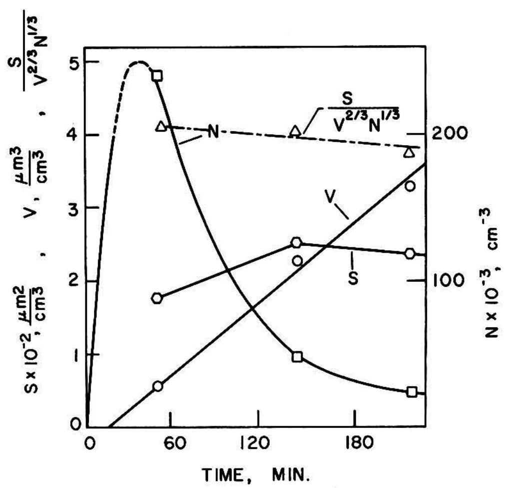

Figure 6. Evolution of N, S, V, and $S/V^{2/3}N^{1/3}$ for Run 2. Growth pattern is similar to Run 1 in Figure 3

creasing size. It is also of interest that the higher conversion rate in Run 2 has a consequence that the equilibrium surface area—i.e., the surface area necessary to accommodate the condensable vapors—is higher. When we consider the previously discussed experimental data, we propose that the chronological evolution of a photochemically formed aerosol in an initially particle-free chamber may be characterized in the following three points (Figure 8):

The initial strong increase of a total number concentration is a manifestation of photochemical nucleation. The nucleation continues over an extended period of time ranging from several minutes to hours.

When the aerosol concentration reaches a sufficiently high value, the particles start to interact by coagulation. The maximum concentration is attained when the production rate, Q (particles/sec), is equal to the coagulation rate K_pN^2.

With further growth, the aerosol surface area approaches a value which is sufficient to accommodate all the photochemically produced vapor, and the nucleation rate diminishes. The decay of the number concentration is then entirely due to coagulation while the increase of the volume fraction is determined by the condensation rate.

Photochemical Aerosol Formation in Presence of Foreign Nuclei—Heterogeneous Nucleation

In the previous section, we have been concerned with the aerosol formation in an initially particulate free system. For sake of reproducibility, such systems were used by most investigators in smog-chamber studies. However, it was pointed out, as well as experimentally verified by Goetz and Pueschel (1967), that the presence of foreign nuclei may alter significantly the behavior of photochemical gas-particle conversion. They also suggested that the system with foreign nuclei is of most practical importance since in the lower atmosphere such nuclei are always present. Unfortunately, the numerous tests by Goetz and Pueschel with the large number of parameters they varied, did not provide a clear pattern by which foreign nuclei interact with the gas-particle conversion process. Evidently, the nature of heterogeneous nucleation is rather complex, and it depends primarily on the size distribution and surface properties of the foreign nuclei as well as on the concentration and chemical composition of the reacting gaseous species.

It seems that the experimental data and the intuitive arguments discussed in the first section of this paper and further data discussed next may provide further insight into the photochemical gas-particle conversion process in a heterogeneous system.

The experimental data discussed previously have revealed that the volumetric gas-particle conversion rate for a given run was uniquely associated with an equilibrium surface area. Furthermore, with increasing gas particle conversion rate, the equilibrium surface also increases. We may now argue that the surface area attained for each run is imposed on the aerosol system by the production rate of the convertible species—i.e., by a gaseous reaction. In that case, the equilibrium surface area for each conversion rate is the minimum surface area necessary to ac-

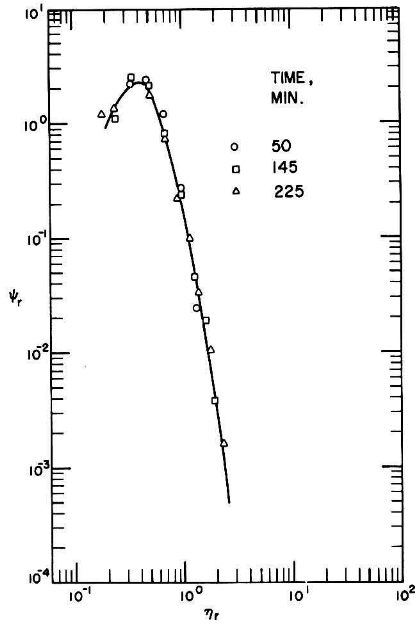

Figure 7. Nondimensionlized size distributions for coagulating and condensing transition regime aerosols (0.01 $\mu m \leq D_p \leq$ 0.1 μm) for Run 2. This dimensionless spectrum is broader than the spectrum for the free molecular regime (Figure 4)

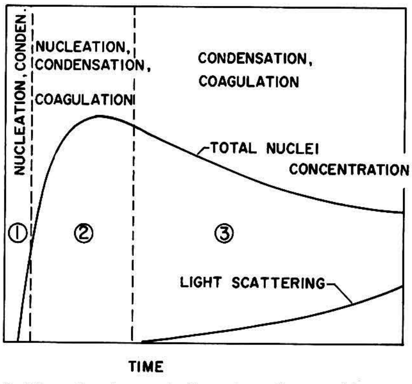

Figure 8. Time development of condensation nuclei concentration and light scattering in an initially particle-free chamber containing an aerosol produced by a photochemically reacting mixture

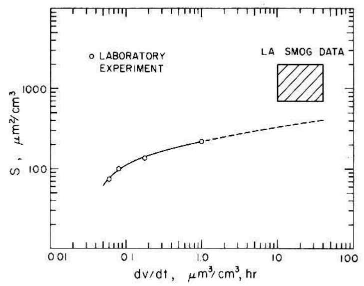

Figure 9. Experimental values for "equilibrium surface area" at various aerosol formation rates dV/dt. Size distribution of Los Angeles smog aerosol in morning hours is such that surface area available for condensation is more than sufficient to accommodate the supersaturated vapors

commodate the condensable photochemical reaction products.

A plot of the laboratory experimental data of the measured volumetric conversion rate dV/dt vs. the equilibrium surface area, S, is shown in Figure 9. The data shown are from the same experiments discussed in the first section of this paper.

It is suggested that the data in Figure 9 may provide at least qualitatively a criterion which determines the nature of photochemical gas-particle conversion in a heterogeneous system, the system being defined by a total aerosol surface area, S, and by volumetric conversion rate dV/dt.

The area below the curve is thought to represent the condition when surface area is not sufficient to accommodate the photochemical reaction products. In this region, there is a steady buildup of convertible species in the gas phase, up to the point of self-nucleation. In the region above the curve, the surface area of the foreign nuclei is generally more than sufficient to accommodate photochemical reaction products—i.e., the nucleation is heterogeneous.

Photochemical Aerosol Formation in Atmosphere

There is experimental evidence from three sources that the presence or absence of foreign nuclei can determine whether there would be nucleation in the atmosphere during smog formation.

Husar et al. (1972) reported no evidence of homogeneous nucleation during the relatively heavy smog episodes studied. Although there was evidence of considerable gas-particle conversion, apparently there were always sufficient foreign nuclei furnished by such sources as the automobile providing adequate surface for deposition of the condensing vapors.

As a consequence, in the Los Angeles basin, the total nucleus count is dominated by the intensity and frequency of ground sources and not by photochemical self-nucleation. This is also evidenced by the strip-chart recording (Figure 10) of the total nucleus count obtained in Pasadena in 1969. As shown in Figure 10, the maximum nucleus concentrations occur during the morning and afternoon rush hours and not during the peak of the aerosol mass concentration at noontime. Typically, in the Los Angeles basin between 10:00 a.m. and 12:00 noon, the conversion rates were estimated to be about 10–40 $\mu m^3/cm^3$ hr (Husar et al., 1972). In the same period, the measured total surface area was between 700 and 2000 $\mu m^2/cm^3$. These values are entered as a shaded area in Figure 9. The location of the shaded area is above the line of "minimum necessary surface area"—i.e., in the region of heterogeneous nucleation which is consistent with the available experimental evidence.

On the other hand, experimental data of Hogan (1968) indicate that in sparsely populated rural areas, the conversion of gases to particles by solar radiation is a major source of Aitken nuclei, and it is of dominating influence in the total nuclei trend. He illustrates his suggestion by a plot of the diurnal Aitken nuclei concentration changes which rose from about 7000/cm^3 at 6:00 in the morning to about 20,000/cm^3 at 12:00 and decayed during the afternoon and night hours. Evidently, at the location studied by Hogan, the nuclei population was insufficient to accommodate the convertible vapors, and the conversion process was homogeneous.

Figure 11 shows the results of an experiment in which photochemical conversion was permitted to take place both with and without the normal ambient nuclei.

On a light smoggy day (October 23, 1971), a transparent balloon was inflated with particulate free ambient air and irradiated by natural solar radiation. As expected, the total nucleus count in the balloon rose from near zero to $2 \times 10^5/cm^3$ in 10 min and then decayed slowly (Figure 11). Then the balloon was cleaned and inflated with unfiltered atmospheric air. The monitoring of the irradiated balloon (containing the nuclei) revealed that with the normal number of nuclei present, no detectable self-nucleation occurred. Thus, in a system with sufficient foreign nuclei present, the vapor deposition occurs preferentially on the existing foreign nuclei—i.e., the nucleation is heterogeneous.

Conclusion

The driving force for the photochemical gas-particle conversion is a gaseous photochemical reaction which produces the gas to particle-convertible species. Depending on the availability of foreign nuclei, the concentration of these species may be relaxed by deposition on the existing particles. This is the case when there is sufficient amount of aerosol surface area present to accommodate the con-

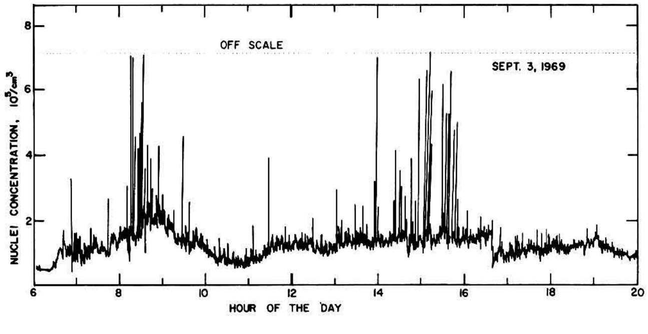

Figure 10. Instantaneous readings of total nuclei concentration. "Baseline" indicates concentration of aged aerosol passing over Pasadena; spikes are manifestation of local sources

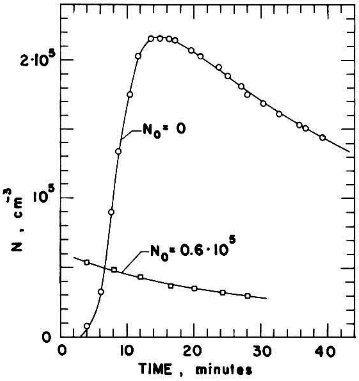

Figure 11. Photochemical nucleation measurement in initially particle-free system (N_O = 0) and in a system with foreign nuclei ($N_O = 0.6 \times 10^5$ cm^{-3})

vertible vapors. On the other hand, if the aerosol surface area is not sufficient, then the result is a buildup of concentration, which ultimately leads to self-nucleation. There is evidence that in the atmosphere both homogeneous self-nucleation, as well as heterogeneous nucleation on foreign nuclei, may occur. In the polluted Los Angeles atmosphere for instance, the growth on foreign nuclei dominates the gas-particle conversion.

A logical and much needed extension of this work would have to include the simultaneous measurement of complete size distributions as well as the chemical composition of gaseous and particulate matter.

Acknowledgment

The authors gratefully acknowledge the helpful comments of S. K. Friedlander of the California Institute of Technology.

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Vertical Distribution of Photochemical Smog in Los Angeles Basin

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■ Aircraft soundings of oxidant concentration and temperature in the vertical section from the Santa Monica coastline inland to the San Bernardino area are analyzed. In addition to the polluted layer confined beneath the temperature inversion, laminae of pollution are detected within the inversion layer with concentrations of oxidant as high as those observed in the ground-based smog layer. It is hypothesized that the upper layers of pollution are formed when a portion of the smog moving up the heated mountain slopes that bound the basin on the north moves out horizontally from the slopes at elevations between the top and bottom of the inversion.

In the spring and summer of 1970 a series of measurements of the oxidant concentration from the surface up to 6000 ft was made in a transect from Santa Monica to San Bernardino, Calif. These observations were taken to supplement similar data being obtained across the San Bernardino Mountains in a study of the ozone damage to ponderosa pines sponsored by the University of California's Project Clean Air (Edinger et al., 1972). The data represent what is probably the most detailed description of the vertical distribution of oxidant from coast to inland mountains yet obtained for the South Coast basin.

The earliest measurements of oxidant aloft in Los Angeles were carried out in 1954 by the Air Pollution Foundation (Neiburger et al., 1955). A blimp was used to obtain measurements at a few levels below, within, and above the temperature inversion at three locations: Dominguez, downtown Los Angeles, and Pasadena. The concentrations observed below the inversion tended to be somewhat higher than those within and above as one might expect considering the hindrance to vertical mixing provided by the inversion layer. In 1965 a series of soundings by chemiluminescent ozonesondes was made at Pt. Mugu, about 50 miles west of downtown Los Angeles. At this location the maximum ozone concentrations occurred above the base of the inversion (Lea, 1968b). This lead to a follow-up investigation at Pt. Mugu, 1967, in which comparisons were made between soundings at Pt. Mugu and Pasadena. Again the ozone maximum was above the inversion base at Pt. Mugu, and in some instances layers of ozone were observed above Pasadena (Lea, 1968a), within the inversion.

The present data are in sufficiently dense array so that a continuous field of oxidant concentrations can be constructed in the vertical section from coast to mountains and compared with the position of the inversion base and top as revealed in the vertical temperature field. Portrayed is a vertical distribution of pollution that confirms Lea's earlier findings and further illuminates the pattern from the coast inland to the basin's mountainous perimeter.

Observational Technique

To obtain dense data in a vertical section, a light plane was equipped to record continuously the oxidant concentration, temperature, and elevation. It was flown along the line from Santa Monica at the coast to Rialto-Miro, an airport just short of the San Bernardino Mountains as indicated on Figure 1. At the west end the plane made a low pass above the ocean, climbed to 6000 ft at a point midway between the coast and El Monte airport, descended to El Monte making a low pass over the runway, and then proceeded to the next airport, Cable (near Pomona), again attaining 6000 ft at the midpoint, and finally to Rialto-Miro in the same fashion. This procedure provides six slant soundings between the coast and San Bernardino, about one every 12 miles. This path was flown four times a day, first flight at 9:00 am, the last at 4:00 pm. Flights were made on June 18, 19, and 20, 1970.

The oxidant was measured by a Mast Model 724-2 Ozone Meter, the temperature by a rapid response platinum wire thermometer, and the height by a Rosemount Model 84OE 3E altimeter.

Results

The observations will be displayed in two ways: in the form of a few typical soundings at different locations and times of day and in the form of the observed fields of potential temperature and oxidant concentration analyzed in the vertical section from the coast inland at three different times of day.

Soundings

The first sounding (Figure 2) displays the classical case of pollutants produced at the surface being effectively trapped below an inversion layer. It presents the conditions at the inland terminus of the vertical section, Rialto-Miro, at 4:30 pm, June 20. Below the inversion base the oxidant concentration is nearly constant with height at about 0.25 ppm. In the first few hundred feet of the inversion, the concentration drops abruptly to values below 0.1 ppm. The temperature lapse rate in the polluted layer is dry adiabatic, the result of convective mixing initiated by the heating from below encountered by the air as it passed over the coastal plain and through the connecting inland valleys. The small (1°C) excursions in the temperature trace in this mixed layer occur where the airplane encountered rising convective elements. The upper limits of this convective mixing is reached at the base of the inversion. Above that, strong atmospheric stability damps out vertical stirring motions, and the vertical diffusion of pollutants from below is effectively blocked.

Figure 3 is a picture taken at 5000 ft (2000 ft above the

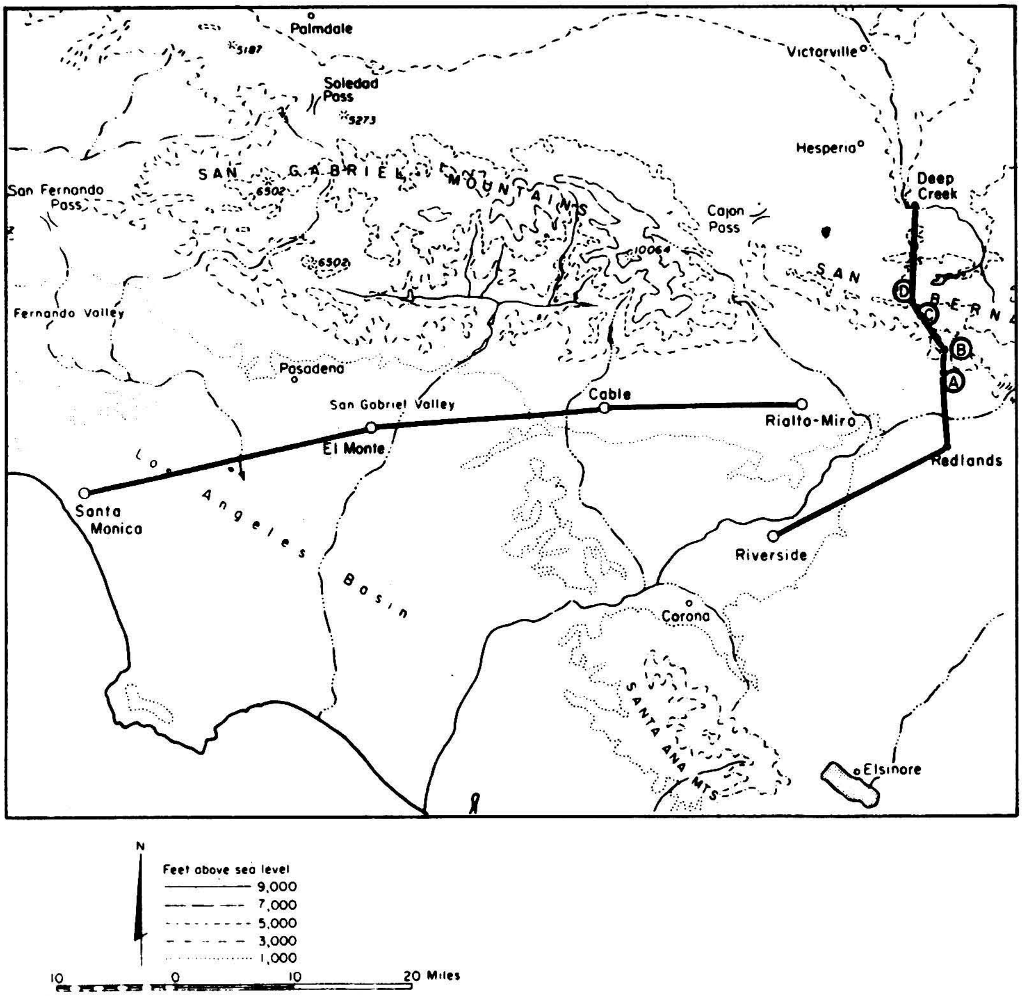

Figure 1. Map of Los Angeles basin showing flight path

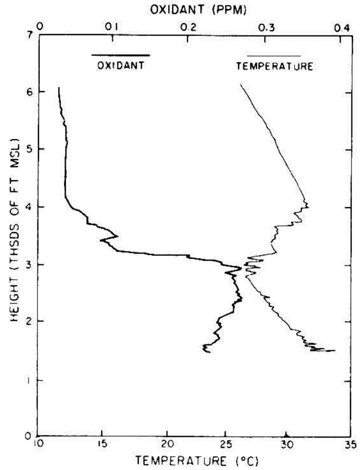

Figure 2. Temperature and oxidant soundings, Rialto-Miro, 4:20 pm, June 20, 1970

Figure 3. Picture of east end of San Gabriel Mountains, taken looking northwest from 5000 ft near Rialto-Miro, 4:20 pm, June 20, 1970

top of the polluted layer) near Rialto-Miro at the time the above sounding was being recorded. The view is to the northwest and shows the east end of the San Gabriel Mountains rising above the polluted layer. The polluted layer, 1500 ft in depth, completely obscures the terrain below.

Soundings taken at the coastal terminus of the section, like those of Lea at Pt. Mugu, show the maximum concentrations in the inversion layer, but the observed concentrations are much higher than those reported by Lea. Figure 4 displays a sounding that began near the ocean surface off Santa Monica and slants upward toward downtown Los Angeles. Uniform concentrations of magnitude less than 0.1 ppm are recorded throughout the depth of the marine layer. In the inversion are several oxidant layers, one with a concentration in excess of 0.2 ppm. In the layer above the top of the inversion, the concentration is very low and practically constant with height. This sounding illustrates the multilayered distribution of oxidant sometimes observed in the inversion layer. Such a heterogeneous distribution in the vertical is possible because of the strong stability there and the associated lack of vertical mixing motions. Note the depth and strength of the inversion. It spans a height interval of 3000 ft through which the temperature increases by 15°C. Contrast it with the markedly modified vertical temperature structure at Rialto-Miro (Figure 2) where the inversion has been reduced to only 1000 ft in thickness and a 5°C temperature difference.

In some instances it is possible to distinguish by eye the different polluted layers within the inversion layer. Figure 5 shows a sounding for such a case. Two peaks in the oxidant concentration are apparent within a strong deep temperature inversion, one near its base the other near its center. (The sounding did not extend to the surface because the extremely low visibility precluded a landing at El Monte.) The visibility was quite good, however, in the layer between these two maxima. Figure 6 is a picture taken at 2500 ft in this relatively unpolluted stratum. The ridge line of the San Gabriel Mountains is faintly seen through the upper polluted layer and the city below is practically obscured by the lower layer, but the mountains at the 2500 ft level are clearly seen.

The last sounding, Figure 7, describes the most heavily and completely polluted inversion layer encounted in the three-day observation period. Strong discontinuities in the vertical oxidant distribution occur at both the base and top of the temperature inversion. The inversion itself was

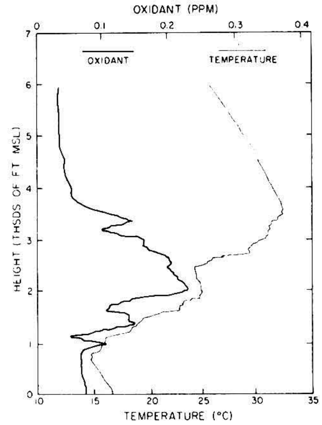

Figure 4. Temperature and oxidant soundings, Santa Monica, 1:28 pm, June 20, 1970

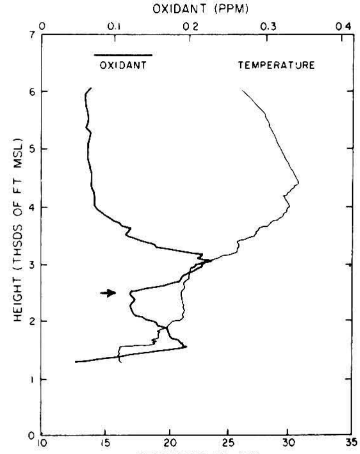

Figure 5. Temperature and oxidant soundings, El Monte, 9:25 am, June 20, 1970

unique in that it had exceptionally strong stability at both its top and bottom. This condition was observed at El Monte in the late afternoon, June 20. The oxidant concentration from ground level up to the base of the inversion was slightly less than 0.1 ppm. At the center of the inversion layer it reached values in excess of 0.37 ppm. Above the top of the inversion the concentration was even lower than it was below the inversion.

Vertical Sections

Figures 8 through 13 present the data for June 20 in the form of vertical sections of the fields of potential temperature and oxidant concentration. Potential temperature is used instead of temperature so that it becomes easy to discriminate between regions of stability and instability. Increase of potential temperature with increasing height denotes stability, decrease denotes instability.

The thermal fields, represented in terms of isentropes, lines of constant potential temperature, have the characteristic features found in previous investigations of the marine layer and inversion over coastal southern California (Edinger, 1959 and 1963). The air beneath the inversion base is well mixed during the daytime hours due to surface heating producing a near adiabatic lapse rate of temperature which appears in the vertical sections as a layer of nearly constant potential temperature. A shallow layer at the ground actually is unstable (superadiabatic). Through the marine (subinversion) layer, vertical mixing takes place quite readily, heat and pollutants introduced at the surface being diffused upward to the base of the temperature inversion. Potential temperatures within this mixed layer increase with distance inland from the coast, evidence of the longer history over heated land of the inland air. Also the depth of the mixed layer is seen to increase with distance inland in the noon and afternoon sections, the result of the daytime erosion of the bottom of the inversion layer by the convective mixing motions within the marine layer. This effect is not yet noticeable in the morning sounding, at which time surface heating is just beginning.

The very marked stability of the inversion layer is revealed by the close vertical packing of the isentropes. The absence of a strong horizontal temperature gradient in the inversion such as that in the marine layer reveals the restriction to the vertical transport of heat provided by this exceptionally stable layer. The widely spaced, relatively irregular isentropes in the upper portion of the sections indicate that the atmosphere above the inversion layer is

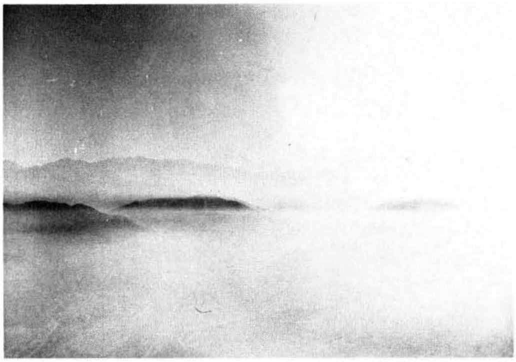

Figure 6. Picture taken in unpolluted layer between two polluted laminae near El Monte, looking north at 2500 ft, 9:25 am, June 20, 1970

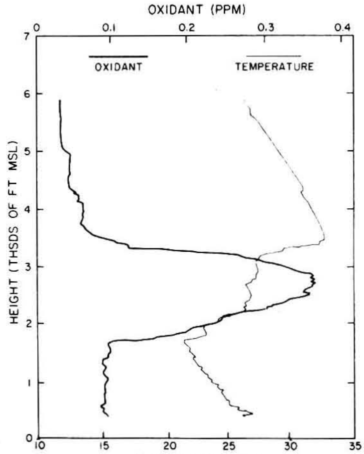

Figure 7. Temperature and oxidant soundings, El Monte, 4:54 pm, June 20, 1970

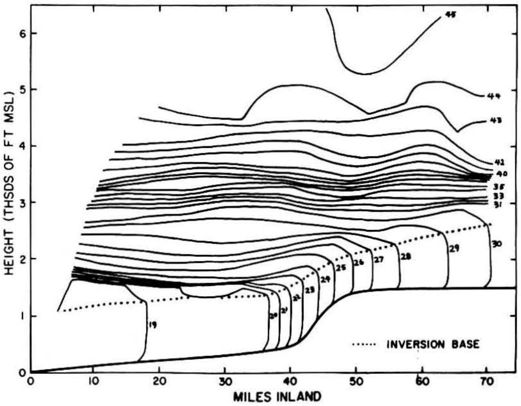

Figure 8. Field of potential temperature (°C) in the vertical cross section from Santa Monica to Rialto-Miro, 9:00 am, June 20, 1970

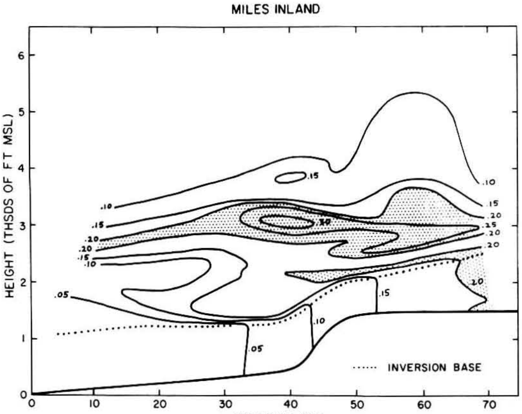

Figure 9. Field of oxidant concentrations (ppm) in the vertical cross section from Santa Monica to Rialto-Miro, 9:00 am, June 20, 1970

one of rather weak stability, bordering on neutral stability.

In summary the thermal distribution in the vertical section normal to the coast shows an inversion that decreases in thickness from the coast inland and one which has a horizontal upper surface. It also indicates that the well-mixed layer below the inversion, in general, increases in depth during the hot midday hours and then begins shallowing in the afternoon.

Figures 9, 11, and 13 display the distribution of oxidant concentration in the sections for the three different times of day. Looking first at the layer beneath the inversion, the marine layer, concentrations tend to increase with distance inland, particularly in the morning and afternoon, reaching values in excess of 0.2 ppm at Rialto-Miro. At midday this is true only for the half of the section adjacent to the coast. The 0.2-ppm value is reached at East Los Angeles and from there inland to Rialto-Miro oscillates about this value. The horizontal and vertical gradients in the concentration within the layer are small compared to those observed at the base of the temperature inversion.

Perhaps the most striking feature of the distribution of oxidant is the occurrence of concentrations within the inversion layer of the same magnitude as those beneath it. The configuration within the inversion is nonuniform, containing multiple layers and strong vertical gradients. Above the inversion the oxidant concentration is at the 0.1-ppm level or below and quite uniform relative to that in the inversion and marine layers.

The vertical distribution of potential temperature and oxidant concentration for the other two days, June 18 and 19, not shown here, are substantially the same as for June 20. All reveal the layers of oxidant within the inversion as well as the other general features in the layers above and below.

Interpretation

The distribution of the oxidant below the inversion conforms to what might be expected in a convectively mixed layer (capped by an inversion) which is being advected inland on a sea breeze over a nonhomogeneous source area of great extent such as the Los Angeles basin. The increase in concentration with distance inland in the morning reflects the fact that the parcels found farthest inland are those with the longest history over source areas. They also are the parcels whose pollutants have participated in photochemical reactions for the longest period of time.

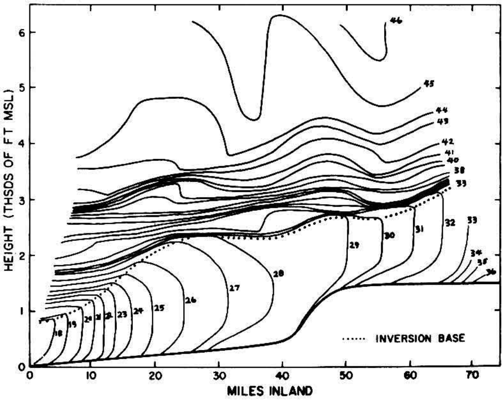

Figure 10. Field of potential temperature (°C) in the vertical cross section from Santa Monica to Rialto-Miro, 12:00 noon, June 20, 1970

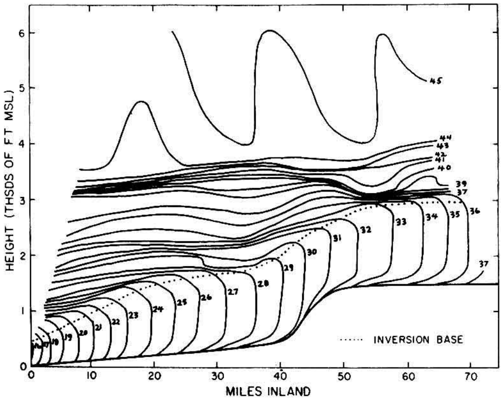

Figure 12. Field of potential temperature (°C) in the vertical cross section from Santa Monica to Rialto-Miro, 4:30 pm, June 20, 1970

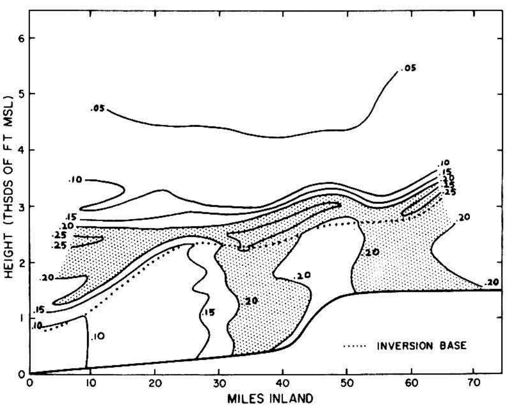

Figure 11. Field of oxidant concentrations (ppm) in the vertical cross section from Santa Monica to Rialto-Miro, 12:00 noon, June 20, 1970

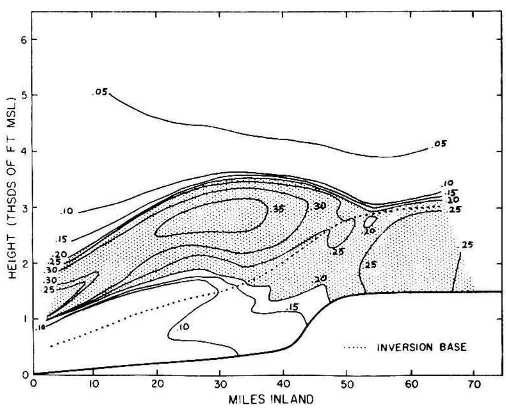

Figure 13. Field of oxidant concentrations (ppm) in the vertical cross section from Santa Monica to Rialto-Miro, 4:30 pm, June 20, 1970

The increase in concentrations just downwind of the Los Angeles metropolitan area at noon could be interpreted as the arrival there of pollutants produced by Los Angeles city traffic during the morning rush hour. Further advection inland of this reacting mass of pollutants brings the maximum concentration of oxidant beneath the inversion to the eastern end of the section by late afternoon.

The appearance of oxidant within the inversion layer in concentrations as high as those in the mixed layer beneath the inversion is difficult to explain in terms of vertical mixing. Perhaps where it is the very lowest portion of the inversion layer that has the high oxidant concentration, the pollution may have been carried there by convective mixing. As pointed out by Edinger (1963) this lowest part of the inversion where the lapse rate is only weakly negative may be interpreted as the uppermost part of the convective layer, an accumulation of convective debris (thermal elements that reach the top of the mixed layer with a slight excess of potential temperature relative to the layer's average). Extensive layers of high oxidant concentration completely internal to the inversion cannot be explained in this way.

Horizontal injection of pollutants in the vicinity of the heated mountain slopes could be invoked as a likely mechanism. That part of the polluted mixed layer which contacts the mountains becomes heated and moves up the slopes. When the inversion layer is deep and strong, as during these three days, a large part of this polluted air rising in convective flow up the slopes does not get warm enough to penetrate the inversion completely. Instead it attains densities intermediate between those at the base and top of the inversion and moves out away from the slopes as spreading laminae of pollution interior to the inversion. Here in the absence of turbulent mixing motions it persists without further diffusion in the vertical.

It appears that the inversion can serve as a reservoir for photochemical smog in cases such as these. Furthermore the previous detection of oxidant in the inversion by Lea and by Neiburger suggests that the situation is not rare. The appearance of a polluted inversion layer as far west as Pt. Mugu indicates just how persistent layers of pollutants can be once encapsulated in a layer of great stability. The author has photographed smog layers within the inversion in many parts of the basin and as far at sea as Santa Barbara Island, 50 miles southwest of Santa Monica. The trajectories of these upper layers of photochemical smog, subsequent to their injection into the inversion, depend upon the pattern of winds at the level of the inversion.

When the wind in the inversion is westerly, smog injected along the slopes of the San Gabriels is carried eastward where some of it encounters the slopes of the San Bernardino Mountains. Data taken by the array of instruments on the slopes of these mountains and by instrumented aircraft during the June 18, 19, and 20 field experiment indicated that the maximum concentration of oxidant occurred at the 3500-ft level, just about at the top of the temperature inversion. It can be hypothesized that part of the explanation may be the delivery to the slope at inversion height of photochemical smog which has traveled from the south slopes of the San Gabriels without being further diluted by vertical mixing motions or depleted chemically through contact with materials at the ground. The decrease in concentration above 3500 ft on the slopes can be ascribed to the active convection and dilution in the only slightly stable layer above the inversion.

It is instructive to speculate on the fate of the upper polluted layers in the inversion as they move into the San Gorgonio Pass. Typically the inversion is finally destroyed by heating from below during the day on the mountain slopes and in the passes, accounting for the marked vertical dilution of visible smog at the mountains ringing the basin along its inland perimeter. But there have been some reports of high oxidant concentrations in the Coachella Valley at night east of San Gorgonio Pass. The sea breeze continues to move air through the pass for some hours after sundown, hours during which there is no convective mixing and during which drainage winds are developing down the slopes of the mountains. It is conceivable that upper laminae of smog encountering the slopes on both sides of the pass on this evening remnant of the sea breeze can become part of the drainage winds which will deliver the polluted air relatively undiluted by mixing motions to the floor of the Coachella Valley. And the polluted layer below the inversion on the basin side of the pass at sundown may move through to the valley as a stable (no longer convective) layer to deliver higher concentrations than those delivered during the daytime when convection destroyed the inversion and allowed mixing to many thousands of feet on the desert side of the pass.

Conclusions

Photochemical smog can occur in high concentrations within the temperature inversion above the Los Angeles basin. Pollution found in the very lowest part of the inversion can reach that level via daytime convective mixing and can be construed as convective debris in the uppermost part of the polluted marine layer. Layers of pollution found in the middle and upper parts of the inversion cannot be accounted for in this fashion but can have as their source the pollution moving up the heated slopes of the mountain ranges peripheral to the basin. Once injected into the inversion, this pollution is no longer subject to convective mixing motions and maintains high concentrations. Wind patterns at inversion level may determine its subsequent history and eventual departure from the basin. If this brings it in contact with high terrain at night, it may be returned to low elevations on drainage winds, within or outside the basin. If this contact occurs during the day, convective mixing on the heated slopes will disperse it vertically. On the other hand some of this inversion-bound pollution may be returned to the ground during the daytime over the basin by fumigation if there is sufficient subsequent erosion of the inversion layer from below by convection.

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Mathematical Modeling of Urban Air Pollution

General Theory

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■ The fundamental theory of urban air pollution modeling is developed. A number of points are considered including: The definition of the mean and random components of the wind velocity field, the necessary conditions for obtaining conventional Eulerian and Lagrangian models, the proper inclusion of nonlinear chemical reactions in a model, the nature of the spatial and temporal averages implicit in the computed concentrations, and the requirements for simulating photochemical smog formation in an urban area.

The development of urban air pollution models has been a subject of interest for a number of years. Unfortunately, most of the published modeling studies have eschewed the theoretical problems associated with the proper description of atmospheric diffusion and have concentrated instead on techniques for utilizing conventional Gaussian plume and diffusion equation models. Before the capabilities of the various models and the meaning of their predictions can be assessed, four fundamental aspects of air pollution modeling must be considered:

The precise definition of the mean and random components of the wind velocity field that enters into a model

The necessary conditions for obtaining various conventional model forms from the general theory of turbulent diffusion

The proper way in which description of the rates of chemical reactions among pollutants enters a model

The nature of the averaging implicit in the computed concentrations—i.e., over what volume of space and period of time are the concentrations averaged

We will consider each of these aspects, our objective being to place within proper perspective the various approaches to air pollution modeling and to delineate those problems in need of further attention.

The simulation of urban air pollution is essentially the problem of describing the behavior of a number of chemically reactive species in the turbulent atmospheric boundary layer. Consider N chemically reactive constituents in a fluid. The concentration of each constituent must satisfy the continuity equation,

$$\frac{\partial c_i}{\partial t} + \frac{\partial}{\partial X_\alpha}(u_\alpha c_i) = D_i\left(\frac{\partial^2 c_i}{\partial X_\alpha \partial X_\alpha}\right) + R_i(c_1, \ldots, c_N, T) + S_i(X, t) \qquad i = 1, 2, \ldots, N \quad (1.1)$$

where u_α is the α-component of the wind velocity, D_i is the molecular diffusivity of species i in air, R_i is the rate of formation or depletion of species i by chemical reaction, T is the temperature (a function of location and time), and S_i is the rate of injection of species i from sources. We follow the summation convention in which repeated Greek subscripts in a term indicate summation over the three components of that term. Since pollutants occur in general at parts-per-million concentrations, their presence does not influence the meteorology. Consequently, the fluid velocities u_α can be considered independent of the c_i. This might not be true if a polluted layer were so concentrated that absorption, reflection, and scattering of radiation by the pollutants resulted in alterations of the fluid behavior. From this point on we will not include the effect of temperature on R_i.

For reasons to be discussed later, it is necessary to represent the wind velocity $\mathbf{u} = (u_1, u_2, u_3)$ in the form $\mathbf{u} = \hat{\mathbf{u}} + \mathbf{u}'$, where $\hat{\mathbf{u}}$ and $\mathbf{u}'$ are deterministic and random components, respectively. The deterministic component $\hat{\mathbf{u}}$ and the statistical properties of $\mathbf{u}'$ may be determined either from observations or from a numerical simulation of the fluid dynamics. We will subsequently consider a means of determining these two components. Thus, Equation 1.1 becomes

$$\frac{\partial c_i}{\partial t} + \frac{\partial}{\partial X_\alpha}[(\hat{u}_\alpha + u_\alpha')c_i] = D_i\frac{\partial^2 c_i}{\partial X_\alpha \partial X_\alpha} + R_i(c_1, \ldots, c_N) + S_i(\mathbf{X}, t) \quad (1.2)$$

Because u_α' is a random variable, Equation 1.2 represents a set of stochastic differential equations—i.e., corresponding to each sample function u_α' there is a c_i satisfying Equation 1.2. Thus, c_i is itself a random variable, which can be characterized by a probability density function. The probability density function for c_i cannot be determined in general, so we concentrate on the moments of the distribution of c_i. The first moment of c_i is its ensemble average $\langle c_i(\mathbf{X},t)\rangle$. Ensemble averaging of Equation 1.2 yields

$$\frac{\partial\langle c_i\rangle}{\partial t} + \frac{\partial}{\partial X_\alpha}(\hat{u}_\alpha\langle c_i\rangle) + \frac{\partial}{\partial X_\alpha}\langle u_\alpha' c_i'\rangle = D_i\frac{\partial^2\langle c_i\rangle}{\partial X_\alpha \partial X_\alpha} + \langle R_i(\langle c_1\rangle + c_1', \ldots, \langle c_N\rangle + c_N')\rangle + S_i(\mathbf{X}, t) \quad (1.3)$$

Let us consider the form of $\langle R_i(\langle c_1\rangle + c_1', \ldots, \langle c_N\rangle + c_N')\rangle$. Suppose that among the N species M chemical reactions are occurring. For elementary reactions we may express R_i as

$$R_i = \sum_{j=1}^{M}\nu_{ij}k_j\prod_{l=1}^{N}c_l^{\beta_{lj}} \quad (1.4)$$

where ν_{ij} is the stoichiometric coefficient for species i in reaction j, k_j is the reaction rate constant for reaction j, and β_{lj} is the reaction order of species l in reaction j.

In chemical reactions among air pollutants the presence of very reactive species, such as free radicals, lead to some reactions being very much faster than others. A common approach to problems of this type is the pseudosteady state approximation in which very reactive species, usually present in low concentrations, are assumed to be formed and destroyed at approximately equal rates at each instant of time. If it can be assumed that the induction period for the pseudosteady state is very short compared to the time scales of the molecular and turbulent transport terms in Equation 1.2, then for those species in pseudosteady state, $R_i = 0$. This leads to algebraic equations for the pseudosteady state species in terms of the other species, which when ensemble-averaged yields

$$\left\langle\sum_{j=1}^{M}\nu_{ij}k_j\prod_{l=1}^{N}(\langle c_l\rangle + c_l')^{\beta_{lj}}\right\rangle = 0 \qquad i = 1, 2, \ldots, L \quad (1.5)$$

where the number of species in pseudosteady state $L < N$. If the total reaction order

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$$\sum_{1}^{N} \beta_{lj} \leq 2$$

then Equation 1.5 can be written as

$$\sum_{j=1}^{M} \nu_{ij} k_j \prod_{l=1}^{N} \langle c_l \rangle^{\beta_{lj}} + \sum_{j=1}^{M} \nu_{ij} k_j \left\langle \prod_{l=1}^{N} c_l'^{\beta_{lj}} \right\rangle = 0 \qquad (1.6)$$

$$i = 1, 2, \ldots, L$$

These L equations are then coupled to the $(N\text{-}L)$ Equations 1.3 for the species not in pseudosteady state (the accumulating species). In Equation 1.3, for the accumulating species

$$\langle R_i(\langle c_1 \rangle + c_1', \ldots, \langle c_N \rangle + c_N') \rangle =$$

$$\sum_{j=1}^{M} \nu_{ij} k_j \prod_{l=1}^{N} \langle c_l \rangle^{\beta_{lj}} + \sum_{j=1}^{M} \nu_{ij} k_j \left\langle \prod_{l=1}^{N} c_l'^{\beta_{lj}} \right\rangle \qquad i = L + 1, \ldots, N \quad (1.7)$$

Equations 1.3 and 1.6 now contain new dependent variables,

$$\langle u_\alpha' c_\alpha' \rangle \text{ and } \left\langle \prod_{l=1}^{N} c_l'^{\beta_{lj}} \right\rangle$$

so that now there are more unknowns than equations. This, in essence, is the closure problem associated with the Eulerian description of turbulent diffusion. A number of approximate solutions to the closure problem have been proposed (the principal ones are discussed in a paper by Kraichnan,. 1962) but each leads to an equation for the concentration statistics which is accurate for only a limited class of problems. Among other approximate solutions is the gradient transport or mixing length hypothesis which leads to the semiempirical diffusion equation (to be discussed later).

By contrast, in the Lagrangian approach, we attempt to describe the concentration statistics in terms of the statistical properties of the displacement of particles in the fluid. The difficulty in the Lagrangian approach lies not in a closure problem but in determining the statistics of the particle displacements. Also, this approach is not readily applicable to situations involving nonlinear chemistry. Nevertheless, because of the severity of the Eulerian closure problem, we shall consider a Lagrangian formulation as the basis for urban air pollution models. We begin with a discussion of the determination of wind velocities.

Definition of Deterministic and Stochastic Velocity Components

The first problem with which we must deal is the definition of the deterministic and stochastic velocity components, $\hat{u}_\alpha$ and u_α'. To illustrate the importance of this problem, suppose we have a puff of pollutant of known concentration distribution $c(\mathbf{X}, t_0)$ at time t_0. In the absence of chemical reaction and other sources, and if we assume molecular diffusion to be negligible, the concentration distribution $c(\mathbf{X}, t)$ at some later time t is described by the so-called advection equation:

$$\frac{\partial c}{\partial t} + \frac{\partial}{\partial X_\alpha}(u_\alpha c) = 0 \qquad (2.1)$$

If we solve Equation 2.1 with $u_\alpha = \hat{u}_\alpha$, and compare the solution with observations we would find in reality that the material spreads out more than predicted. The extra spreading is, in fact, what is referred to as turbulent diffusion and results from the influence of the stochastic component u_α' which we have ignored. Now let us solve Equation 2.1 with the precise velocity field u_α. We should then find that the solution agrees exactly with the observations (assuming, of course, that molecular diffusion is negligible), implying that if we knew the velocity field precisely at all locations and times, there would be no such phenomenon as turbulent diffusion. Thus, turbulent diffusion is an artifact of our lack of complete knowledge of the true velocity field. Consequently, one of the fundamental tasks in turbulent diffusion theory is to define the deterministic and stochastic components of the velocity field.

As we noted, **u** may be derived either from observations or from the solution of a fluid dynamic simulation model. In either case the velocities are known only at discrete points in space. This raises the question of whether these discrete values of **u** are sufficient to describe **u** at all points in space and time as required by Equation 1.1.

Assume that the three-dimensional velocity field is sampled on a network of grid points with separations $\Delta X_1 = d_1$, $\Delta X_2 = d_2$, and $\Delta X_3 = d_3$. The measured wind velocities can then be represented by $u_\alpha{}^m(n_1d_1, n_2d_2, n_3d_3, t)$. From these discrete measurements we wish to construct $u_\alpha(X_1, X_2, X_3, t)$. Let us assume that the measurements $u_\alpha{}^m$ are free of error. We can then invoke a three-dimensional form of the sampling theorem (Papoulis, 1965; Lamb, 1971b), a basic result in communications and sampled-data control theory. According to this theorem, if the wind velocities do not have wave number components greater than π/d_i, $i = 1,2,3$, then $u_\alpha(\mathbf{X},t)$ can be completely reconstructed from $u_\alpha{}^m(n_1d_1, n_2d_2, n_3d_3, t)$ using the relationship

$$u_\alpha(\mathbf{X}, t) = \sum_{n_1}\sum_{n_2}\sum_{n_3} u_\alpha{}^m(n_1d_1, n_2d_2, n_3d_3, t) \prod_{i=1}^{3} \frac{\sin[(\pi X_i/d_i) - \pi n_i]}{[(\pi X_i/d_i) - \pi n_i]} \qquad (2.2)$$

Let us explore the implications of Equation 2.2. To reconstruct $\mathbf{u}(\mathbf{X},t)$ exactly, the wave numbers associated with **u** must not exceed π/d_i. Wave numbers are the inverse of wavelengths, which can be thought of as the sizes of turbulent eddies. In a typical urban area a lower limit on d_i for weather stations is at best 1 km. Thus, in order for Equation 2.2 to hold, no turbulent eddies must exist with sizes smaller than about 2 km ($2\pi/\lambda_{\min} = \pi/d_{\min}$). However, we know that in the atmosphere there are eddies as small as 10^{-4} km. Instead of using $u_\alpha{}^m$ from weather stations, we could perform a numerical simulation of the fluid dynamics. A typical mesh spacing for such a solution might be 0.1 km. In that case, Equation 2.2 would be valid as long as there are no eddies smaller than 0.2 km. Clearly, we would be moving in the right direction as d_i decreases, but if the smallest eddies are indeed 10^{-4} km, we would need $d_i \simeq 10^{-4}$ km. Such a fine grid, either for actual measurements or numerical solution is obviously impossible. Thus, Equation 2.2 can only give that portion of the velocity field with wave number less than π/d_i. That part of the velocity field containing wave numbers greater than π/d_i must remain unknown and be treated as random.

We therefore let $\hat{u}_\alpha$ be the value computed from Equation 2.2. However, to use Equation 2.2 to determine $\hat{u}_\alpha$, we must filter out the components of $u_\alpha{}^m$ with wave numbers greater than π/d_i. This requires that we obtain information on spatial scales of the turbulence at a given time from continuous velocity records at fixed locations. Unfortunately, this cannot be done in general. Nevertheless, we need some simple way of estimating spatial scales of motion from time scales of motion in order to filter out the smaller spatial scales from $u_\alpha{}^m$.

Perhaps the simplest approach to this problem is the following. First, we hypothesize that the time scale τ_i of a perturbation in u_i is roughly proportional to the spatial scale of the perturbation. Therefore, let us say that

$$0(\tau_i) = 0([|\kappa|\bar{u}_i]^{-1}) \qquad (2.3)$$

where $\kappa = (\kappa_1, \kappa_2, \kappa_3)$ is the wave number vector of the perturbation and $\bar{u}_i$ is some characteristic velocity, say

$$\bar{u}_i = \frac{1}{V}\int_V u_i(\mathbf{X}, t)d\mathbf{X} \tag{2.4}$$

where V is a volume with dimensions comparable to the d_i's. The magnitude of the wave number vector, $|\kappa|$, is roughly a measure of the inverse of the magnitude of the spatial eddy sizes. Next, we examine the coherence functions of the velocity records measured at neighboring wind stations. From these functions we estimate the period, τ_m, say, of the eddy with wave number components $\kappa_i = \pi/d_i$, $i = 1, 2,$ or 3. Then, in view of the hypothesis (2.3), all we need do is filter each velocity record (consisting of three velocity components) to remove all frequencies greater than π/τ_m.

Assuming Equation 2.3 is valid, once a time scale τ_i for each velocity component is determined, the data $u_\alpha{}^m$ can be filtered by well-known techniques (Jenkins and Watts, 1968) to produce a velocity record $\tilde{u}_\alpha{}^m$, which satisfies the conditions of Equation 2.2. Then, Equation 2.2 can be used to give $\hat{\mathbf{u}}(\mathbf{X},t)$. Since we then know $\mathbf{u}(n_1d_1, n_2d_2, n_3d_3, t)$, the true velocity, and $\hat{\mathbf{u}}(\mathbf{X},t)$, the deterministic velocity (not just at the measuring points but everywhere), the $\mathbf{u}'$ are defined exactly at the measuring points where they can be analyzed for their statistical properties. Assuming the statistics of the $\mathbf{u}'$ values are spatially smooth, we can interpolate the statistics of $\mathbf{u}'$ over the entire field.

Having defined $\hat{\mathbf{u}}$ and $\mathbf{u}'$, we now return to the determination of the mean concentration by Equation 1.3. In spite of the fact that we now know both $\hat{\mathbf{u}}$ and the statistics of $\mathbf{u}'$, the determination of the statistics of c_i from the statistics of $\mathbf{u}'$ is hindered by the closure problem. As we have noted, there is at present no generally valid solution to this problem. We therefore turn to a Lagrangian approach in the next section where we assume that in place of $\hat{\mathbf{u}}$ and the statistics of $\mathbf{u}'$, we have knowledge of $\hat{\mathbf{u}}$ and the statistics of the Lagrangian velocity $\mathbf{v}'$. Here $\mathbf{v}'$ represents the velocity of a particle measured with respect to a coordinate system moving with velocity $\hat{\mathbf{u}}$ starting from the point of release of the particle.

Equations Governing Mean Concentration of Particles in Turbulent Flow

To avoid the closure problem associated with the Eulerian approach, we will derive the form of Lagrangian models for turbulent diffusion and chemical reaction. We begin by considering a single particle which is at location $\mathbf{X}'$ at time t'. The subsequent motion of the particle can be described by its trajectory, $\mathbf{X}[\mathbf{X}', t'; t]$. Let $\psi(\mathbf{X}, t)$ be the probability density function for finding the particle within an infinitesimal volume centered at $\mathbf{X}$ at time t. For generality, we can assume that the initial position of the particle is not known precisely but rather is given in the form of a probability density function, $\psi(\mathbf{X}', t')$. The probability of finding the particle at $\mathbf{X}$ at t is simply the product of the probability that the particle undergoes a displacement from $\mathbf{X}'$ to $\mathbf{X}$ in (t', t) and the probability that the particle was at $\mathbf{X}'$ at t', integrated over all $\mathbf{X}'$. If $Q(\mathbf{X},t|\,\mathbf{X}',t')$ is the conditional probability that if the particle was at $\mathbf{X}'$ at t' it is at $\mathbf{X}$ at t, then

$$\psi(\mathbf{X}, t) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} Q(\mathbf{X}, t|\,\mathbf{X}', t')\psi(\mathbf{X}', t')d\mathbf{X}' \tag{3.1}$$

If we assume, in addition, that the particle may decay according to a first-order rate law, the "lifetime" of an individual particle is exponentially distributed. If the decay coefficient is a function of time, $A(t)$, then the probability that the particle will not decay in the time interval (t', t) is

$$\exp\left(-\int_{t'}^{t} A(\tau)d\tau\right).$$

For such a particle, the probability of a transition from $\mathbf{X}'$ to $\mathbf{X}$ is simply the product of $Q(\mathbf{X}, t|\mathbf{X}', t')$ and the probability that during the time interval it does not decay. Thus, in this case, Equation 3.1 becomes

$$\psi(\mathbf{X}, t) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} Q(\mathbf{X}, t|\,\mathbf{X}', t')\psi(\mathbf{X}', t') \exp\left(-\int_{t'}^{t} A(\tau)d\tau\right)d\mathbf{X}' \tag{3.2}$$

The density function, ψ, is relevant only when a single particle is present. Suppose, however, that an arbitrary number n of particles are initially present and that the position of the ith particle is given by the density function $\psi_i(\mathbf{X}, t)$. In this case it can be shown (Lamb, 1972b) that the ensemble mean of the concentration $c_{\Delta V}(\mathbf{X}, t)$ averaged over a sample volume ΔV centered at $\mathbf{X}$ is given by

$$\langle c_{\Delta V}(\mathbf{X}, t)\rangle = \frac{1}{\Delta V}\sum_{i=1}^{n}\int_{\Delta V} \psi_i(\mathbf{X}', t)dV(\mathbf{X}') \tag{3.3}$$

Hence, the so-called point concentration $c(\mathbf{X}, t)$, corresponding to an infinitesimal sample volume ΔV, has the ensemble mean value

$$\langle c(\mathbf{X}, t)\rangle = \sum_{i=1}^{n}\psi_i(\mathbf{X}, t) \tag{3.4}$$

By expressing the probability density $\psi_i(\mathbf{X}', t')$ in Equation 3.2 in terms of the known initial particle distribution $\langle c(\mathbf{X}_0, t_0)\rangle$ and the known spatial-temporal distribution of particle sources $S(\mathbf{X}', t')$, say in units of particles per volume per time, and then substituting the resulting expression into Equation 3.4, we obtain the following general formula for the mean concentration:

$$\langle c(\mathbf{X}, t)\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} Q(\mathbf{X}, t|\mathbf{X}_0, t_0)\langle c(\mathbf{X}_0, t_0)\rangle \exp\left(-\int_{t_0}^{t} A(\tau)d\tau\right)d\mathbf{X}_0 + \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{t_0}^{t} Q(\mathbf{X}, t|\mathbf{X}', t')S(\mathbf{X}', t') \exp\left(-\int_{t'}^{t} A(\tau)d\tau\right)dt'd\mathbf{X}' \tag{3.5}$$

This is the fundamental relationship for the mean concentration of a species which can decay exponentially in a turbulent flow in which there are sources. The determination of $\langle c(\mathbf{X}, t)\rangle$, given $\langle c(\mathbf{X}_0, t_0)\rangle$ and $S(\mathbf{X}', t')$, rests on the evaluation of the transition density $Q(\mathbf{X}, t|\mathbf{X}_0, t_0)$. We might note that if the turbulence is stationary and homogeneous $Q(\mathbf{X}, t|\mathbf{X}_0, t_0) = Q(\mathbf{X} - \mathbf{X}_0; t - t_0)$—i.e., the transition density depends only on the displacements in time and space and not on where the particle is or when it was introduced into the flow. In the case, empirical data indicate that the transition density $Q(\mathbf{X} - \mathbf{X}_0; t - t_0)$ is marginally and perhaps jointly normal (Batchelor, 1949),

$$Q(\mathbf{X} - \mathbf{X}_0; t - t_0) = \frac{1}{(2\pi)^{3/2}|\mathbf{P}|^{1/2}} \exp\left\{-\frac{1}{2}\zeta^T\mathbf{P}^{-1}\zeta\right\} \tag{3.6}$$

where ζ^T is the transpose of the column vector ζ which has elements

$$\zeta_i = X_i - X_{i_0} - \langle X_i - X_{i_0}\rangle \qquad i = 1, 2, 3 \tag{3.7}$$

and where $\mathbf{P}^{-1}$ and $|\mathbf{P}|$ are the inverse and determinant, respectively, of the covariance tensor $\mathbf{P}$,

$$P_{ij} = \langle\zeta_i\zeta_j\rangle \tag{3.8}$$

If the coordinate axes are the principal axes of the tensor $\mathbf{P}$, then $P_{ij} = 0$ for $i \neq j$. We assume that the mean displacements $\langle X_i - X_{i0}\rangle$ are due only to the deterministic velocity

$$\langle X_i - X_{i_0}\rangle = \int_{t_0}^{t} \hat{u}_i(\mathbf{X}', t')dt' \tag{3.9}$$

where $\hat{\mathbf{X}}'$ is the particle position at t' if the only velocity were $\hat{u}_i$.

If $P_{ij} = 0$ for $i \neq j$, Equation 3.6 becomes, for $\tau = t - t_0$,

$$Q(\mathbf{X} - \mathbf{X}_0; t - t_0) = \frac{1}{(2\pi)^{3/2}[P_{11}(\tau)P_{22}(\tau)P(\tau)]^{1/2}} \exp\left(-\frac{1}{2}\sum_{i=1}^{3} \frac{\zeta_i^2}{P_{ii}(\tau)} \right) \quad (3.10)$$

If, in addition, there is no mean flow, $\langle X_i - X_{i0} \rangle = 0$, and ζ_i is replaced by $(X_i - X_{i0})$. We often denote the diagonal elements of $\mathbf{P}$, $P_{ii}(\tau)$, by $\sigma_i^2(\tau)$. If the turbulence is also isotropic, there is no preferred direction and $\sigma_i^2(\tau) = \sigma^2(\tau)$.

Let us consider some special cases of Equations 3.5 and 3.6:

(a) Instantaneous point source at $\mathbf{X}_0$ which emits unit concentration of pollutant with a reflecting barrier at $X_3 = 0$ (the ground). No decay of pollutant.

$$\langle c(\mathbf{X}, t) \rangle = \frac{1}{(2\pi)^{3/2}\sigma_1(\tau)\sigma_2(\tau)\sigma_3(\tau)} \exp\left[-\frac{(X_1 - X_{10})^2}{2\sigma_1^2(\tau)} - \frac{(X_2 - X_{20})^2}{2\sigma_2^2(\tau)} \right] \times \left\{ \exp\left[-\frac{(X_3 - X_{30})^2}{2\sigma_3^2(\tau)} \right] + \exp\left[-\frac{(X_3 + X_{30})^2}{2\sigma_3^2(\tau)} \right] \right\} \quad (3.11)$$

If, in addition, there is a mean wind $\hat{u}_1 = U$ in the direction of the X_1 axis, the first argument of the first exponential in Equation 3.11 becomes $-(X_1 - X_{10} - U\tau)^2/2\sigma_1^2(\tau)$.

(b) Continuous point source of unit strength at $\mathbf{X}_0$ with $\hat{u}_1 = U$, $\hat{u}_2 = \hat{u}_3 = 0$. Reflecting barrier at $X_3 = 0$. No decay of pollutant.

$$\langle c(\mathbf{X}, t) \rangle = \int_0^t \frac{1}{(2\pi)^{3/2}\sigma_1(\tau)\sigma_2(\tau)\sigma_3(\tau)} \exp\left[-\frac{(X_1 - X_{10} - U\tau)^2}{2\sigma_1^2(\tau)} - \frac{(X_2 - X_{20})^2}{2\sigma_2^2(\tau)} \right] \times \left\{ \exp\left[-\frac{(X_3 - X'_{30})^2}{2\sigma_3^2(\tau)} \right] + \exp\left[-\frac{(X_3 + X'_{30})^2}{2\sigma_3^2(\tau)} \right] \right\} dt' \quad \tau = t - t' \quad (3.12)$$

Since the source is continuous we want the solution as $t \rightarrow \infty$. At steady state, there is no time dependence so we must convert from travel time τ to distance $X_1 - X_{10}$. Then, the σ_i^2 becomes a function of distance from the source, $X_1 - X_{10}$. Letting $t \rightarrow \infty$ in Equation 3.12 gives

$$\langle c(\mathbf{X}) \rangle = \frac{1}{2\pi\sigma_2\sigma_3 U} \exp\left[-\frac{(X_2 - X_{20})^2}{2\sigma_2^2} \right] \times \left\{ \exp\left[-\frac{(X_3 - X_{30})^2}{2\sigma_3^2} \right] + \exp\left[-\frac{(X_3 + X_{30})^2}{2\sigma_3^2} \right] \right\} \quad (3.13)$$

This result is the so-called Gaussian plume equation for a source of unit strength.

The formulas in (a) and (b) are the classic relationships for diffusion in homogeneous turbulence. The continuous Gaussian plume formulas have been used extensively in predicting pollutant dispersion from point and line sources. They have been fairly successful in predicting long-time averages of concentrations near the source ($X_1 - X_{10} < 10$ km) under steady meteorological conditions when used in conjunction with empirically determined values of the σ_i^2, such as from the Pasquill-Gifford curves (Pasquill, 1962; Slade, 1968; Turner, 1969). Although rigorously these formulas do not apply in nonstationary, inhomogeneous turbulence, they can provide reasonable order of magnitude estimates in many practical circumstances. These formulas are used not only for their simplicity but also because $Q(\mathbf{X}, t|\mathbf{X}_0, t_0)$ is practically impossible to determine either experimentally or theoretically in nonstationary, inhomogeneous turbulence. Perhaps the only feasible way of determining Q is by numerical simulation of turbulent flows, such as reported by Lamb (1971a) who used the fluid simulation model of Deardorff (1970).

When nonlinear chemical reactions are occurring the Gaussian puff and plume formulas cannot be used, although for very slow reactions Friedlander and Seinfeld (1969) have extended the Lagrangian similarity theory of Batchelor to enable inclusion of such reactions. In general, however, these formulas cannot be used as the basis of a general urban air pollution model. Let us return to Equation 3.5 in an effort to develop a general Lagrangian model.

One of the disadvantages of using Equation 3.5 in practice is that it requires a tremendous amount of computational effort if the time interval, $t - t_0$, is large and there are many particle sources. This is explained by the fact that Equation 3.5 essentially treats each particle individually from the time that the particle is produced to the time that the calculations end. The computational effort is rewarded, however, by the achievement of high resolution descriptions of the spatial and temporal variations in the particle concentration statistics. If one is willing to sacrifice part of this resolution or if a fluid simulation model is used to reduce the scales of the turbulent velocity components, the computing time required by Equation 3.5 can be reduced. Let us see how this might be done.

Consider the situation in which the random component of the velocity of any particle, $v_i(t)$, has a correlation function $R_{ij}(t; \tau) = \langle v_i(t)v_j(t + \tau) \rangle$ which vanishes sufficiently rapidly with increasing τ that a time scale

$$T_{ij} = \frac{1}{\langle v_i(t)v_j(t) \rangle} \int_0^\infty R_{ij}(t; \tau) d\tau \quad (3.14)$$

exists for all values of t and all possible points $(\mathbf{X}', t')$ of release of the particle. Under this condition it is to be expected that the motion of any particle at any time t will be statistically independent of its motions prior to the time $t - \Delta t$ where

$$\Delta t >> \max_{i,j} T_{ij} \quad (3.15)$$

In particular, given a sequence of times $t_1, t_2, \ldots t_n = n\Delta t$, where Δt satisfies Equation 3.15, we may expect that the conditional density function $Q(\mathbf{X}_n, t_n|\mathbf{X}_{n-1}, t_{n-1}, \ldots, \mathbf{X}_0, t_0)$ which gives the probability that the particle is at $\mathbf{X}_n$ at t_n given that it was at $\mathbf{X}_{n-1}$ at t_{n-1}, and so forth, satisfies

$$Q(\mathbf{X}_n, t_n|\mathbf{X}_{n-1}, t_{n-1}, \ldots, \mathbf{X}_0, t_0) = Q(\mathbf{X}_n, t_n|\mathbf{X}_{n-1}, t_{n-1}) \quad (3.16)$$

In this case the particle displacements constitute a Markov process and $Q(\mathbf{X}_n, t_n|\mathbf{X}_s, t_s)$ satisfies the Chapman-Kolmogorov equation

$$Q(\mathbf{X}_n, t_n|\mathbf{X}_s, t_s) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} Q(\mathbf{X}_n, t_n|\mathbf{X}_m, t_m) Q(\mathbf{X}_m, t_m|\mathbf{X}_s, t_s) d\mathbf{X}_m \quad (3.17)$$

$$n > m > s$$

Noting that $Q(\mathbf{X}, t|\mathbf{X}', t')$ in Equation 3.5 can be replaced by $Q(\mathbf{X}_n, t_n|\mathbf{X}_s, t_s)$, we can combine Equations 3.5 and 3.17 to yield

$$\langle c(\mathbf{X}_n, t_n) \rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} Q(\mathbf{X}_n, t_n|\mathbf{X}_{n-1}, t_{n-1}) \langle c(\mathbf{X}_{n-1}, t_{n-1}) \rangle \times \exp\left(-\int_{t_{n-1}}^{t_n} A(\tau) d\tau \right) d\mathbf{X}_{n-1} +$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{t_{n-1}}^{t_n} Q(\mathbf{X}_n, t_n|\mathbf{X}_p, t_p)S(\mathbf{X}_p, t_p) \times \exp\left(- \int_{t_p}^{t_n} A(\tau)d\tau\right)dt_p d\mathbf{X}_p \quad (3.18)$$

Equation 3.18 is a general relation for the mean concentration of exponentially decaying particles under the restriction that Δt is significantly greater than the Lagrangian time scale of the turbulence. We would like to reduce Equation 3.18 to the differential equation forms for $\langle c(\mathbf{X}, t)\rangle$ more commonly encountered. To do this, we must make additional assumptions. First, it is necessary to assume that temporal variations in $S(\mathbf{X}, t)$ and $A(t)$ are small compared to Δt and that spatial variations in $S(\mathbf{X}, t)$ are gradual, namely

$$\frac{1}{S(\mathbf{X}, t)}\frac{\partial S}{\partial t} << \frac{1}{\Delta t} \quad (3.19)$$

$$A(t) << \frac{1}{\Delta t} \quad (3.20)$$

$$\frac{1}{S(\mathbf{X}, t)}\frac{\partial S}{\partial X_i} << [\Delta t^2(\langle v_i^2\rangle + \hat{u}_i^2)]^{-1/2} \quad (3.21)$$

Secondly, we must assume that the spatial and temporal inhomogeneities in the turbulence are of such scales that the transition density, Q, of a particle released anywhere in the fluid is the Gaussian density for travel times t in the range $0 \leq t \leq \Delta t$. Actually, this condition is probably automatically satisfied when Equation 3.15 is true. Thus, over each interval of Δt a particle behaves as though it were in a field of stationary homogeneous turbulence. We can refer to such a situation as locally stationary and homogeneous turbulence. Quantitatively, the fluid velocity components should satisfy the following conditions:

$$\frac{1}{\langle u_i'(\mathbf{X}, t)u_j'(\mathbf{X}, t)\rangle}\frac{\partial}{\partial t}\langle u_i'(\mathbf{X}, t)u_j'(\mathbf{X}, t)\rangle << \frac{1}{\Delta t} \quad (3.22)$$

$$\frac{1}{\hat{u}_i(\mathbf{X}, t)}\frac{\partial \hat{u}_i(\mathbf{X}, t)}{\partial t} << \frac{1}{\Delta t} \quad (3.23)$$

$$\frac{1}{\langle u_i'(\mathbf{X}, t)u_j'(\mathbf{X}, t)\rangle}\frac{\partial}{\partial X_k}\langle u_i'(\mathbf{X}, t)u_j'(\mathbf{X}, t)\rangle << \frac{1}{[(R_{kk} + \hat{u}_k^2\Delta t)\Delta t]^{1/2}} \quad (3.24)$$

$$\frac{1}{\hat{u}_i(\mathbf{X}, t)}\frac{\partial \hat{u}_i(\mathbf{X}, t)}{\partial X_k} << \frac{1}{[(R_{kk} + \hat{u}_k^2\Delta t)\Delta t]^{1/2}} \quad (3.25)$$

Under these conditions the transition density $Q(\mathbf{X}_n, t_n|\mathbf{X}_{n-1}, t_{n-1})$ can be written $Q(\Delta\mathbf{X}|\mathbf{X})$, the transition probability that the particle will be displaced a distance $\Delta\mathbf{X}$ from $\mathbf{X}$ during Δt. In addition, this transition density will be Gaussian.

Under all of the above conditions, Equation 3.18 takes the form

$$\langle c(\mathbf{X}, t + \Delta t)\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} Q(\Delta\mathbf{X}|\mathbf{X} - \Delta\mathbf{X}) \exp(- A(t)\Delta t) \times [\langle c(\mathbf{X} - \Delta\mathbf{X}, t)\rangle + \Delta t S(\mathbf{X} - \Delta\mathbf{X}, t)]d(\Delta\mathbf{X}) \quad (3.26)$$

The objective is to derive a differential equation for $\langle c(\mathbf{X}, t)\rangle$ from Equation 3.26.

Expanding $\langle c(\mathbf{X}, t + \Delta t)\rangle$, $Q(\Delta\mathbf{X}|\mathbf{X} - \Delta\mathbf{X})$, $\langle c(\mathbf{X} - \Delta\mathbf{X}, t)\rangle$, $\exp(- A(t)\Delta t)$ and $S(\mathbf{X} - \Delta\mathbf{X}, t)$ in terms of Taylor series about the point $(\mathbf{X}, t)$, we obtain

$$\langle c(\mathbf{X}, t + \Delta t)\rangle = \langle c(\mathbf{X}, t)\rangle + \frac{\partial\langle c\rangle}{\partial t}\Delta t + O(\Delta t^2) \quad (3.27)$$

$$Q(\Delta\mathbf{X}|\mathbf{X} - \Delta\mathbf{X}) = Q(\Delta\mathbf{X}|\mathbf{X}) - \frac{\partial Q}{\partial X_\alpha}\Delta X_\alpha + \frac{1}{2}\frac{\partial^2 Q}{\partial X_\alpha \partial X_\beta}\Delta X_\alpha \Delta X_\beta - \ldots \quad (3.28)$$

$$\langle c(\mathbf{X} - \Delta\mathbf{X}, t)\rangle = \langle c(\mathbf{X}, t)\rangle - \frac{\partial\langle c\rangle}{\partial X_\alpha}\Delta X_\alpha + \frac{1}{2}\frac{\partial^2\langle c\rangle}{\partial X_\alpha \partial X_\beta}\Delta X_\alpha \Delta X_\beta - \ldots \quad (3.29)$$

$$\exp(- A(t)\Delta t) = 1 - A(t)\Delta t + O(\Delta t^2) \quad (3.30)$$

$$S(\mathbf{X} - \Delta\mathbf{X}, t) = S(\mathbf{X}, t) - \frac{\partial S}{\partial X_\alpha}\Delta X_\alpha + \frac{1}{2}\frac{\partial^2 S}{\partial X_\alpha \partial X_\beta}\Delta X_\alpha \Delta X_\beta - \ldots \quad (3.31)$$

Substituting Equations 3.27–3.31 into 3.26, we obtain

$$\frac{\partial\langle c\rangle}{\partial t}\Delta t + O(\Delta t^2) = -\langle c\rangle A(t)\Delta t - [1 - A(t)\Delta t]\frac{\partial}{\partial X_\alpha}(\langle c\rangle\langle\Delta X_\alpha\rangle) + \frac{1}{2}(1 - A(t)\Delta t)\frac{\partial^2}{\partial X_\alpha \partial X_\beta}(\langle c\rangle\langle\Delta X_\alpha \Delta X_\beta\rangle) + S(\mathbf{X}, t)\Delta t - \frac{\partial}{\partial X_\alpha}(S\langle\Delta X_\alpha\rangle)\Delta t + O(\langle\Delta X_\alpha \Delta X_\beta \Delta X_\gamma\rangle) + O(\langle\Delta X_\alpha \Delta X_\beta\rangle\Delta t) \quad (3.32)$$

We must now evaluate $\langle\Delta X_\alpha\rangle$ and $\langle\Delta X_\alpha \Delta X_\beta\rangle$. The mean displacement in a time interval Δt is

$$\langle\Delta X_\alpha\rangle = \hat{u}_\alpha(\mathbf{X}, t)\Delta t \quad (3.33)$$

The mean square displacement tensor is defined by

$$\langle\Delta X_\alpha \Delta X_\beta\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\Delta X_\alpha \Delta X_\beta Q(\Delta\mathbf{X}|\mathbf{X})d(\Delta\mathbf{X}) \quad (3.34)$$

On the basis of the assumption that Q is Gaussian and using Equation 3.33, we can write

$$\langle\Delta X_\alpha \Delta X_\beta\rangle = K_{\alpha\beta}(\mathbf{X}, t)\Delta t + \hat{u}_\alpha(\mathbf{X}, t)\hat{u}_\beta(\mathbf{X}, t)\Delta t^2 \quad (3.35)$$

where

$$K_{\alpha\beta} = \langle v_\alpha v_\beta\rangle T_{\alpha\beta} + \langle v_\beta v_\alpha\rangle T_{\beta\alpha} \quad (3.36)$$

Substituting Equations 3.33 and 3.35 into 3.32, dividing by Δt, and letting $\Delta t \rightarrow 0$, we obtain

$$\frac{\partial\langle c\rangle}{\partial t} + \frac{\partial}{\partial X_\alpha}(\hat{u}_\alpha\langle c\rangle) = \frac{1}{2}\frac{\partial^2}{\partial X_\alpha \partial X_\beta}(\langle c\rangle K_{\alpha\beta}) - A\langle c\rangle + S \quad (3.37)$$

which is recognized as the Fokker-Planck equation corresponding to the random process represented by Equation 3.26 (Chandrasekhar, 1954). We should point out that to achieve the limit $\Delta t \rightarrow 0$, we must consider Δt (and, for that matter, all time variables in Equation 3.32) as having been nondimensionalized by an arbitrary time scale T. The limit $\Delta t \rightarrow 0$ is then achieved by letting $T \rightarrow \infty$.

If the coordinate axes coincide with the principal axes of the $K_{\alpha\beta}$ tensor, or if the turbulence is isotropic, then $K_{\alpha\beta} = 0$, $\alpha \neq \beta$, and Equation 3.37 reduces to the customary diffusion equation

$$\frac{\partial\langle c\rangle}{\partial t} + \frac{\partial}{\partial X_\alpha}(\hat{u}_\alpha\langle c\rangle) = \frac{1}{2}\frac{\partial^2}{\partial X_\alpha \partial X_\alpha}(K_{\alpha\alpha}\langle c\rangle) - A\langle c\rangle + S \quad (3.38)$$

When we go one step further and assume that $K_{\alpha\alpha}$ is spherically symmetric and constant throughout space, we find that Equation 3.38 reduces to

$$\frac{\partial\langle c\rangle}{\partial t} + \frac{\partial}{\partial X_\alpha}(\hat{u}_\alpha\langle c\rangle) = K\frac{\partial^2\langle c\rangle}{\partial X_\alpha \partial X_\alpha} - A\langle c\rangle + S \quad (3.39)$$

where

$$K = \frac{1}{2}K_{\alpha\alpha}$$

In spite of the fact that Equations 3.37–3.39 are expressed in an Eulerian coordinate frame, they are based on Lagrangian statistics, as can be seen from the definition of the "diffusivity" $K_{\alpha\beta}$. From a strictly mathematical point of view, Equations 3.37–3.39 are valid only for infinitely large time scales T. From a practical standpoint, however, it is necessary only that $T \gg \Delta t$. Also, we have already seen that $\Delta t \gg \max T_i$, so we conclude that

$$\max_{i,j} T_{ij} << \Delta t << T \quad (3.40)$$

The basic Lagrangian Equation 3.5 applies only to linearly reactive particle species, because in deriving the fundamental relationship, Equation 3.2, on which this equation is based, we assumed that the chemical reactions occur independently of the particle displacements. This assumption is clearly not always valid for nonlinear reactions where the reaction speed is determined by the frequency of particle collisions. To handle this case using Lagrangian statistics is very complicated (Lamb, 1972c), but it appears that this approach may be the only way at present whereby the complex and important microscale transport and reaction phenomena which occur in the vicinity of point and line sources can be described. However, the Lagrangian theory for nonlinear processes appears to be too complex to provide a viable basis for modeling macroscale features of the concentration distribution in urban atmospheres. For this job any one of the Equations 3.37–3.39 may be used.

Regarding these equations, we point out that each may be applied to certain nonlinearly reactive substances owing to the assumptions in Equations 3.19–3.21 on which each of these equations rests.

By virtue of these assumptions the temporal and spatial variations in the mean concentration field are so much larger in scale than the Lagrangian time scale $\tau = \max T_{ij}$ and the average distance $L = [(\hat{u}_i^2 + \langle v_i^2 \rangle)\tau^2]^{1/2}$ that a particle travels in time τ that the collision frequency, and hence nonlinear reaction rate, experienced by any particle during any period τ, is independent of the particle's path and moreover is just that frequency, or reaction rate, which is appropriate for the local mean concentration. Thus, we may use the terms $A\langle c_i \rangle$ and S_i to represent not only the linear reaction rate and strength of the systematic sources, respectively, of the ith species, but also the sources and sinks resulting from the nonlinear chemical reactions among the N species. Specifically, the term $A\langle c_i \rangle$ can represent all those reactions which deplete species i,

$$A(t)\langle c_i \rangle = \left\{ \sum_{j=1}^{M'} \nu_{ij} k_j \prod_{l=1}^{N} \langle c_l \rangle^{\beta_{lj}} \right\} \langle c_i \rangle, \qquad (3.41)$$

and similarly $S_i(\mathbf{X}, t)$ can represent the formation of species i by reactions among the other species present,

$$S_i(\mathbf{X}, t) = \sum_{j=1}^{M''} \nu_{ij} k_j \prod_{\substack{l=1 \\ l \neq i}}^{N} \langle c_l \rangle^{\beta_{lj}}. \qquad (3.42)$$

It turns out that the values of τ and L, characteristic of the atmosphere, are so large that conditions in Equations 3.19–3.21 are grossly violated near isolated sources such as smoke stacks and highways. As a result Equations 3.37–3.39 provide only an approximate description of the macroscale features of the mean concentration distribution because they completely ignore the effects of the microscale phenomena (mentioned earlier) induced by such sources. Since these microscale phenomena can have a profound effect upon the large-scale concentration features in cases where nonlinear reactions are active, we may expect that Equations 3.37–3.39 will prove to be inadequate for simulating chemically reacting air pollution until some method is devised for parameterizing the effects of the microscale phenomena in terms of the large scale concentration distribution. This is one of the important problems of air pollution modeling which remains to be solved.

Semiempirical Equation of Atmospheric Diffusion

The most common approach to problems of atmospheric diffusion has been based on the Eulerian description of Equation 1.3, together with two assumptions that An eddy diffusivity tensor $\bar{K}_{\alpha\beta}$ exists, defined by

$$\langle u_\alpha' c_i' \rangle = -\overline{K}_{\alpha\beta} \frac{\partial \langle c_i \rangle}{\partial X_\beta} \qquad (4.1)$$

and that if reactions are occurring, moments of the form $\langle c_i' c_j' \rangle$ can be neglected. Generally it is assumed that $\overline{K}_{\alpha\beta} = 0$ for $\alpha \neq \beta$. Then Equation 1.3 becomes

$$\frac{\partial \langle c_i \rangle}{\partial t} + \frac{\partial}{\partial X_\alpha}(\hat{u}_\alpha \langle c_i \rangle) = \frac{\partial}{\partial X_\alpha}\left(\overline{K}_{\alpha\alpha}\frac{\partial \langle c_i \rangle}{\partial X_\alpha}\right) + R_i(\langle c_1 \rangle, \ldots, \langle c_N \rangle) + S_i(\mathbf{X}, t) \qquad (4.2)$$

It can be shown (Lamb, 1972a) that the two above assumptions, and hence Equation 4.2, are probably valid provided that in addition to Equations 3.19, 3.21, and 3.22–3.29, the following condition is met: that the time scale of the fastest reaction described by $R(c_1, \ldots c_N)$ be much larger than the Lagrangian time scale, τ, of the turbulence. This list of restrictions is essentially identical to that which was placed on Equation 3.38, so as far as applicability is concerned, Equations 3.38 and 4.2 are identical. The only significant difference between these two equations lies in their diffusion terms. In Equation 3.38, $K_{\alpha\alpha}$ is dependent strictly on the Lagrangian statistics of the turbulence while in Equation 4.2, $\bar{K}_{\alpha\alpha}$ is an Eulerian parameter—i.e., a function of each point in space, which is to be determined by empirical data. However, since the Lagrangian properties on which the $K_{\alpha\alpha}$ are dependent are very difficult to measure directly, the $K_{\alpha\alpha}$ are usually determined by using them as parameters for fitting the solution of Equation 3.38 to empirical concentration data. This same procedure is used to determine the $\bar{K}_{\alpha\alpha}$ so that all in all there is little significant difference between Equations 3.38 and 4.2. Because of the empirical nature of the diffusivities, the accuracy of both equations is also dependent on the degree to which the conditions of the problem to which these equations are applied correspond to the conditions under which the diffusivities were measured.

As we have already pointed out, Equations 4.2 and 3.37–3.39 apply only to time and space scales which are much larger than the corresponding scales τ and L of the turbulence. Thus, to regard these as so-called point equations is to imply that a "point" has spatial dimensions much larger than $L_i (i = 1, 2, 3)$ and that an "instant" is a period long compared to τ. Let these minimum resolvable scales be denoted by l_i and T—i.e., $l_i \gg L_i$, $T \gg \tau$. Now in applications where the chemistry is nonlinear, analytic solutions are not available for these equations so they must in general be solved numerically. Depending on the type of computer available, it may prove infeasible to select a difference grid with space increments $\Delta X_i = l_i$ and a time increment $\Delta t = T$. When intervals $\Delta X_i > l_i$ and/or $\Delta t > T$ are necessary, an additional problem arises in connection with the nonlinear terms.

To illustrate the nature of this problem, we consider for convenience the one-dimensional equation

$$\frac{\partial \langle c(X, t) \rangle}{\partial t} = K_X \frac{\partial^2 \langle c \rangle}{\partial X^2} - k\langle c \rangle^2 + S(X, t) \qquad (4.3)$$

with K_X a constant.

Suppose we solve this equation numerically using $\Delta t = T$ and $\Delta X > l_X$. Since a discrete grid with spacing ΔX cannot resolve features of $\langle c(X, t) \rangle$ which have wave number components $\kappa > \pi/\Delta X$ (by virtue of the sampling theorem mentioned earlier), the difference equation representation of Equation 4.3 which we solve numerically can describe only the variations in $\langle c(X, t) \rangle$ which have wave number scales $\kappa \leq \pi/\Delta X$. Moreover, the difference equation cannot account for the effects of perturbation in either $\langle c \rangle$ or S with $\kappa > \pi/\Delta X$. One way of remedying this situation is to filter from both $\langle c \rangle$ and S all wave numbers greater than $\pi/\Delta X$. This can be done by space averaging as follows:

$$\langle \tilde{c}(X, t) \rangle \equiv \frac{1}{2\,\Delta X}\int_{X-\Delta X}^{X+\Delta X} \langle c(X', t) \rangle dX' \qquad (4.4)$$

with a similar definition for $S(X, t)$. If $a(\kappa, t)$ and $b(\kappa, t)$ are the Fourier transforms of $\langle c \rangle$ and S, respectively—i.e.,

$$\langle c(X, t) \rangle = \int a(\kappa, t)e^{i\kappa X}d\kappa, \text{ and so forth} \qquad (4.5)$$

then it is easy to show that the corresponding transforms of $\langle \tilde{c} \rangle$ and $\tilde{S}$ are $\tilde{a}(\kappa, t) = (\sin \kappa\Delta X/\kappa\Delta X)a(\kappa, t)$, $\tilde{b}(\kappa, t) = (\sin \kappa\Delta X/\kappa\Delta X)b(\kappa, t)$. Due to the nature of the weighting function $\sin \kappa\Delta X/\kappa\Delta X$, $\tilde{a}$ and $\tilde{b}$ are virtually zero for values of $\kappa > \pi/\Delta X$, and thus $\langle \tilde{c} \rangle$ and $\tilde{S}$ have properties which are compatible with our difference equation version of Equation 4.3. Our aim, then, is to use the difference equation to obtain the space averaged concentration $\langle \tilde{c} \rangle$.

To obtain the differential equation for $\langle \tilde{c} \rangle$ we could average Equation 4.3 in the manner of Equation 4.4, but this task is more easily performed in wave number space. We substitute Equation 4.5 and the corresponding relationship between S and $b(\kappa, t)$ into Equation 4.3 and obtain for the case of $k = 0$,

$$\frac{\partial a(\kappa, t)}{\partial t} = -K_X\kappa^2 a(\kappa, t) + b(\kappa, t) \qquad (4.6)$$

Multiplying by $\sin \kappa\Delta X/\kappa\Delta X$ we get

$$\frac{\partial \tilde{a}}{\partial t} = -K_X\kappa^2\tilde{a} + \tilde{b}$$

the inverse of which yields

$$\frac{\partial \langle \tilde{c} \rangle}{\partial t} = -K_X\frac{\partial^2 \langle \tilde{c} \rangle}{\partial X^2} + \tilde{S} \qquad (4.7)$$

In other words, for linear problems $\langle \tilde{c} \rangle$ satisfies an equation identical to that governing $\langle c \rangle$ with the forcing term in the former case being the space averaged source distribution.

The situation is entirely different, however, when nonlinear terms are present in Equation 4.3. Placing Equation 4.5 and the analogous expression for S into Equation 4.3, we get

$$\frac{\partial a(\kappa, t)}{\partial t} = -K_X\kappa^2 a(\kappa, t) - k\int a(\kappa - \kappa')a(\kappa')d\kappa' + b(\kappa, t) \qquad (4.8)$$

It is immediately clear from this equation that in contrast to the linear problem, the low wave number components of $\langle c \rangle$ which comprise $\langle \tilde{c} \rangle$ are affected, through the nonlinear term, by all wave number components of $\langle c \rangle$. This presents the difficult problem of representing the effect on $\langle \tilde{c} \rangle$ of the high wave number components of $\langle c \rangle$ which lie outside the spectrum of $\langle \tilde{c} \rangle$ and are unresolvable by the difference grid. There is no rigorous solution to this problem because there is no exact way of expressing the effects on $\langle \tilde{c} \rangle$ of subgrid scale variations in S in terms of $\tilde{S}$ and $\langle \tilde{c} \rangle$. Perhaps by solving the concentration equation in wave number space (Equation 4.8 in the present instance), we could treat a larger range of the spectral components of the concentration and source distribution explicitly and thereby reduce to a negligible level the effects of the subgrid scale or truncated components. Obviously, one can conceive of problems in which it would be infeasible to eliminate the subgrid scale effects by this method. What is needed in the long run is a suitable heuristic parameterization of the effects of the unresolvable fluctuations. The development of such a parameterization will be the topic of a future study.

Simulation of Chemically Reacting Air Pollution

In the previous sections we have developed both Lagrangian and Eulerian descriptions of air pollutant behavior.

The question now arises—what do the restrictions on the use of the Lagrangian and Eulerian models mean in practice? To answer this question, we consider the problem of simulating photochemical smog, which is undoubtedly the most challenging current problem in air pollution modeling. The first step is the formulation of a kinetic mechanism for photochemical smog—i.e., the determination of a functional form for R_i.

The nature and characteristics of atmospheric contaminants suggest certain difficulties in the formulation of a kinetic mechanism of general validity. First, there is multiplicity of stable chemical species in the atmosphere. Most species are present at very low concentrations, thereby creating major problems in detection and analysis. A number of atmospheric constituents, in fact, probably remain unidentified. Second, there are a large number of short-lived intermediate species and free radicals which participate in an enormous number of individual chemical reactions. However, while we must admit to only a partial understanding of atmospheric reaction processes, it remains essential that we attempt to formulate quantitative descriptions of these processes suitable for inclusion in an overall simulation model.

A suitable mechanism must not be overly complex, since computation times for the integration of the basic model, in which the mechanism is to be imbedded, are likely to be excessive. On the other hand, too simplified a mechanism may omit important reaction features. A major issue in this regard is that the mechanisms predict the behavior of a complex mixture of many hydrocarbons, yet do so with a paucity of detail. The goal, then, is to achieve acceptable accuracy in prediction without an undue computational burden.

Kinetic mechanisms that have been proposed fall into two general categories: detailed mechanisms for photooxidation of a single hydrocarbon and compact generalized mechanisms for a complex mixture. Detailed mechanisms which attempt to account for the history of all species generated must be ruled out for three reasons. First, while the aim of those developed thus far has been completeness of description, this thoroughness has been achieved through the inclusion of a number of reaction steps that involve free radicals. Unfortunately, knowledge of the rates of these reactions is imprecise. Furthermore, when several free radical reactions are included in a mechanism, the flexibility in the choice of rate constants is increased, as each imprecisely known parameter can be varied independently in the process of matching prediction and experiment. To the extent that detailed mechanisms possess this flexibility in parameterization, the validity of comparison of prediction and experiment is diminished. Second, computation time is a limiting factor in the solution of the coupled partial differential equations that comprise the overall airshed model. The inclusion of a detailed mechanism in such a model greatly increases the computational burden and is to be avoided if at all possible.

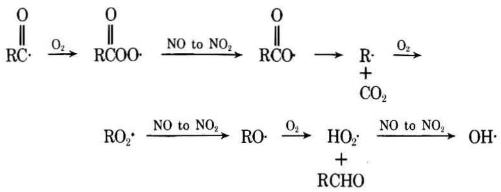
Finally, the decision to develop and implement a detailed mechanism implies the desire to represent reaction processes as accurately as is feasible. Thus, a relatively large number of reaction steps must be incorporated in the description of the dynamics of consumption of a particular hydrocarbon, such as propylene. Reaction dynamics will, however, vary for the many hydrocarbon species present in the atmosphere. If, for example, 30–40 steps are required to describe propylene kinetics, and 50 hydrocarbon species, each having unique dynamics, are believed to exert a significant impact on atmospheric reaction processes, one is faced with an intractable representation of the system.

To summarize, then, we require a mechanism which: describes reaction rate phenomena accurately over a specified range of concentrations, is a parsimonious representation of the actual atmospheric chemistry, in the interest of minimizing computation time, and can be written for general hydrocarbon species, with the inclusion of variable stoichiometric coefficients, to permit simulation of the behavior of the complex hydrocarbon mixture that actually exists in the atmosphere. In short, we seek a mechanism which incorporates a balance between accuracy of prediction and ease of computation.

The two mechanisms which fulfill the above requirements for suitability and have been most successful in simulating smog chamber data are those of Eschenroeder and Martinez (1972) and Hecht and Seinfeld (1972). The Hecht-Seinfeld mechanism is reproduced in Table I.

We might note a few points concerning this mechanism. All reactive hydrocarbons have been lumped into one fictitious species, called HC. Also, all of the peroxy radicals (those capable of oxidizing NO to NO_2) are lumped into the species $RO_2\cdot$. Note that $RO_2\cdot$ is merely symbolic of these radicals; some may not contain exactly two oxygen atoms. In reactions 9–11, the stoichiometric coefficients α, β, and δ govern the growth of the total peroxy radical population, whereas γ and ϵ describe the amount of aldehyde production.

If CO and H_2O are present, we treat $HO_2\cdot$ and $RO_2\cdot$ as separate species; in the absence of CO and H_2O, both are included in $RO_2\cdot$. In the latter case the coefficient, θ, cannot be interpreted exactly as the fraction of $RO_2\cdot$ which is $HO_2\cdot$. This is because peroxy radicals other than $HO_2\cdot$ can ultimately be degraded to $OH\cdot$. For example, the history of a typical acyl ($R\dot{C}O$) radical arising from atomic oxygen attack on an olefin might be



Thus, an original acyl radical participates in the conversion of three molecules of NO to NO_2 with an OH radical resulting.

The mechanism in Table I has four accumulating species: NO, NO_2, HC, and O_3. The following species are in pseudosteady stage: O, $OH\cdot$, $HO_2\cdot$, $\dot{R}O_2\cdot$, HNO_2, HNO_3, and RCHO are products, while CO and H_2O are generally present in great excess and can be considered of constant concentration. The dynamics of a batch system will then be described by four differential equations.

Earlier, we developed relative criteria for validity of the Lagrangian models based on time scales. Our main concern with the photochemical smog mechanism is the time scales associated with the system. A measure of the time scale for the chemical reaction system is given by the eigenvalues of the reaction rate equations. [The eigenvalues λ_i, $i = 1, 2, \ldots, n$, of a system of n ordinary differential equations are those of the $n \times n$ Jacobian matrix J, the i, j element of which is $\partial R_i/\partial c_j$ and are the n solutions of the equation, $det(J - \lambda I) = 0$.]

Table I. Generalized Mechanism for Photochemical Smog

Reactions	Rate constants, ppm, min
1. $NO_2 + h\nu \rightarrow NO + O$	$0.355\ min^{-1}$
2. $O + O_2 + M \rightarrow O_3 + M$	$2.76 \times 10^6\ min^{-1a}$
3. $O_3 + NO \rightarrow NO_2 + O_2$	$21.8\ ppm^{-1}\ min^{-1}$
4a. $O_3 + NO_2 \rightarrow NO_3 + O_2$	$6 \times 10^{-3}\ ppm^{-1}\ min^{-1}$
4b. $NO_3 + NO_2 \rightleftarrows N_2O_5$	
4c. $N_2O_5 + H_2O \rightarrow 2HNO_3$	
5. $NO + NO_2 + H_2O \rightarrow 2HNO_2$	$2.5 \times 10^{-3}\ ppm^{-1}\ min^{-1b}$
6. $HNO_2 + h\nu \rightarrow NO + OH\cdot$	$5 \times 10^{-3}\ min^{-1}$
7. $CO + OH\cdot \xrightarrow{O_2} CO_2 + HO_2\cdot$	$2 \times 10^2\ ppm^{-1}\ min^{-1}$
8. $HO_2\cdot + NO_2 \rightarrow HNO_2 + O_2$	$1 \times 10^1\ ppm^{-1}\ min^{-1}$
9. $HC + O \rightarrow \alpha\ RO_2\cdot$	$3.1 \times 10^4\ ppm^{-1}\ min$ $(\alpha = 5)$
10. $HC + O_3 \rightarrow \beta RO_2\cdot + \gamma\ RCHO$	$1.7 \times 10^{-2}\ ppm^{-1}\ min^{-1}$ $(\beta = 1.9)$
11. $HC + OH\cdot \rightarrow \delta\ RO_2\cdot + \epsilon\ RCHO$	$1 \times 10^4\ ppm^{-1}\ min^{-1}$ $(\delta = 0.2; \epsilon = 0.22)$
12. $RO_2\cdot + NO \rightarrow NO_2 + \theta\ OH\cdot$	$1.8 \times 10^3\ ppm^{-1}\ min^{-1}$
13. $RO_2\cdot + NO_2 \rightarrow$ PRODUCTS	$10.\ ppm^{-1}\ min^{-1}$
14. $HO_2\cdot + NO \rightarrow NO_2 + OH\cdot$	$1.8 \times 10^3\ ppm^{-1}\ min^{-1}$

NOTE: It is possible to combine Reactions 4a–4c as

$$O_3 + NO_2 \xrightarrow[\substack{NO_2\\H_2O}]{4} 2HNO_3$$

in which the overall rate is that of Reaction 4a, the rate-controlling step.

[a] Pseudofirst order.

[b] Pseudosecond order.

First we consider a measure of the time scale for the fastest reactions in the system. Perhaps the most characteristic set of fast reactions in the smog system are reactions 1–3, the principal inorganic reactions. Consider the dynamics of a system initially consisting of pure NO_2 and in which only reactions 1–3 are occurring. The system is described by three differential equations (one each for NO_2, O, and O_3). At $t = 0$ the largest nonzero eigenvalue is $-2 \times 10^6\ min^{-1}$, the pseudofirst-order rate constant for Reaction 2 in Table I. Thus, the time required for this system to reach steady state is the order of 10^{-6} min. Clearly, the steady state approximation for oxygen atoms is valid. Similar calculations will confirm the steady state approximation for the other radical species in Table I.

Now consider the full mechanism in Table I. Our objective is to determine under what conditions the reaction rates, R_{NO2}, R_{NO}, R_{O3} and R_{HC}, corresponding to this mechanism and the parameters in Table I can be included in Equation 3.38, the basic Lagrangian model. To include these reaction rates, perhaps split into $-A\langle c_i \rangle + S(\langle c_1 \rangle, \ldots, \langle c_N \rangle)$, the time scale for the system must satisfy Equations 3.19 and 3.20. As we noted, a measure of the time scale of the system is its eigenvalues. For the mechanism in Table I, the four eigenvalues at three values of time are given in Table II. The system is characterized by a wide separation in the magnitudes of the eigenvalues. The large negative eigenvalue corresponds to processes taking place on time scales much faster than the rate determining steps. (It is important to note that in spite of the fact that we have employed the steady state approximation for free radicals, we still have a wide separation in the λ's.) After 1 min, the component of the linearized solutions corresponding to λ_1 will have a magnitude the order of e^{-30}, and will be negligible. Thus, the important rate-determining eigenvalue is λ_2, which is of the order of 10^{-2}.

In considering Equation 3.38, λ_2 assumes the role of $A(t)$. The condition in Equation 3.20 implies, then, that

Table II. Eigenvalues of Mechanism in Table I

t, min	λ_1	λ_2	λ_3	λ_4
1.3	−33.1	4.63×10^{-2}	1.24×10^{-4}	1.28×10^{-7}
60.3	−21.2	3.51×10^{-2}	$4.83 \times 10^{-4} - 6.59 \times 10^{-4}i$	$4.83 \times 10^{-4} + 6.59 \times 10^{-4}i$
119	−21.5	-8.98×10^{-3}	$-2.04 \times 10^{-2} - 1.71 \times 10^{-2}i$	$-2.04 \times 10^{-2} + 1.71 \times 10^{-2}i$

NOTE: Initial conditions used were $C_{NO_2}(0) = 0.04$, $C_{NO}(0) = 1.5$, $C_{O_3}(0) = 0$, $C_{HC}(0) = 3.0$.

Δt must be the order of 10 min or less. Fortunately, this estimate is consistent with Equation 3.40, since max T_{ij} is generally the order of 1 min. This estimate of $A(t)$ corresponds to the initial conditions in Table II. These were chosen as typical of those in a smoggy atmosphere.

Therefore, we can conclude that Equation 3.38 will represent a valid urban air pollution model for photochemical smog as long as the concentration field is smooth (Equation 3.21) and the concentrations are at levels such that the rate-determining eigenvalue allows us to use a Δt of the order of 10 min.

To meet these requirements it will be necessary to space-average the source inputs to remove steep gradients in concentration as would result, for example, from freeways and power plants. This point has been mentioned. We reiterate that the parameterization of strong localized sources of reactive material for inclusion in a large simulation is still an important unsolved problem.

A description of the simulation of photochemical smog in the Los Angeles basin by means of numerical solution of the semiempirical equations of atmospheric diffusion is given by Roth et al. (1971) and Seinfeld et al. (1972).

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Received for review May 3, 1972. Accepted October 4, 1972. Presented at the Symposium on Science in the Control of Smog, California Institute of Technology, Pasadena, Calif., November 1971. Work performed in part at the University of California, Los Angeles, with Federal funds from the Environmental Protection Agency under grant number AP 1200-1, and in part at the California Institute of Technology with the aid of a gift from the John A. McCarthy Foundation.

INDUSTRY TRENDS

J. F. Pritchard has signed a letter of intent with the Coastal States Energy Co. to construct a substitute natural gas (SNG) plant near Corpus Christi, Tex. The plant, subject to approval by the Federal Power Commission, will cost more than $30 million and will be the world's largest single-train SNG plant.

Chemico has received a $9.25 million turn-key contract to design and build a sulfuric acid plant for Kennecott Copper's Hurley, N.M., smelter facility. The double absorption acid plant will serve as a pollution abatement facility.

Ingersoll-Rand has created an environmental division with initial product and systems capabilities in waste water treatment. The division has plans for new products in solids separation late this year.

Waste Resources Corp. (Philadelphia, Pa.) has filed a shelf registration with the Securities and Exchange Commission consisting of a million shares of common stock. The company said the new registration was necessary when it became obvious that the original filing of 350,000 must be "substantially supplemented" to keep pace with planned expansion.

Fluor Corp. and Lucas American Recyclers announced that Fluor Utah, a Fluor Corp. subsidiary, will have an exclusive license to market, design, and construct Lucas Cyclonic Waste Furnace Systems in the United States. Lucas American holds the patents for the Lucas system, developed in Wednesbury, England.

Resources Conservation Co. (RCC) has begun a six-month test of its evaporative desalination process under an $80,000 contract from the Office of Saline Water. The test is being conducted at OSW's Roswell, N.M., facility.

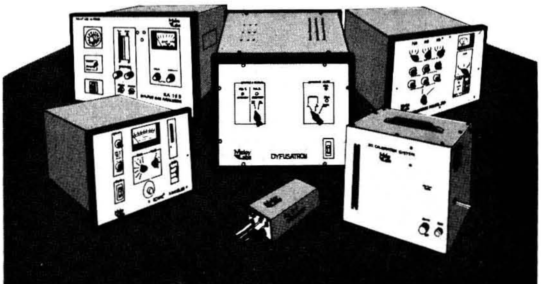
Intercomp Resource Development and Engineering, Inc. (Houston, Tex.), has formed an environmental evaluation division to consolidate the atmospheric diffusion and model development activities of the company.

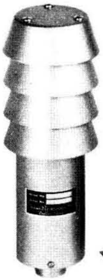
Rollins International, Inc. has agreed to acquire Clark, Dietz & Associates Engineers, Inc., a national engineering firm specializing in environmental protection. Terms were not announced.

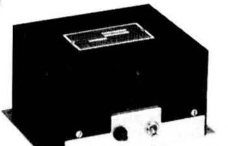
Radiation and Environmental Materials, Inc. (Santa Monica, Calif.) has changed its name to REM Scientific, Inc. REM makes a full line of air monitoring instruments, featuring chemiluminescence technology.

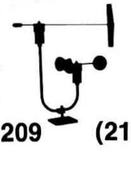
Babcock and Wilcox has sold its 15th boiler to Central Power and Light Co.—this one a 105-mW steam generator with NO_x control for the No. 3 unit of the Laredo Power Station, Laredo, Tex. The contract amounts to about $2.5 million. NO_x control is by the gas recirculation method.

American Society for Testing and Materials says it's compiling a list of coastal laboratories conducting seawater corrosion tests. Laboratories wishing to be included on the list should write Dr. Kenneth G. Compton, School of Marine and Atmospheric Sciences, 10 Rickenbacker Causeway, Miami, Fla. 33149.





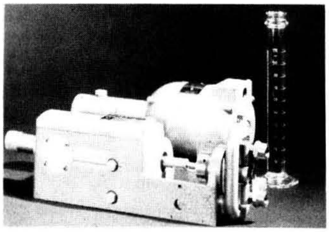




NEW PRODUCTS

Buffer device

Unique buffer device designed to protect gas meters from damage resulting from high-speed float overtravel is now standard equipment in new line of meters. Buffer, made of Teflon, protects meters designed primarily for gas (compressible fluid) applications. Meter Engineering &Mfg., Inc. **61**



Pumps

MPL series of medium-sized, versatile metering pumps is designed for laboratory work or a wide range of industrial uses. Models are available in either single or dual assemblies with either plunger for high pressure, or hydraulically backed diaphragm for low-pressure pumpheads. Wide range of accessories is available. Ace Industrial Division. **62**

Sewer cameras

Permanent, stereoscopic record of sewers and pipelines comes from portable underground camera. Accurate footage measuring system pinpoints exact location of each photo. Costs only about one third as much as television inspection devices, both initially and operationally. Underground Surveys Corp. **63**

Process recorder

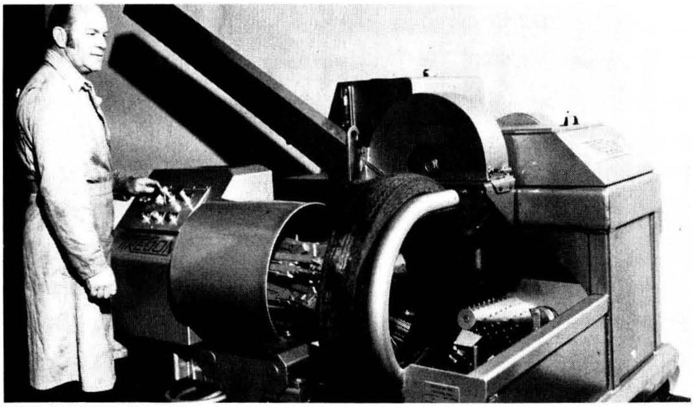
Instrument is new 6-in. strip chart recorder for either linear or nonlinear solution conductivity measurements in either single- or overlapping dual-pen form or in 2,3,6, and 12 multipoint versions. Beckman Instruments **64**

Relay control unit

Solid state relay control unit is a dual-channel on/off controller designed for use with company's Model 50 series of pH, ORP, conductivity, and temperature meters. Unit accepts 0-5 vDC signals from one or two sources. It provides two outputs, one per channel, capable of supplying 5 amps of 115-V line power. Great Lakes Instruments, Inc. **65**

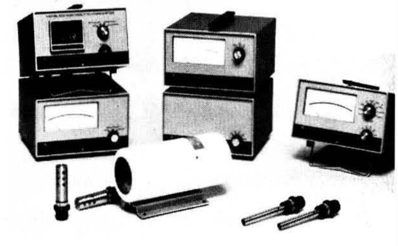
Pump module

New module is designed for use with company's hollow fiber devices, but can also be used for any laboratory application requiring closely regulated fluid or gas delivery. Rates from 3-35 ml/min, 15-150 ml/min or 100-1680 ml/min depending on pumphead selected. Fluids pumped at pressures up to 25 psi and gases up to 15 psi. Generates vacua up to 600 mm Hg. Bio-Rad Laboratories, Inc. **66**



Tire shredder

Machine automatically reduces 800-1400 tires per 8-hr shift, into chips that can be varied from ¼ to 2 in.^{2} The bead hoop is not cut and is rejected from the machine after the 10-sec chipping cycle for each tire. AIM Corp. **67**



Humidity instruments

Complete line of equipment for measuring humidity in all of its basic forms—web bulb, percent relative humidity, dew point temperature and ppm water vapor—is offered with linear display and recorder output voltages. Engineered for continuous usage. General Eastern Corp. **68**

Clean benches

Series of horizontal-flow clean benches boasts HEPA filter permanently sealed into an integral module, with integrity of seal between module and plenum assured by a sealed, flexible duct. Filter replacement is easily accomplished by inexperienced personnel. Tenny Engineering, Inc. **69**

Air purifier

Wall-mounted, recirculating purifier removes dust, odors, and other contaminants from air in individual rooms. Unit has washable dust filter and an inch-thick bed of activated charcoal. Barnebey-Cheney **70**

Sound absorbers

Unique, hanging sound absorbers are recommended for use where accoustical ceilings are impractical. Cylindrical shape gives more surface area and better sound attenuation than conventional flat absorbers. Insul-Coustic/Birma Corp. **71**

Scavenger

Sawfish cuts through weed infestations, picks up floating debris or trash, and loads refuse onto barge. Can work in as little as 10 in. of water. Aquamarine Corp. **72**

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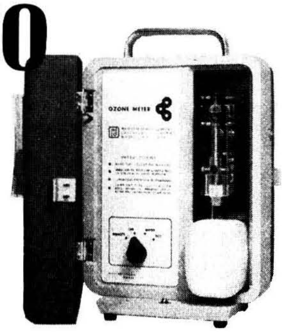


Mounting kit

Universal mounting kit for attaching company's pneumatic and electric actuators on any ½- to 2-in. ball valve, comes in four versions, depending on valve size and actuator type. Construction is carbon steel. Worcester Controls Corp. **73**

Printer

New self-contained, solid-state print unit reliably and automatically averages and prints concentration readings from pollution monitoring equipment in digital form for long periods unattended. Eliminates need for laborious review and compilation of data from strip chart recorders. Spectra Systems **74**

Filter probe

Nonclogging filter probe is designed for drawing off gas samples from stacks and flues. Filters out micron-sized particles of fly ash, sulfates, and other particulates as gas flows through. Probe is cleaned in place by air blowback. Bendix Filter Div. **75**

Oxygen meter

Portable low-cost dissolved oxygen meter has 6-in. scale reading concentrations from 0–15 ppm, 0–120% saturation and temperatures from 0–50°C. Teflon membrane covers silver electrodes in probe which senses oxygen polarographically. Chemtrix, Inc. **76**

Emissions analyzer

Analyzer allows continuous monitoring CO, CO_2, unburned O_2 and can be used with 2-cycle, 4-cycle, diesel, and gasoline engines of all sizes. Connects directly to exhaust pipe. Megatech Corp. **77**

Vacuum regulator

High-performance vacuum regulator is intended primarily for use in emission testing instrumentation. Installation would be between dry gas meters and vacuum sources in an emission sampling train. Control is effective at gas flow rates from ½ to 3 cfm and maintains pressure to within 0.05 in. Hg over an operating range of 8–18 in. Hg. Western Precipitation Div., Joy Mfg. Co. **78**

Conductivity monitor

New 7075 electrolytic conductivity monitor is a simplified instrument, giving direct indication of dissolved solids in water by either specific conductance or specific resistance methods. Built-in calibration circuit allows fast comparison checks with preset mark on the dial. Circuitry is all solid state with feedback-stabilized amplifier to minimize drift. Leeds & Northrup **79**

NEW LITERATURE

Analysis services. Free price list details services available from company in field of water analysis and waste water analysis. Company's services include consultation, program development, sampling, and analysis. Princeton Chemical Research **91**

Installation manual. Manual provides calculation factors tor installing ultraviolet air intake or exhaust purification systems using tubular germicidal uv lamps. American Ultraviolet Co. **92**

Gratings. Bulletin announces product line of replica diffraction gratings available after company's first entry into the field in 10 years. Baird-Atomic **93**

Liquid waste treatment. Comprehensive brochure on industrial liquid waste treatment systems outlines company's latest product technology in packaged and custom-designed units for a broad spectrum of applications including treatment of chrome and cyanide wastes, ion exchange, evaporation, electrochemical destruction, and the like. Industrial Filter & Pump Mfg. Co. **94**

Laser catalog. Four-page brochure summarizes features of high energy, high repetition-rate neodymium YAG laser system. Performance specs of the Q-switched lasers are given. International Laser Systems, Inc. **95**

Case history. Booklet entitled "A Story on Handling Plant Wastes," tells how downtime and maintenance costs have been reduced in the waste disposal operations of a large chemical plant. Morris Pumps, Inc. **96**

Catalog. New Mikro-Products catalog includes a wide range of equipment for air pollution control and dust recovery, as well as for particle size reduction and separation. MikroPul Div., Slick Corp. **97**

OSHA requirements. Bulletin describes ways of meeting a wide variety of OSHA requirements by using rubber products. Hecht Rubber Corp. **98**

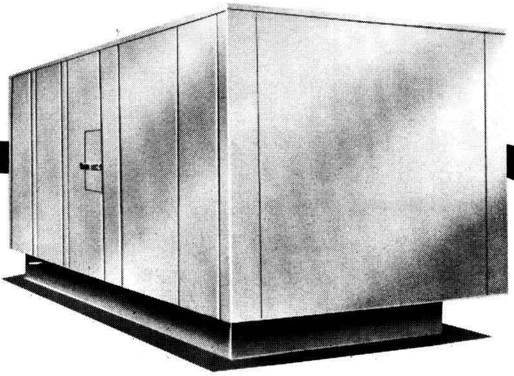
Catalog. New, fully illustrated catalog features a complete line of equipment for controlling, recording, and measuring temperatures. Includes complete line of totally interchangeable thermister probes and a section on lab tools. Laboratory Specialists Ltd. **99**

Furnaces. Catalog details company's full line of electric furnaces for lab and production use. Temperatures of units vary up to 2350°F with standard capacities up to 12 ft^3. Hotpack Corp. **100**

Water pollution. New catalog describes line- and battery-operated instruments for both fresh- and salt-water ecological studies, oceanography, and pollution analysis. Beckman Instruments, Inc. **101**

Pumps. Folder gives details of 44 typical installations of company's pumps. Reference guide tells which pump to use for specific applications, lists operating conditions and diagrams installation patterns. Kenco Pump **102**

(Continued on page 266)



Treatment capabilities. Bulletin describes company's capabilities in the field of air and water pollution abatement. Also tells of mobile treatment service which can test out proposed pollution abatement regimen before expensive equipment is bought. Andco Environmental Processes, Inc. **103**

Impact statements. Brochure defines company's specific services to clients centering around preparation of environmental impact statements for both terrestrial and aquatic environments. Firm also does contract research, water quality testing, consultation, and management. New England Research, Inc. **104**

Color standards. Series of interchangeable color comparators for more than 40 water tests by visual comparison makes sampling and measurement of environmental contaminants easy without sacrificing high accuracy. Lovibond of America, Inc. **105**

Catalog. Catalog listing 2500 chemicals including inorganic and organometallic research chemicals, ultrapure metals, AR reagents, and lab accessories is available from company. Apache Chemicals, Inc. **106**

Boron. Comprehensive 58-page hardback book entitled "The Ecological Significance of Boron," is available for distribution to libraries, colleges and universities, regulatory agencies, and other public agencies dealing with water quality criteria. Write direct to Mr. E. D. Lemon, Manager of Environmental Affairs, U.S. Borax, 3075 Wilshire Blvd., Los Angeles, Calif. 90075

Publication list. The 1972–1973 list of ASTM publications gives the more than 600 publications of the American Society for Testing and Materials dealing with standardized testing methods and materials specifications. To request single, free copy, write direct on letterhead to ASTM, 1916 Race St., Philadelphia, Pa. 19103

Films. Comprehensive and detailed listing of films on environment tells of free-loan 16-mm color and black and white movies available for showing to community groups and schools. Modern Talking Picture Service, 2323 New Hyde Park Road, New Hyde Park, N.Y. 10040 (Write direct.)

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BOOKS

The Water's Edge: Critical Problems of the Coastal Zone. Bostwick H. Ketchum, Ed. xx + 393 pages. The MIT Press, 28 Carleton St., Cambridge, Mass. 02142. 1972. $3.95, paper.

Proceedings of the Workshop on Critical Problems of the Coastal Zone, held in May 1972. This report represents the professional judgment of the participants on the problems created by man's use of coastal resources. Includes guidelines and recommendations for actions which can be taken to ameliorate, correct, or improve present or predicted deterioration of the coastal environment.

Environmental Affairs. Michael B. Meyer, Ed. Environmental Affairs, Inc., Boston College Law School, Brighton, Mass. 02135. Published quarterly. $18 annually, paper.

Purpose of the journal is to help environmental specialists stay abreast of environmental developments in a number of fields and disciplines. Covers basic policy considerations, new scientific and technological developments, and new legal and political ideas.

The Coastal Zone of Delaware. xxxvi + 464 pages. Publications Office, College of Marine Studies, University of Delaware, Newark, Del. 19711. 1972. $10, paper.

Contains information on the present status, trends, and problem areas of the Delaware coastal zone. Stresses various methods available to the state for regulating certain activities and for acquiring critical areas in the coastal zone. This document is the final report of Delaware Governor Russell Peterson's Task Force on Marine and Coastal Affairs.

Green Land—Clean Streams. R. Michael Stevens et al. xiv + 226 pages. Center for the Study of Federalism, Temple University, Philadelphia, Pa. 19122. $7.50, paper.

Description and analysis of the current experience with the techniques of land treatment of waste water. Covers high-volume treatment and disposal; treatment, conversion of pollutants into resources, and potential reuse; treatment by infiltration through a soil-plant cover medium or treatment by overland flow on the surface of a soil-plant cover medium. Describes over 40 different land disposal facilities.

The Spoils of Progress: Environmental Pollution in the Soviet Union. Marshall I. Goldman. xi + 372 pages. The MIT Press, 28 Carleton St., Cambridge, Mass. 02142. 1972. $7.95, hard cover.

The author describes abuses of water, air, land, and raw materials in Russia, analyzing the forces that have brought about the current situation and describing both the drawbacks and advantages of state control and conservation. Contains appendices of selected laws on the environment, the Conservation Law of the Russian Republic, and the Water Law 1970.

Environmental Engineering and Sanitation. 2nd ed. Joseph A. Salvato, Jr. xviii + 919 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1972. $24.95, hard cover.

First published in 1958 as Environmental Sanitation; now expanded and revised to reflect new interests in, and concerns for, the environment. Emphasizes practical applications of sanitary and engineering theory and principles to environmental control in urban, suburban, and rural communities. Author emphasizes the importance of considering the effect of new projects or construction on natural resources and people and vice versa.

Ionizing Radiation: Levels and Effects. A Report of the United Nations Scientific Committee on the Effects of Atomic Radiation. Vols. 1 and 2. iv + 497 pages. United Nations, Sales Section, New York, N.Y. 1972. $12.50, paper.

Reviews the following subjects: environmental radiation, doses from medical radiation, doses from occupational exposure, miscellaneous sources of ionizing radiation, genetic effects of ionizing radiation, effects of radiation on the immune response, experimental induction of neoplasms by radiation, and radiation carcinogenesis in man.

Directory of Environmental Consultants. Bill Bate, Ed. 46 pages. Directory Press, P.O. Box 8002, St. Louis, Mo. 63108. 1972. $6.00, paper.

Directory is an attempt to ensure that adequate review of all environmental programs can be made by any group. Lists professionals who have offered free consulting services—reviewing prepared reports, collecting small amounts of additional data, and suggesting weaknesses in present programs.

Energy, Economic Growth, and the Environment. Sam H. Schurr, Ed. viii + 232 pages. The Johns Hopkins Press, Baltimore, Md. 21218. 1972. $10, hard cover.

Contains eight papers whose authors view the energy-economic growth-environment controversy from widely different vantage points. Covers society's requirements to assure both social and biological survival, rising energy consumption, and meeting the increasing demand for energy while achieving desirable environmental objectives as well.

Scrubber Handbook. xxvi + 791 pages. National Technical Information Service, U.S. Dept. of Commerce, Springfield, Va. 22151. 1972. $13.50, paper.

Represents an effort to present the best available engineering information on scrubbers. Covers fundamental principles and then covers generally applicable design methods. Handbook was prepared by Ambient Purification Technology, Inc. (Riverside, Calif.) under contract to EPA.

Proceedings of the 1972 National Incinerator Conference. 353 pages. The American Society of Mechanical Engineers, 345 E. 47 St., New York, N.Y. 10017. 1972. $25, paper.

Contains 33 papers representing more than 10 years effort by the ASME to bring together those people interested in the technology of solid waste processing and disposal. Covers incinerator design, operation, environmental considerations, and the type of refuse disposed of by incinerators.

Particulate Polycyclic Organic Matter. Committee on Biologic Effects of Atmospheric Pollutants. xiii + 361 pages. Printing and Publishing Office, National Academy of Sciences, 2101 Constitution Ave., Washington, D.C. 20418. 1972. $7.75, paper.

Report dealing with contract with EPA to produce background documents for pollutants, including particulate polycyclic organic matter. Committee attempts to interpret, evaluate, and reconcile the immense amount of information available, especially that concerning carcinogenic effects of particulate polycyclic organic matter.

The Complete Ecology Fact Book. Philip Nobile, John Deedy, Eds. xx + 472 pages. Doubleday & Co., Inc., 277 Park Ave., New York, N.Y. 10017. 1972. $10, hard cover.

Brings together hard-to-find information in a compilation of ecology statistics gathered from the United Nations, U.S. government, private industry, foundations, and individual sources. Covers population, endangered species, pollution, detergents, food, pesticides, nonrenewable mineral wastes, and solid wastes. Appendices list court decisions, conservation agencies and organizations, foundations, and publications.

Science, Scientists and Society. William Beranek, Jr., Ed. vii + 199 pages. Bogden & Quigley, Inc., 19 N. Broadway, Tarrytown-on-Hudson, N.Y. 10591. 1972. $2.95, paper.

Book of lectures to stimulate scientists to take time to consider their possible roles in society. Presentations by Arie J. Haagen-Smit, Norman H. Brooks, and James J. Morgan on different aspects of the environment.

Marine Ecology, Vol. 1, Part 3. Otto Kinne, Ed. 544 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1972. $34, hard cover.

Intended as an exhaustive systematic exposition summarizing and evaluating information obtained thus far on living systems in the sea and littoral areas. Intended for individuals professionally concerned with life in the marine environment—investigators, engineers, teachers, students, administrators, and businessmen.

Population, Resources, Environment. Paul R. Ehrlich, Anne H. Ehrlich. xiv + 509 pages. W. H. Freeman and Co., 660 Market St., San Francisco, Calif. 94104. 1972. $9.50, hard cover.

Revised and updated edition of the Ehrlichs' first text in environmental studies. Latest edition includes more detailed coverage of demography, a new treatment of energy resources, and a fuller discussion of poisons in the environment.

The Environmental Future. Proceedings of the First International Conference on Environmental Future. Nicholas Polunin, Ed. xiv + 660 pages. Barnes & Noble Books, 10 E. 53rd St., New York, N.Y. 10022. 1972. $32.50, hard cover.

Proceedings of Conference held in Finland in 1971. The object of the Conference was to bring together, for free discussion, as complete a range of leading experts as possible, covering between them all the main aspects of environmental study and implications.

Analysis of Industrial Wastewaters. K. H. Mancy, W. J. Weber, Jr. 149 pages. John Wiley & Sons, Inc., 605 Third Ave., New York, N.Y. 10016. 1972. $6.95, paper.

Reprinted from Treatise on Analytical Chemistry. Discusses certain operating principles that are useful as guidelines for analyzing waste waters. Proper control of treatment processes and evaluation of the pollution potential of industrial waste waters are highly dependent on precise and accurate measurement of impurities.

The Automobile Cycle: An Environmental and Resource Reclamation Problem. U.S. Environmental Protection Agency. 115 pages. Superintendent of Documents, U.S. Govt. Printing Office, Washington, D.C. 20402. 1972. $1.25, paper.

Revision of a report prepared for the President's Council on Environmental Quality. Covers potential remedies for recycling problems and positive and negative incentives and stimulants.

Geology of Soils: Their Evolution, Classification, and Uses. Charles B. Hunt. 344 pages. W. H. Freeman & Co., 660 Market St., San Francisco, Calif. 94104. 1972. $12.50, hard cover.

Introductory text for future specialists in geology, soil science, engineering, ecology, and hydrology. Aims at comprehensive understanding of the environment at ground level. Describes interrelationships among the development and distribution of soils, the physical and biological properties of soils, and the factors that engineers must consider when working with the ground.

Institutional Arrangements for International Environmental Cooperation. x + 74 pages. National Academy of Sciences, 2101 Constitution Ave., Washington, D.C. 20418. 1972. $3.50, paper.

Report considers ways in which international organizations can deal with problems of a deteriorating environment. Prepared by the Academy's Committee for International Environmental Programs.

Pollution Control in the Marine Industries. Thomas F. P. Sullivan, Ed. 350 pages. International Association for Pollution Control, Suite 303, 4733 Bethesda Ave., N.W., Washington, D.C. 20014. 1972. $25, paper.

Proceedings of conference held in 1972. Describes the entire field of marine pollution control. Supplies information, with appropriate commentaries, for those who are presently involved in the marine field such as vessel owners and operators, ship builders, naval architects, marine equipment and service suppliers, and those who hope to supply services or equipment to this new part of the marine industry in the future.

Population, Resources, and the Environment. Ronald G. Ridker, Ed. 377 pages. Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. 1972. $4.25, paper.

Volume 3 of Research Reports of the Commission on Population Growth and the American Future. Report conclusion is that there is nothing to be gained by a further increase in population in the U.S., so far as resources and the environment are concerned.

Erosion and Sediment Control—An Annotated Bibliography. 16 pages. American Society of Agricultural Engineers, 2950 Niles Rd., St. Joseph, Mich. 49085. 1972. $4.00, paper.

The 34 referenced items include papers presented at ASAE meetings, articles appearing on various ASAE publications, and of other groups such as the American Water Resources Association, the American Society of Civil Engineers, and the Soil Conservation Society of America. A synopsis is included wth each entry to describe the subject matter of the reference.

Air Pollution and Industry. R. D. Ross, Ed. xviii + 489 pages. Van Nostrand Reinhold Co., 450 W. 33rd St., New York, N.Y. 10001. 1972. $18.95, hard cover.

Reference and guide designed to help the plant engineer identify and solve air pollution problems. Book includes contributions from industry, government, and university personnel in treating the problem of air pollution at the industrial level. Intended for engineers, chemists, chemical engineers, metallurgists, mechanical engineers, and everyone involved in plant operation, as well as educators, executives, and government officials.

Wastewater Engineering: Collection, Treatment, Disposal. Metcalf & Eddy, Inc. xiii + 782 pages. McGraw-Hill Book Co., 330 W. 42nd St., New York, N.Y. 10036. 1972. $19.50, hard cover.

Text containing up-to-date treatment of waste water engineering for the undergraduate student, the graduate student, and the practicing engineer. Presented so that the reader will be able to apply the fundamentals to the solution of collection, treatment, and disposal problems.

Ecology, Pollution, Environment. Amos Turk, Jonathan Turk, Janet T. Wittes. ix + 217 pages. W. B. Saunders Co., W. Washington Sq., Philadelphia, Pa. 19105. 1972. $3.95, paper.

Book could be used for a course in environmental science or as a supplement to a course in biology or chemistry. Covers two aspects of environmental science; first, it presents the actual subject matter in this field —relevant background material in the physical sciences where it is needed so that previous formal training is not required. Second, a discussion of social problems and issues shows that various scientific and economic factors must be taken into account prior to environmental decisions.

Forest Land Use and the Environment. Richard M. Weddle, Ed. 150 pages. Montana Forest and Conservation Experiment Station, School of Forestry, Univ. of Montana, Missoula, Mont. 59801. 1972. $3.25, paper.

Contains nine articles discussing current forest management practices and their impact on the environment. Also provides an understanding of the social, political, economic, and administrative considerations which underlie these practices. Each of the authors is a specialist in his own field.

Emissions from Internal Combustion Engines and Their Control. D. J. Patterson, N. A. Henein. vii + 355 pages. Ann Arbor Science Publishers, Inc., P.O. Box 1425, Ann Arbor, Mich. 48106. 1972. $18.75, hard cover.

Covers the chemical and chemical engineering aspects of the subject as well as mechanical engineering. Delineates the fundamentals of combustion and emission formation in both homogeneous and heterogeneous combustion systems. Intended as an introductory text in combustion engine emissions and their control. Designed for the engineer, research worker, or student who is concerned with the theory and practice of engine and vehicle emission control.

Environmental Law, 2nd Ed. Arnold W. Reitze, Jr. North American International, P.O. Box 28278, Central Station, Washington, D.C. 20005. 1972. $19.95, hard cover.

Principal additions in the second edition include 20 more cases, four sample complaints, a subchapter on noise, a section on deep well injection, and an expanded chapter on environmental policy. Updating was to mid-July, 1972. Covers laws in air pollution, water pollution, solid wastes and recycling, noise, environmental policy, and litigation.

RESOURCEFUL TOPICS FOR ENVIRONMENTAL BETTERMENT

1. ENVIRONMENTAL PROTECTION

Emil T. Chanlett, University of North Carolina at Chapel Hill. 1973, 608 pages (tent.), $15.50 (tent.).

ENVIRONMENTAL PROTECTION is man-centered. This book describes the rationale for the management and protection of our land, air, water and energy resources. The consequences of mismanagement of the major environmental components are examined at three levels: 1) effects on health, 2) effects on comfort, convenience, efficiency and esthetics, and 3) effects on the balance of ecosystems and of renewable resources. Although scientific and engineering principles are stressed, the material is presented in a clear, non-mathematical manner to facilitate understanding by relatively divergent groups.

2. THERMAL COMFORT: Analysis and Applications in Environmental Engineering

P. O. Fanger, Technical University of Denmark. 1973, 244 pages (tent.), $12.95.

A novel and rational basis for heating and air conditioning technology is introduced in this unique book, the first to deal exclusively with thermal comfort for man. Based on the results of recent research work, the book deals with conditions for thermal comfort, methods of assessing thermal environments, and principles for performing thermal analyses of enclosures based on comfort criteria.

3. CITIES AND GEOLOGY

Robert F. Leggett, former Director, National Research Council of Canada. 1973, 460 pages (tent.), $14.50.

Designed for courses in urban or environmental geology, environmental studies, and city planning/urban development, this text utilizes examples, illustrations, and case histories from around the world to demonstrate the significance of geology in solving problems of urban growth. The author emphasizes the value of engineering-geological maps, as well as the work of state (and other) geological surveys.

4. WATER RESOURCES ENGINEERING, Second Edition

Ray K. Linsley and **Joseph B. Franzini,** both of Stanford University. 1972, 662 pages, $17.50. *Solutions Manual.*

Covering the full spectrum of water management, this edition contains new information on reference data, computer solutions, and added problems in metric units. Hydrologic concepts, legal aspects of water, open and closed channels, dams and spillways, and engineering economy are discussed.

5. WASTEWATER ENGINEERING: Collection, Treatment, Disposal

Metcalf & Eddy Incorporated, Boston, Massachusetts. 1972, 768 pages, $19.50. *Solutions Manual.*

In this single volume, the wide body of knowledge encompassing the rapidly expanding field of wastewater engineering has been consolidated. Useful both as a text and as a reference manual for practicing engineers, the text has been prepared by professors and engineers engaged in the design, construction and operation of wastewater engineering facilities.

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MEETING GUIDE

March 19–20 Washington, D.C.
1973 AIA-CEC Public Affairs Conference. American Institute of Architects and Consulting Engineers Council

Discussion topics will include controlling demands for energy, implications of OSHA, and other items. *Contact:* AIA-CEC Public Affairs Conference, 1155 15th St., N.W., Washington, D.C. 20005

March 19–23 Columbus, Ohio
Mid-West Workshop in Environmental Science. Ohio State University

Contact: John Lindamood, Dept. of Food Science and Nutrition, Ohio State University, 2121 Fyffe Rd., Columbus, Ohio 43210

March 19–23 Anaheim, Calif.
Corrosion 73 International Forum. National Association of Corrosion Engineers

Many technical sessions include environmental considerations. *Write:* National Association of Corrosion Engineers, 2400 West Loop South, Houston, Tex. 77027

March 20–22 Lake Kiamesha, N.Y.
Flexible Vinyls and Human Safety: An Objective Analysis. Society of Plastics Engineers

Will cover effects of phthalic acid ester plasticizers on human health as well as the environmental aspects of the use of lead, cadmium, mercury, and antimony in plastics colorants and stabilizers. *Write:* Roger P. Fox, Society of Plastics Engineers, 656 W. Putnam Ave., Greenwich, Conn. 06830

March 21–24 Logan, Utah
Symposium on Environmental Biogeochemistry. Utah State University and others

Will emphasize the cooperation of soil scientists, organic geochemists, and biologists in contributing to solving contemporary environmental problems. *Contact:* J. Skujins, Ecology Center, Utah State University, Logan, Utah 84322

March 23–25 Chicago, Ill.
National Symposium on the Future Status of Earth Resources in Society. National Assoc. of Geology Teachers

Contact: Musa Qutub, Symposium Chairman, Dept. of Earth Sciences, Northeastern Illinois University, Bryn Mawr at St. Louis Ave., Chicago, Ill. 60625

March 26–27 Orlando, Fla.
Seminar on Sanitary Landfilling in High Water Table Areas. Orange County, Fla. and EPA

Purpose of the seminar is to disseminate information on Orange County's demonstration projects and other major projects on solid waste disposal in high water table areas. *Contact:* Dennis Fenn, Project Officer, EPA, 5555 Ridge Ave., Cincinnati, Ohio 45268

March 26–28 Syracuse, N.Y.
Food Processing Waste Management Conference. EPA, Cornell University, and National Canners Association

Focus will be on results of research and practical applications dealing with waste water management in the food processing industry. *Contact:* Agricultural Waste Management Program, 1973 Conference Committee, 207 Riley Robb, Cornell University, Ithaca, N.Y. 14850

March 28–30 Des Moines, Iowa
Soil Conservation Society of America. National Conservation Tillage Conference

Contact: H. Wayne Pritchard, Director, Soil Conservation Society of America, 7515 N.E. Ankeny Rd., Ankeny, Iowa 50021

March 29–30 St. Louis, Mo.
Greater St. Louis Section of APCA. Specialty Conference

Titled "Design, Operation, and Maintenance of High Efficiency Particulate Control Equipment." *Write:* James G. Richeson, District Manager, Carborundum Co. The Pangborn Corp., 10406 Manchester, Kirkwood, Mo. 63122

March 29–30 Knoxville, Tenn.
Third Annual Industrial Air Pollution Control Conference. University of Tennessee and APCA

Contact: Joseph R. Duncan, Program Chairman, University of Tennessee, Dept. of Civil Engineering, Knoxville, Tenn. 37916

April 1–3 San Antonio, Tex.
National Petroleum Refiners Association. 71st Annual Meeting

Sessions on environmental requirements and associated costs. *Contact:* National Petroleum Refiners Assoc., Suite 802, 1725 Desales St., N.W., Washington, D.C. 20036

April 1–5 Kansas City, Mo.
Food Seminar Workshop. EMA, FDA, USDA, OSHA, EPA

Contact: Environmental Management Association, 1710 Drew St., Clearwater, Fla. 33515

April 1–6 Pacific Grove, Calif.
Environmental Needs as Part of the Quality System in Construction. Engineering Foundation

Fee: $175. *Contact:* Engineering Foundation, 345 E. 47th St., New York, N.Y. 10017

April 2–5 Anaheim, Calif.
Institute of Environmental Sciences. 19th Annual Technical/Tutorial Meeting and Equipment Exposition

Will provide a forum for exchange between educational, industrial, and governmental activities to impart U.S. environmental programs with realism. *Write:* Institute of Environmental Sciences, 940 E. Northwest Hwy., Mt. Prospect, Ill. 60056

April 4–5 Edgewood Arsenal, Md.
Fourth Annual Symposium on Environmental Pollution. American Ordnance Assoc.

Theme will be "Reclamation and Disposal of Hazardous Materials." *Contact:* Commander Arthur Sullivan, USN (Ret.), American Ordnance Assoc., Union Trust Bldg., 740 15th St., N.W., Washington, D.C. 20005

April 5–9 Washington, D.C.
CIMAC 73—10th International Congress on Combustion Engineering. ASME and others

Covers field of internal combustion engines, environmental problems, alternative fuels, etc. *Contact:* ASME, 345 E. 47th St., New York, N.Y. 10017

April 8–11 Washington, D.C.
Second National Symposium on State Environmental Legislation. Council of State Governments

Contact: Council of State Governments, Iron Works Pike, Lexington, Ky. 40505

April 8–13 Dallas, Tex.
American Chemical Society. 165th ACS National Meeting

Write: A. T. Winstead, ACS, 1155 Sixteenth St., N.W., Washington, D.C. 20036

April 10–12 Charlotte, N.C.
1973 Textile Engineering Conference. American Society of Mechanical Engineers

Includes papers on environmental control in the textile industry. *Write:* ASME, 345 E. 47th St., New York, N.Y. 10017

April 16–18 Huron, Ohio
Sixteenth Conference on Great Lakes Research. International Association for Great Lakes Research.

Covers physical, chemical, biological, engineering, and socio-economic problems of the Great Lakes. *Contact:* Charles E. Herdendorf, Center for Lake Erie Area Research, 484 W. 12th Ave., Columbus, Ohio 43210

April 19 Virginia Beach, Va.
Third Commonwealth Air Pollution Control Workshop and Exhibit. State Air Pollution Control Board and Va. Port Authority

A forum for exchanging environmental information, including new advances in air pollution control techniques. *Contact:* Tony Mason, Virginia Port Authority, 1600 Maritime, Norfolk, Va. 23515

April 23–27 Washington, D.C.
National Meeting on Complete WateReuse. American Institute of Chemical Engineers and EPA

Sessions will cover the broad topics of engineering, administration, economics, and public. *Contact:* Larry Cecil, Chairman, Water Section, Environmental Division, AIChE, 345 E. 47th St., New York, N.Y. 10017

April 25–27 Palm Beach Shores, Fla.
American Nuclear Society and Marine Technology Society. National Topical Meeting

Theme "The Ocean, Nuclear Energy & Man." *Contact:* M. Jack Ohanian, Chairman, Dept. of Nuclear Engineering, University of Florida, Gainesville, Fla. 32601.

April 26–27 Durham, N.C.
National Symposium on Ultimate Disposal of Wastewaters and Their Residuals. Research Triangle Universities and others

Sessions on land disposal, marine disposal, sludge handling, design practice, recovery, and recycling. *Contact:* F. E. McJunkin, Associate Director, Water Resources Research Institute, North Carolina State Univ., 124 Riddick Bldg., Raleigh, N.C. 27607

April 28 Chicago, Ill.
Second Annual National Symposium on Societal Problems of Water Resources. Illinois Earth Science Assoc. and American Water Resources Assoc.

Contact: Musa Qutub, Symposium Chairman, Northeastern Illinois Univ., Bryn Mawr at St. Louis Ave., Chicago, Ill. 60625

April 29–May 2 St. Louis, Mo.
National Association for Environmental Education. 1973 Annual Meeting

Write: National Association for Environmental Education, P.O. Box 1295, Miami, Fla. 33143

April 29–May 2 Houston, Tex.
Fifth Annual Offshore Technology Conference. American Institute of Chemical Engineers and others

Session topics include: environmental conservation, control of oil spills, remote sensing and navigation, and other subjects. *Contact:* Offshore Technology Conference, 6200 N. Central Expressway, Dallas, Tex. 75206

April 29–May 3 New Orleans, La.
American Oil Chemists' Society. 64th Annual Spring Meeting.

Includes discussions on pollution abatement—control of dust, water, hydrocarbons, and proteins. *Write:* AOCS Headquarters, 508 S. Sixth St., Champaign, Ill. 61820

May 1–3 Lafayette, Ind.
28th Annual Purdue Industrial Waste Conference. Purdue University

Will cover numerous phases of industrial waste treatment through research, design, operations, and/or case history aspects. *Write:* David W. Hawkins, Civil Engineering Dept., Purdue Univ., West Lafayette, Ind. 47907

May 8 Paramus, N.J.
Third Annual Industrial Air Pollution Seminar. Rossnagel & Associates

Covers control equipment displays and papers directed toward engineers in textile, printing, plating, food processing, foundry, odor, acid, chemical, dust industries. *Write:* W. B. Rossnagel, Director, Rossnagel & Associates, 1999 Rt. 70 (E. Marlton Pike), Cherry Hill, N.J. 08003

May 15–17 Toronto, Ont., Canada
Second Annual Pollution Control Show. Pollution Control Association of Ontario

Conference will take a practical approach to pollution control in terms of economics and legislation. *Write:* Dianne C. Warnick, Public Relations Coordinator, Ontario Marketing Productions Ltd., 111 Bond St., Toronto 200, Toronto, Ont.

May 20–25 Boston, Mass.
Annual American Industrial Hygiene Conference. American Industrial Hygiene Association and others

Conference will feature the latest in R&D in the field of worker protection. *Write:* E. Lynn Schall, Managing Director, American Industrial Hygiene Association, 210 Haddon Ave., Westmont, N.J. 08108

May 22–24 Washington, D.C.
Environmental Impact on the Textile Industry Symposium. American Association of Textile Chemists and Colorists

Will cover environmental problems, solutions, and economics; government regulations; OSHA regulations; and action taken by the textile industry. *Contact:* AATCC Technical Center, P.O. Box 12215, Research Triangle Park, N.C. 27709

Courses

March 19–23 Austin, Tex.
Advanced Water Pollution Control: Biological Waste Treatment. University of Texas at Austin

Write: Engineering Institutes, P.O. Box K, University of Texas at Austin, Austin, Tex. 78712

March 26–30 Palo Alto, Calif.
Hydrologic Simulation Workshop. Hydrocomp Inc.

Fee: $375. *Contact:* Hydrocomp Inc., 1502 Page Mill Rd., Palo Alto, Calif. 94304

March 29–30 Milwaukee, Wis.
Water Pollution—Law & Regulation. University of Wisconsin-Extension

Fee: $95. *Contact:* University of Wisconsin-Extension, Dept. of Engineering, 600 W. Kilbourn Ave., Milwaukee, Wis. 53203

March 29–30 Madison, Wis.
Environmental Design. University of Wisconsin—Extension

Fee: $95. *Write:* University of Wisconsin—Extension, Dept. of Engineering, 432 N. Lake St., Madison, Wis. 53706

April 5–6 Madison, Wis.
Industrial Noise Control. University of Wisconsin—Extension

Fee: $95. *Write:* University of Wisconsin—Extension, Dept. of Engineering, 432 N. Lake St., Madison, Wis. 53706

April 16–20 Chicago, Ill.
Stack Sampling. IIT Research Institute

Geared to the engineer, chemist, and/or supervisor in the design and conduct of source sampling programs and interpretation of data. *Write:* Ronald G. Draftz, IIT Research Institute, 10 W. 35 St., Chicago, Ill. 60616

April 16–20 Austin, Tex.
Advanced Water Pollution Control: Physical and Chemical Waste Treatment. University of Texas at Austin

Write: Engineering Institutes, P.O. Box K, University of Texas at Austin, Austin, Tex. 78712

April 16–20 Nashville, Tenn.
Development of Design Criteria for Waste Water Treatment Processes. Vanderbilt University

Seminar will cover two categories: biological waste treatment and physical-chemical waste treatment. Fee: $275. *Write:* W. Wesley Eckenfelder, Box 6222, Station B, Vanderbilt University, Nashville, Tenn. 37235

April 17–18 Los Angeles, Calif.
22nd Annual Instrument Short Course. Southern California Meter Assoc.

Special attention will be given to water, waste, and atmosphere cleanup and control. *Contact:* S. C. Moffitt, c/o McCamey-Jones, Inc., 1403 S. Atlantic Blvd., Los Angeles, Calif. 90022

May 21–25 Bronx, N.Y.
18th Summer Institute in Water Pollution Control. Manhattan College

Two one-week courses offered concurrently in: biological waste treatment and mathematical modeling of natural water systems. Fee: $250. *Write:* Donald J. O'Conner, Environmental Engineering & Science Program, Manhattan College, Bronx, N.Y. 10471

Quarterly Chicago, Ill.
Air Pollution Sampling. Nalco Chemical Co.

Five-day course in the techniques of gaseous sampling and analysis. *Write:* Nalco Chemical Co., 180 N. Michigan Ave., Chicago, Ill. 60601

Plattsburgh, N.Y.
Miner Institute for Man and His Environment. Environmental Studies 101/301

Semester-long course intended to familiarize students with selected environments which involve man in varying degrees. Limited to 40 students. *Contact:* The Director: Environmental Studies 101/301, State University of New York, Miner Institute for Man and His Environment, Plattsburgh, N.Y. 12901

Whitehouse Station, N.J.
Air Pollution Seminars. Root Engineering, Inc.

Seminar offered as part of a complete, custom-tailored air pollution consultation program from stack tests to environmental impact studies. *Write:* Root Engineering, Inc., 3616 U.S. Highway 22, Whitehouse Station, N.J. 08889

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April 15 deadline Washington, D.C.
2nd Joint Conference on Sensing of Environmental Pollutants. Instrument Society of America

Will feature basic phenomenology related to sensors and sensing techniques for measuring land, water, and air environmental quality parameters. *Contact:* M. E. Ringenbach, Director, Engineering Development Laboratory, NOAA/National Ocean Survey, Rockville, Md. 20852

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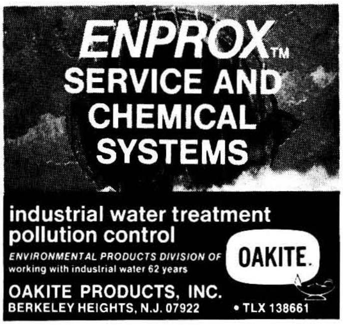

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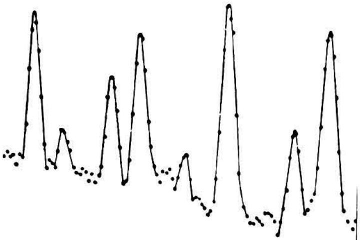

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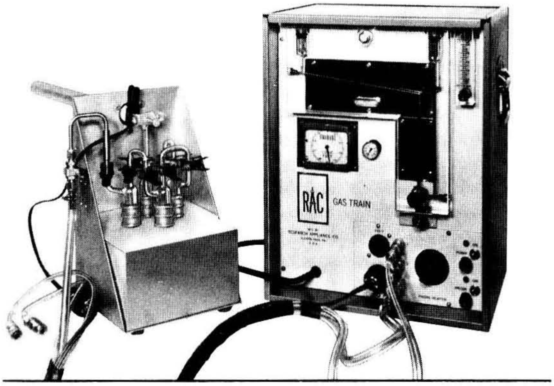
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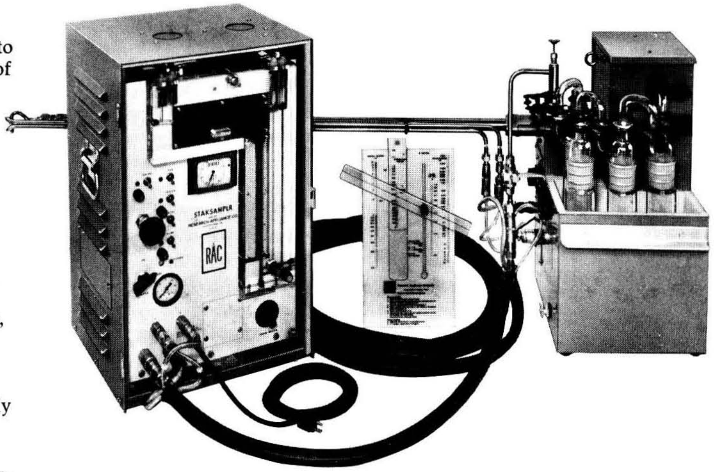
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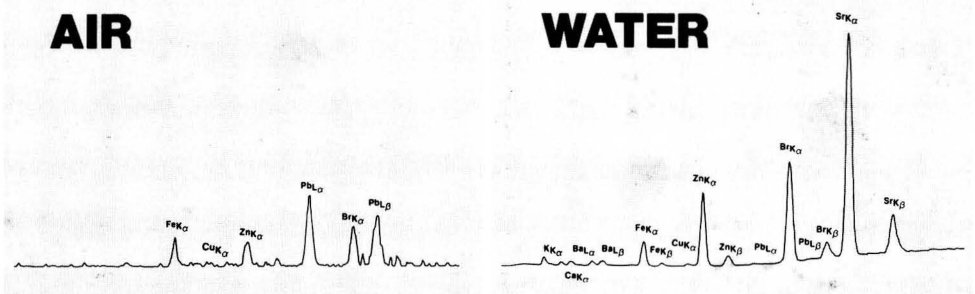

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