Number Four 1984

Oak Ridge National Laboratory
review

WATER: Current Challenges in Energy Research

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VOLUME 17 **NUMBER FOUR 1984**

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COVER CAPTION: The theme of this issue is water, an important subject of investigation at ORNL partly because providing energy for human use consumes water and affects its quality. The water-energy connection is illustrated in the cover photograph of a water wheel (from an abandoned mill) in a stream in East Tennessee. (Photograph by Bill Clark).

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FROM THE EDITOR: Water—Its Wonders, Our Worries

Water, the wondrous stuff of life and one of our most precious resources, has long been a compelling subject. For several years we have heard predictions that scarcity of water, or at least a shortage of clean, safe water, will become the crisis of the 1980s, just as the energy crunch was the crisis of the 1970s. The public worries about water pollution and contamination of drinking water—concerns that recently have led to tough legislation.

Water remains a vital subject for scientific research. Its properties have been studied and exploited for hundreds of years. At Oak Ridge National Laboratory, where energy is the primary focus of study, water has become an important subject of investigation partly because providing energy for human use consumes water and affects its quality. ORNL scientists have focused on many of water's properties, including its ability to remove, store, and transport heat and to dissolve numerous materials. Its ability to serve as a coolant and neutron moderator in nuclear power reactors led to the development of the concept of light-water reactors at ORNL and elsewhere. Water in reactors apparently has another benefit: ORNL studies previously reported in the *Review* and updated in this issue show that because today's reactors are largely water cooled instead of air cooled, they tend to emit significantly less iodine-131 (a hazardous radioactive gas) to the environment following a loss-of-coolant accident such as that at Three Mile Island.

In this issue all the articles touch upon water. Eli Greenbaum writes about photosynthetic reactions that can split water into oxygen and hydrogen, which can be a useful chemical feedstock and a clean fuel. Combustion of less clean fuels such as coal can pollute the water that reaches the earth as precipitation. David Shriner writes about evidence that acid rain in combination with particles and gases (such as ozone) deposited from the atmosphere can inhibit the growth of crops and may be responsible for the long-term decline of forests in the eastern United States. He tells us about a plan to manipulate watersheds to determine how acid precipitation is directly or indirectly related to the acidification of streams and the availability of aluminum, which kills fish.

Geochemist David Cole tells how an understanding of the properties of hot water and its dissolved minerals underground enables geologists to better explore for geothermal systems, natural gas, and ore deposits, and how geologists can mimic, in a very short time, the chemical processes that form rocks.

Epidemiologists and chemists at ORNL are now looking at the issue of drinking water and health. Elaine Zeighami writes about an epidemiological study of Wisconsin farmers that indicates a relationship between use of soft drinking water and increased risk of cardiovascular disease. The study found that hard water, which is high in calcium, appears to lower the risk of death from heart attack and stroke.

Most drinking water in the United States is chlorinated to kill disease-causing bacteria. But chlorine can react with organic matter in water to form potentially hazardous organic compounds. An article in this issue discusses the work of ORNL chemist Bob Jolley, who was the first to identify potentially hazardous organic compounds formed by adding chlorine to wastewater. In addition to his research, he has organized five international conferences on the health and environmental impacts of water chlorination.

Half of the nation's drinking water comes from groundwater. Unfortunately synthetic organic chemicals from industry and farming have contaminated some groundwater sources of drinking water. A book edited by ORNL researchers Curtis Travis and Elizabeth Etnier and summarized in this issue discusses the environmental and legal problems of groundwater pollution. Two sidebars explore the efforts of ORNL scientists to determine the best sites for monitoring groundwater quality and to divert groundwater from a radioactive waste burial area at ORNL.

Basic studies of the structure of water have been carried on at ORNL since the 1940s. X-ray and neutron diffraction studies have allowed researchers to measure the tiny distances between atoms on neighboring molecules of water. The ORNL X-ray data have also been used by radiation physicists elsewhere to obtain enhanced X-ray images for more accurate medical diagnoses.

For a laboratory concerned with energy and environmental problems, water will always be a subject of intensive inquiry. Fusion researchers, for example, will be concerned with finding more efficient, economical methods for extracting deuterium from seawater to fuel fusion devices. Basic researchers can drink to the fact that water and the chemical baggage that this excellent solvent carries will continue to be an intellectual challenge for years to come.—*Carolyn Krause.*

Coal-burning plant in the eastern United States spews sulfur dioxide and nitrogen oxides into the atmosphere. These gases are the main contributors of acidity in rainfall.

Sick and dying Norway spruce trees in a Federal Republic of Germany forest may be victims of acid rain, dry atmospheric deposition, or air pollution. (Photograph by S. E. Lindberg.)

Acid Rain and Dry Deposition of Atmospheric Pollutants: *ORNL Studies the Effects*

By DAVID SHRINER

Acidic precipitation and atmospheric deposition may be involved in the decline of some forests and in the elevation of aluminum levels in streams. ORNL researchers play an important role in pinpointing the effects of atmospheric pollutants on vegetation, fish, and surface waters.

Some lakes in the western Adirondack Mountains of upstate New York no longer support trout. Red spruce trees in forests in Vermont and Tennessee are dying. The Statue of Liberty, other monuments, and many stone buildings are showing signs of decay. Is there a common cause? Many scientists attribute the cause to acid rain, which is formed in the atmosphere by the interaction of moisture with sulfur dioxide and nitrogen oxides emitted primarily by the burning of coal, oil, and gasoline. Others, like many environmental scientists at Oak Ridge National Laboratory, believe that the common thread accounting for these phenomena is indeed pollution of the atmosphere but that the form, pathways, and mechanisms of the causal agents are much more complex than acid rain alone.

For the past ten years atmospheric deposition of sulfur and nitrogen oxides in the form of acid rain has been an issue in the public and political eye. In 1983 the National Acid Precipitation Assessment Program (NAPAP) reported that acid rain may be responsible for fishery losses in some bodies of water and for a decline in tree growth and survival in some forests in New England and southern Appalachia. Because

David S. Shriner is ORNL coordinator for atmospheric deposition research and leader of the Regional Resource Analysis Group of ORNL's Environmental Sciences Division. He holds a Ph.D. degree in plant pathology from North Carolina State University. A native of Spokane, Washington, Shriner also has earned degrees in forest management and plant pathology from the University of Idaho and Pennsylvania State University, respectively. Since coming to ORNL in 1974, he has studied the fate and effects of energy-derived pollutants on terrestrial ecosystems and has assessed regional-scale environmental problems. In 1979 he was cochairman of the ORNL Life Sciences Symposium. With Chet Richmond and Steve Lindberg of ORNL, he was coeditor of the book *Atmospheric Sulfur Deposition*. He is a member of the Federal Interagency Task Force on Acid Precipitation and is chairman of the National Atmospheric Deposition Program. Here, Shriner checks a plot of soybean plants in an open-topped exposure chamber at ORNL's Air Pollution Effects Field Research Facility. Each chamber has a movable cover to exclude ambient rainfall and an activated charcoal filter to exclude ambient gaseous air pollutants such as ozone. The crops in the chamber can also be exposed to simulated rainfall with different levels of acidity (pH). By comparing soybean growth in the chamber under controlled conditions with that under ambient conditions, ORNL scientists have determined that ozone, independent of acid rain, can reduce soybean productivity by about 10%.

the acid rain problem in the eastern United States is attributed largely to fossil fuel combustion, legislation was recently proposed in Congress to require a 10-million-ton reduction in sulfur dioxide emissions from coal-fired power plants. If passed, the measure could have raised consumer electric bills to pay for pollution controls on power plants, primarily those in the Midwest that burn high-sulfur coal. However, on May 2, 1984, a House of Representatives subcommittee rejected the acid rain control legislation by a 10 to 9 vote.

But as rain does not go away, neither will the volatile issue of acid rain. A number of scientific questions still lack definitive answers. For example, no one knows whether sulfur emissions from coal-fired plants in the Midwest are chiefly responsible for the decline of forests in the East or the acidification of some lakes in the Adirondacks that no longer support fish life. Also unclear is whether paying the high price of emission control would eliminate the forest and lake acidification problems in the East. No one knows whether acid rain and dry deposition of sulfuric and nitric oxides are the only causes of change in soils, forests, crops, and aquatic life in streams. And the jury is still out on whether acid rain's impact is reversible or irreversible or even all negative. What is certain is that these difficult questions have provided an "acid test" of the abilities of some of the nation's best and brightest scientists.

During the past ten years, scientists at ORNL have made important contributions toward understanding the transport, deposition, and fate of emissions from human activity, which ultimately contribute to the acid rain problem. Why has ORNL become a major center of research

Dan Richter collects a soil water sample from Walker Branch Watershed. Dale Johnson has found that soils differ dramatically in their ability to hold onto sulfur deposited by acid rain and other forms of atmospheric deposition. If sulfate ions move readily through the soil, they may strip away nutrients and ions of hydrogen and aluminum (which can enter streams, where they can be toxic to fish). In other soils, the sulfate ions are bound by iron and aluminum oxides. Johnson and his colleagues are developing models to predict how long different soils can hold onto sulfur and prevent it from removing forest nutrients.

activity in the science of atmospheric deposition? For one reason, ORNL has a cadre of interested and committed scientists. Equally important, however, has been the long-term commitment of ORNL's government sponsor (now the Department of Energy) to a quantitative understanding of the fundamental processes regulating forested and aquatic ecosystems and of how energy development might affect them. At ORNL that commitment came first in the form of the establishment in 1967 of the Walker Branch Watershed in Oak Ridge. Today ORNL Walker Branch studies are providing one of the nation's longest records of wet and dry deposition inputs and streamflow outputs from an area of forested landscape.

Watershed Nutrient Dynamics

Walker Branch was the site of the first watershed-scale sulfur budget (record of sulfur inputs and outputs) prepared in the United States, a result of efforts in the early 1970s by Environmental Sciences Division (ESD) staff members—namely, Gray Henderson and then me. Since 1977 ESD's Dale Johnson, Dan Richter, and Don Todd have refined the earlier work to improve the understanding of the processes and mechanisms involved in sulfur movement through a forested watershed.

One of Johnson's key contributions to understanding the "big picture"—that is, the regional consequences of sulfur deposition by the descent of dry particles, gases, rain, snow, frost, and dew—has been the recognition that soils differ dramatically in their capacity to retain sulfur deposited from the atmosphere. In some soils, sulfate anions (negatively charged ions) pass readily through the soil and pull away positively charged ions (cations) that have been attached to the negatively charged soil particles. These cations may be nutrients such as calcium and magnesium or hydrogen ions and aluminum. If the sulfate anions from acid rain carry away nutrient cations, forest nutrient reserves are reduced, and tree growth may be inhibited. If the sulfate anions carrying hydrogen ions and aluminum are washed into lakes and streams, they may cause acidification of the streams. Even worse, the introduction of toxic aluminum to lakes and streams can kill fish.

In other soils, such as many of the iron- and aluminum-rich soils of the Southeast, the sulfur becomes bound by iron and aluminum oxides and is retained in the subsurface soil, partially neutralizing the potential negative effects of sulfur deposition on the forest soil system. Research on Walker Branch and collaboration with scientists studying numerous other watersheds throughout the United States have led Johnson and his colleagues to develop models to predict sulfate "breakthrough" in these soil systems—that is, to estimate the finite capacity of the soil to hold onto, or adsorb, sulfate before beginning to export it and associated nutrient cations. Also significant among their findings has been the fact that forest ecosystems appear to selectively conserve limiting nutrient cations (vitally needed nutrients in low supply, such as calcium) while losing nonlimiting cations (nutrients in plentiful supply such as sodium, magnesium, and potassium). Johnson hypothesizes

Mountain stream in the Great Smoky Mountains National Park. How processes on land can affect acidification of mountain streams will be studied at ORNL and other laboratories in the second half of this decade. (Photograph by Ron McConathy.)

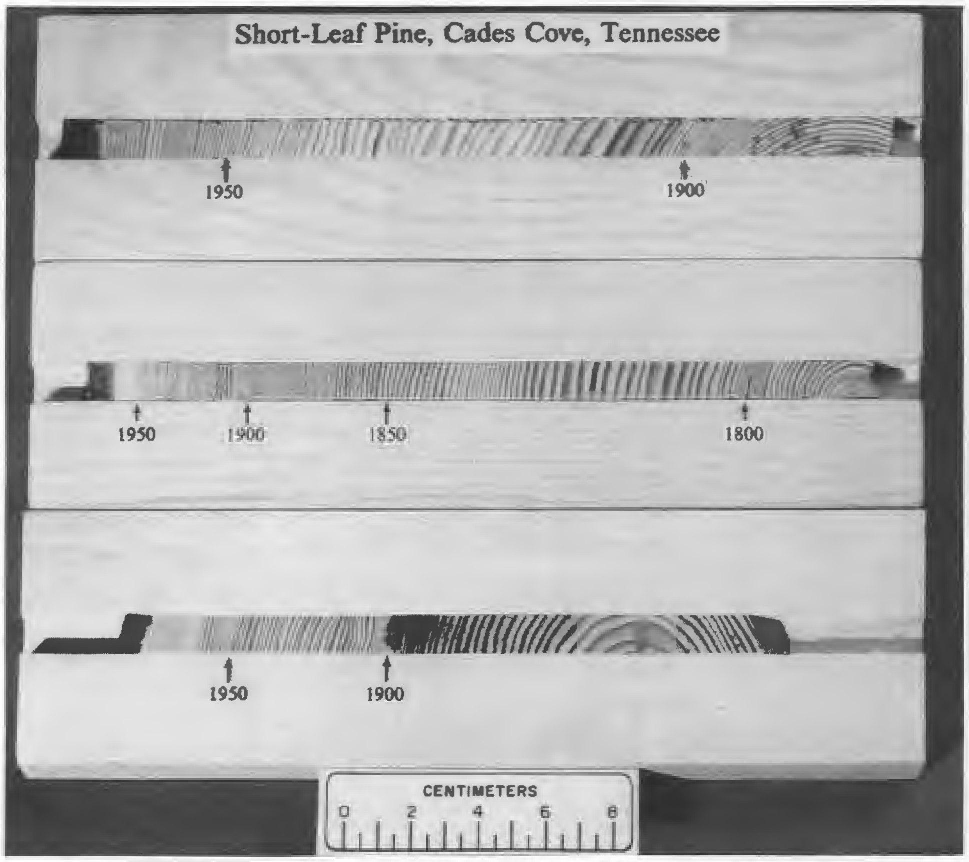
that calcium-poor sites do not lose calcium, because the amount deposited from the atmosphere apparently equals the amount removed by leaching.

A newly funded $7.7-million project for the Electric Power Research Institute (EPRI) focuses on the effects of atmospheric deposition on the forest canopy and soil processes and on the accumulation, cycling, and losses of key elements in forest ecosystems. Johnson and Steve Lindberg (ESD), principal investigators for the project, will study key processes regulating the effects of atmospheric deposition on forest element cycling. In collaboration with scientists from four universities, the National Park Service, and the U.S. Forest Service, they will examine processes regulating the movement of sulfate, nitrate, hydrogen ions, base cations, and aluminum through the forest canopy and soil systems. They will monitor fluxes of these ions and artificially alter inputs of some elements to the soil. The goals of these studies are (1) to assess how much acid deposition changes the supply of forest nutrients and affects forest productivity and (2) to determine if these changes may be related to forest diebacks occurring in some regions of the United States.

The base of information generated by our Walker Branch studies has served as a major impetus in the recent development of a proposed $37-million, six-year program of research on the impact of acid rain on forested watersheds. The goal of the research is to determine why some streams and lakes become acidified while others do not. Environmental researchers will propose to assess how the paths that water follows through the watershed and how biological, geological, and chemical interactions on land and within streams and lakes contribute to stream acidification. This proposed DOE program is being spearheaded by Webb Van Winkle and Robb Turner of ORNL in conjunction with staff members of three sister DOE laboratories—Argonne, Brookhaven, and Pacific Northwest. The program, whose final approval is still pending, will involve additions of simulated acid rain and snow to four watersheds, one each in the Northeast, Southeast, Midwest, and West, beginning in late 1985.

Air Pollution and Forest Growth

In 1982 a large national project to evaluate the potential role of air pollution in forest productivity was launched under the leadership of Sandy McLaughlin. Although there have been numerous reports of isolated cases of reduced tree growth believed to be caused by air



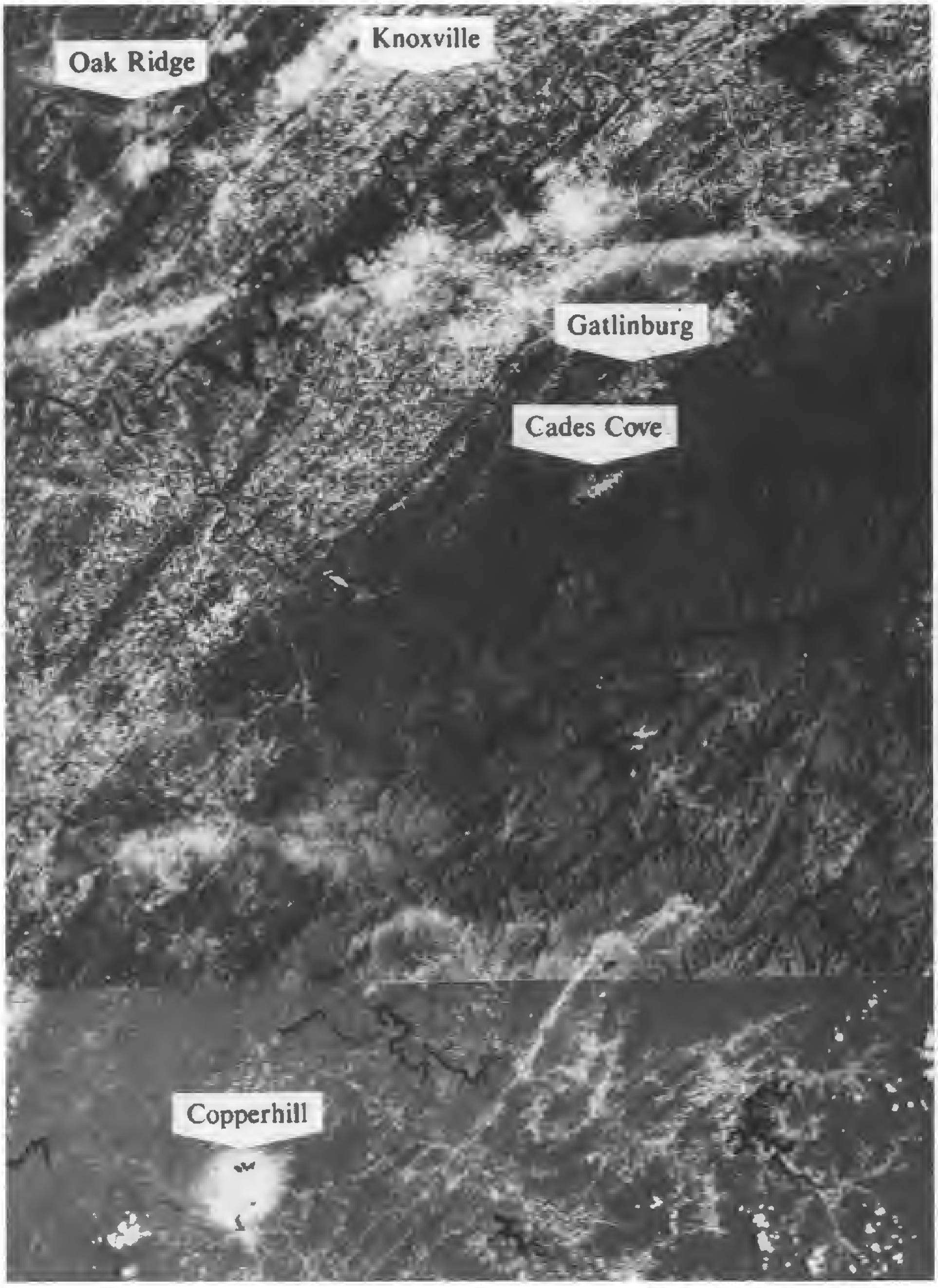
These three shortleaf pine tree cores (mounted in blocks of wood) show suppressed growth in rings formed during the period 1863–1912, when the Copperhill smelter was operating. The cores came from trees in the Smoky Mountains that were downwind from the copper smelter, which emitted sulfur dioxide. Suppressed growth is also seen in rings formed after 1950, possibly due to air pollution.

Dying spruce trees are found throughout the Great Smoky Mountains. The cause is unknown, but scientists have hypothesized that contributing factors may include acid rain, dry atmospheric deposition, and air pollution. (Photograph by S. B. McLaughlin.)

pollution, only recently has the information been available to evaluate regional-scale patterns of forest growth and to examine their correlation with various indices of atmospheric pollution. This information has been obtained by the FORAST (Forest Response to Anthropogenic Stress) project designed and implemented by McLaughlin and coworkers T. J. Blasing, Linda Mann, Ron McConathy, and Dan Duvick as well as collaborators at several eastern universities and government laboratories. The results of this two-year study are now being summarized.

Preliminary findings indicate that for some species there has been a marked and synchronous decrease in the width of annual growth rings formed during the past 20–25 years. The magnitude of the observed growth changes varies between species and with site quality and elevation. Because declining growth may be caused by natural factors such as tree and stand aging and regional changes in climate, this project is attempting to examine spatial and temporal gradients in a variety of possible causative factors. Included among these factors are regional levels of atmospheric pollutants such as sulfur and nitrogen oxides as well as ozone. The limitation of the study is that it cannot establish causal relationships between the decline in forest growth and the specific components of air pollution (such as sulfur dioxide or ozone). Nevertheless, this study's contribution in guiding the development of future research initiatives and in generating testable hypotheses regarding the possible causes for the observed slowdown in forest growth represents a major milestone in understanding the regional impacts of air pollutants.

An additional contribution of the FORAST project has been the development of techniques for using trace element signatures in tree-ring tissues as an index of past air pollution in a region. In May 1984 ESD's Fred Baes and McLaughlin published a paper in *Science* detailing the tree-ring record coinciding with the operation of the copper smelter in Copperhill, Tennessee, during the opening decade of the 20th century. They hypothesized that tree rings in the Great Smoky Mountains National



Landsat satellite imagery of East Tennessee. The bare spot at Copperhill shows the effect of logging and sulfur dioxide pollution on vegetation in this area.

Park (downwind from the smelter, which released large amounts of sulfur dioxide) might yield a correlation between tree growth rates and changes in the level of trace metals, such as iron and titanium (also released from the smelter), in ring tissues.

According to a report in the May 5, 1984, issue of *Science News*, Baes and McLaughlin's study of annual growth rings from shortleaf pine trees in eastern Tennessee shows "increasing metal concentrations since the 1950s and a possibly related decrease in growth during the 1970s." In their paper the ORNL researchers reported that tree rings formed during the 1863–1912 period, when the Copperhill smelter was in operation, showed suppressed growth and increased levels of iron and other metals.

Forest Canopy Interactions

Early work on Walker Branch Watershed suggested that the total amount of sulfur deposited on tree leaves and soil by atmospheric particles, gases, and aerosols (dry deposition) was probably large, but it was difficult to quantify. Since 1976 Steve Lindberg and his coworkers in ESD have played a leading role in the nation's research efforts to measure the extent to which dry deposition is a source of sulfates, nitrates, and trace metals to forested landscapes. More importantly, they have studied the role that the forest canopy plays in capturing materials from wet and dry deposition, such as metals dissolved in acid rain or attached to dry particles. Their innovative approaches to measuring dry deposition on both natural and artificial surfaces have led to increasingly better estimates of the relative contributions made by wet and dry deposition to the total

Studies of the Walker Branch Watershed forest canopy led by Steve Lindberg (above) indicate that as much as half of the deposited elements (such as sulfur) enter the forest ecosystem through dry deposition, that the surface area of the forest canopy significantly influences the seasonal contribution of such deposition to the watershed, and that the deciduous trees of the forest progressively neutralize acid rain percolating through the forest canopy.

deposition of sulfur and trace elements on the Walker Branch Watershed.

In a paper published in the March 26, 1982, issue of *Science*, Lindberg, Ralph Turner of ESD, and Robert Harriss of the National Aeronautics and Space Administration reported that as much as half of the deposited elements, such as sulfur and lead, enter the forest ecosystem through dry deposition, and that reactions between rain and deposited particles on foliage can result in concentrations of toxic metals on leaf surfaces far higher than those occurring in rain alone.

Bill Hoffman, an Oak Ridge Associated Universities visiting professor working with Lindberg, found that the Walker Branch forest canopy progressively neutralizes acid rain percolating through it. Thus the canopy can alter the acidity of precipitation before it reaches forest soils, streams, and lakes.

Possible consequences of these reactions in the canopy, such as disruption of normal nutrient cycling, are now under study by Lindberg and Gary Lovett of ESD. Preliminary indications are that acidic deposition may increase the loss of nutrients from foliage by up to 40% above normal leaching rates. Lovett is also expanding on his recently published studies of cloud water deposition in high-elevation fir forests of New England by making similar measurements in the spruce-fir zones of the Great Smoky Mountains. In his earlier work, he found that these high-elevation forests receive nearly 50% of their total moisture and 70% to 80% of total sulfate and nitrate deposition from cloud water. The extremely high deposition rates may make an important contribution to the death observed among red spruce trees in high-elevation forests in Vermont and Tennessee.

ORNL has maintained a charter membership in the National Atmospheric Deposition Program. This national network of precipitation chemistry monitoring sites, which currently includes approximately 150 monitoring stations across the country, has been adopted as the core of a National Trends Network (NTN) under the sponsorship of the NAPAP program. At the monitoring site at the Oak Ridge National Environmental Research Park, deposition of a full suite of elements by precipitation has been monitored by Jan Coe of ESD both weekly and during rainfall events as a part of the NTN and Multi-State Atmospheric Pollution from Power Plants (MAP3S) programs. Quality-assured data from these networks, which use standardized siting and sampling protocols, form the basis for evaluating atmospheric transport models ultimately needed to establish the relationship between sources of pollution and the deposition of those pollutants at receptor sites of interest.

Acid Rain and Vegetation

Some of ORNL's early studies of the effects of acidic precipitation on vegetation grew out of my Laboratory seed money proposal that was funded in 1975. At that time, ORNL's overall research effort in air pollution effects was in its infancy. The seed money investment in a facility to simulate rainfall in Laboratory greenhouses was a first step toward receiving funds from DOE, the Environmental Protection Agency (EPA), and later EPRI to explore the mechanisms of the effect of acid rain on vegetation.

At the outset, McLaughlin and I recognized that the study of individual pollutants such as ozone, sulfur dioxide, or acid rain in isolation from the influence of simultaneously occurring pollutants would prevent sorting out the principal components of air pollution responsible for long-term regional impacts on plant productivity. Based on that early concept, subsequent research at the Laboratory has focused on pollutant mixtures. McLaughlin, Bill Johnston, George Taylor, and Richard Norby have played a leading role in providing a better understanding of the complex mechanisms involved in plant response to pollutant mixtures.

Early in 1981 Johnston and I began a field study, the first of its kind, to decipher the relative importance of gaseous pollutants, such as ozone, and of acid rain in inhibiting the growth of crops, such as winter wheat and soybeans. Results to date have demonstrated that acid rain alone has little negative effect on the crops studied but that ozone alone reduces crop yield. The combined effect, which is equal to that of the two pollutants added together, results in reduced plant growth. As a result of the combined effect of acid rain and ozone, soybean productivity was 10% lower than that of soybeans protected from the pollutants. Soybeans are apparently more sensitive to acid rain than is winter wheat. At high levels of acid rain, we found that winter wheat actually had improved growth, suggesting that the nitrates in the rain had a fertilizing effect.

Brent Takemoto, a graduate student from Bowling Green State University, is using a diffusion porometer to measure the extent to which soybean leaf pores open up to exchange gas with the atmosphere. Leaf pores normally open up to take in carbon dioxide (CO_2) for photosynthesis, the essential process for plant growth. They also permit uptake of ozone. However, if exposed to a high concentration of ozone, leaf pores tend to close and absorb less CO_2. Ozone also photooxidizes chlorophyll pigment, thus reducing photosynthesis. When ozone impairs photosynthesis, the growth and productivity of exposed plants are inhibited.

Effects on Aquatic Ecosystems

Research at ORNL on the effects of atmospheric deposition on aquatic ecosystems has recently expanded to include a search for the physiological indicators of stress in trout exposed to episodic fluctuations of hydrogen ions in surface waters. This study, also funded by the Laboratory seed money program, involves collaborative work between Marshall Adams of ESD and Carl Burtis of the ORNL Chemical Technology Division (CTD). To date, their work has demonstrated the promising use of blood chemistry as an indicator of the stress of acid rain on trout. They have found that the blood in fish under acid stress has elevated levels of triglycerides and of the isoenzyme SGOT and reduced levels of sodium.

A second project was recently initiated by Jerry Elwood and his coworkers. Their field studies in

The degree to which acids in precipitation enter surface waters is regulated by processes within vegetation canopies and soils.

Chester Richmond, ORNL Associate Director for Biomedical and Environmental Sciences, represents ORNL on the national Interagency Task Force on Acid Precipitation.

ORNL Manages, Synthesizes, and Integrates Acid Precipitation Data

Another area of ORNL research on atmospheric deposition is the synthesis, integration, and assessment of the results from the broad range of research activities currently under way in the National Acid Precipitation Assessment Program (NAPAP). The role of this assessment activity is to pull together as complete a picture as possible of atmospheric deposition patterns and consequences and to provide that technical information to agency policymakers. Dick Olson and Paul Kanciruk of the ORNL Environmental Sciences Division (ESD) and Gloria Caton of the Information Division are helping the program immensely by developing centralized data repositories for the NAPAP assessment team and by coordinating the exchange of all forms of data on emissions, deposition, and natural resources for the federal government's Interagency Task Force on Acid Precipitation.

An important example of this centralized data management responsibility is the role that Kanciruk plays as data administrator for the National Surface Water Survey of the Environmental Protection Agency. During the fall quarter of 1984, some 2000 lakes in the eastern United States were sampled for a variety of chemical parameters indicating sensitivity to surface water acidification. The production of a verified and validated data base of surface water chemistry will be headquartered at ORNL. Once the data have been validated, ORNL staff will work with teams of scientists throughout the country to analyze spatial patterns of surface water chemistry and their statistical relationship to landscape characteristics and deposition patterns potentially responsible for changes in surface water chemistry, such as increased acidity and aluminum content.

The NAPAP program is charged with three congressionally mandated assessments of the present and future risk to the environment from atmospheric deposition. ORNL's roles in answering key questions and in data integration have led naturally to the Laboratory taking a lead role in developing methods for integrated assessment of the acid precipitation issue. For the 1985 assessment, ORNL staff members are involved in a synthesis of the current impact of acid deposition on aquatic and terrestrial ecosystems. In addition, methods for performing a fully integrated assessment of the costs of future levels of atmospheric deposition and the benefits of alternative control options are being developed by a team of scientists drawn from the National Laboratory Consortium (NLC), which is led by ORNL. A major issue of this integrated assessment will be the appropriate expression of uncertainty associated with the aggregation of atmospheric chemistry and transport data, response of receptor systems, and cost-benefit analyses. ESD's Bob Gardner and Virginia Dale are developing methods for

both the southern Appalachians and New England characterize the spatial and temporal patterns of water chemistry in acidic streams, with particular emphasis on the chemistry of aluminum in acidified waters. These studies represent the first of their kind to attempt to relate the chemical and biological effects of headwater stream acidification. The relationships between stream chemical parameters, such as pH (level of acidity), alkalinity, calcium, and aluminum, and biological variables, such as fish density and growth rates, are being determined. The results of this research will permit testing of the general hypothesis that the biological responses to

quantitatively expressing the uncertainty associated with various control options likely to be proposed. For example, they and their colleagues will determine the uncertainty associated with computer model calculations that compare the cost of proposed controls to reduce emissions from power plants in the East and Midwest with the benefit of reducing ecological damage from acid rain in the East.

In late 1984 the Environmental Protection Agency (EPA) sampled about 2000 lakes in the eastern United States for acidity and other parameters. To reach the many lakes that are inaccessible by road and to hasten the collection and analysis of samples, EPA used helicopters.

Using a syringe, Marshall Adams draws blood from a trout. Changes in blood chemistry induced by the fish's exposure to pulses of acidity will be determined by Carl Burtis with a centrifugal fast analyzer. Fish may be exposed to pulses of acidity during rainstorm and snowmelt events. Preliminary findings suggest that fish subjected to acid stress have higher than normal levels of triglycerides and lower than normal levels of sodium in their blood.

Mary Ann Bogle collects a water sample from the Sugar Cove Branch in the Cherokee National Forest on the Tellico Plain. The water will be analyzed as part of a project studying the effects on fish growth and density of changes in surface water chemistry such as increased acidity and aluminum content.

stream acidification are most pronounced in the headwaters and progressively decrease downstream. Hydrologic events such as stormflow and snowmelt typically introduce acidity and aluminum into streams as a pulse, particularly from sensitive forested watersheds. Such pulses may cause considerable acid stress on fish.

A third project, involving Van Winkle, Jim Breck, and Sigurd Christensen of ESD and colleagues at the University of Wyoming will develop and evaluate fish population models that incorporate laboratory data on the combined effects of acidity and aluminum on fish in low-calcium waters (surface waters whose underlying bedrock contains little limestone, which normally neutralizes acids in water).

Future Opportunities for ORNL

During the past year, aided by discretionary funds from ORNL Central Management, Richard Genung and Suman Singh of CTD have begun to evaluate potential opportunities for the Laboratory to contribute innovative technological breakthroughs in pollution control technology. The aim of this technology is to reduce emissions of acidic precipitation precursors such as sulfur dioxide and nitric oxide. Flue gas desulfurization (FGD) technology (scrubbers) available now is costly and limited in its effectiveness. Some utilities, in fact, have argued that mitigation rather than control measures might be cheaper; for example, acidified soils and waters could be neutralized by adding powdered limestone instead of by installing expensive scrubbers on coal-fired power plants to restrict sulfur emissions. Research and development efforts at ORNL and elsewhere are exploring options that may be more efficient and economical than FGD technology, such as coal cleaning and fluidized-bed-combustion and gasification-combined cycles. Several promising ideas have surfaced, such as a membrane separation technique and a one-step flue-gas treatment process. Further development of the most promising of these concepts will be pursued with additional discretionary funds during fiscal year 1985.

Arnold Hunley sprays insecticide on soybean plants to ward away spider mites and army worms. To preserve the experimental crop, the plants are sprayed to prevent disease and insect infestation and are irrigated during periods of extreme drought. University of Tennessee researchers are using some ORNL plots to determine which of 13 different varieties of soybeans are particularly resistant to damage from acid rain and which are particularly sensitive to acid rain.

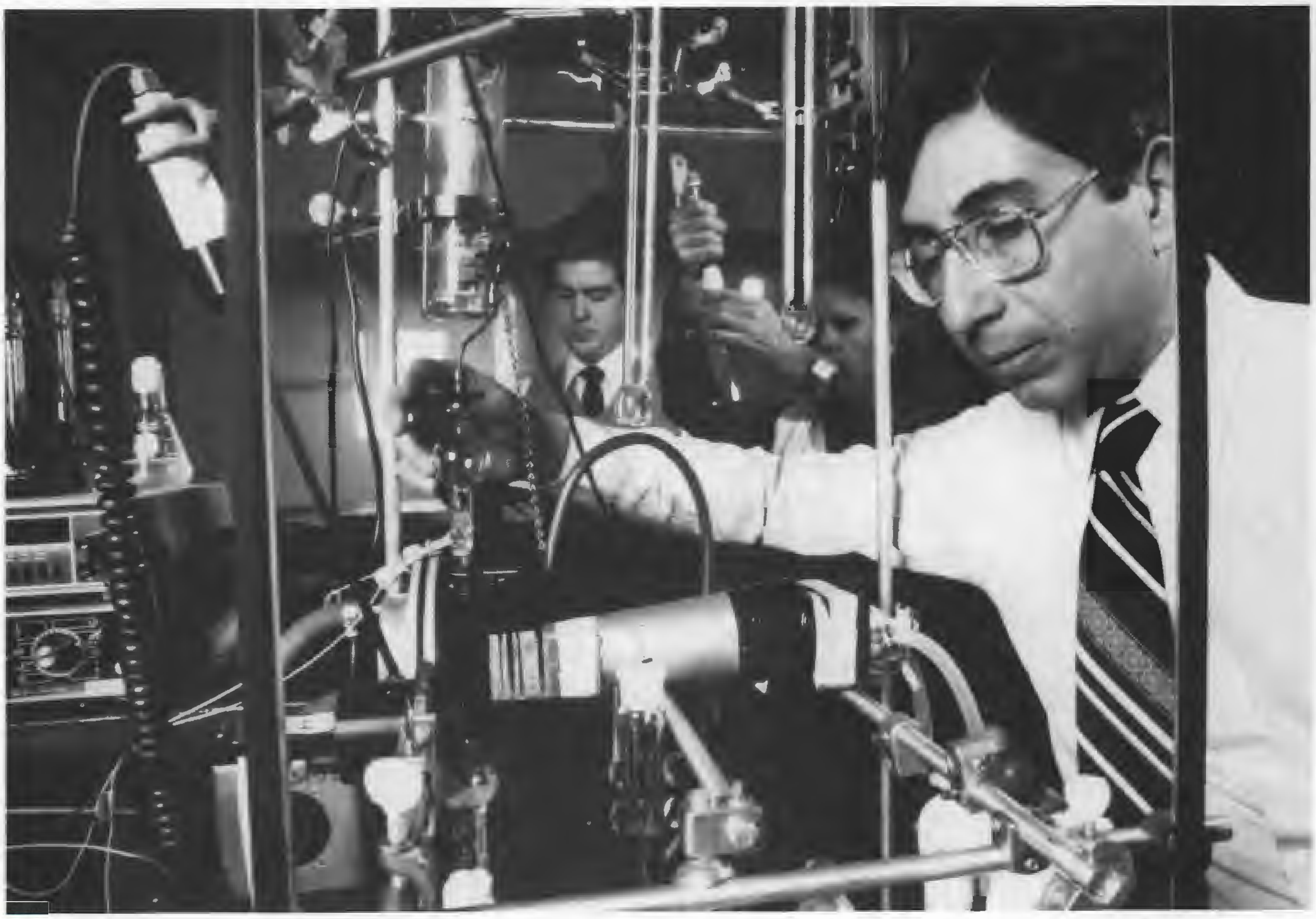
In addition, Bob Honea and Dick Rush of the Energy Division, in conjunction with Richard Durfee of the Computing and Telecommunications Division, are exploring the use of the Laboratory's capability in using Landsat remote-sensing imagery to evaluate whether a link exists between past changes in land use patterns and changes in surface water chemistry.

Conclusion

Atmospheric deposition research in Oak Ridge has resulted in the development of innovative methods for understanding and reducing the impacts of acid rain and sources of dry sulfates. Measurement of dry deposition on forest canopies has been advanced both by direct measurement techniques using surrogate surfaces (for large particles) and by eddy correlation techniques (for small particles and gases), which are being developed by the National Oceanic and Atmospheric Administration's Atmospheric Turbulence and Diffusion Laboratory in Oak Ridge. The unique system developed at ORNL to simulate rainfall over field-grown vegetation while simultaneously excluding ambient rainfall and ambient gaseous pollutants is the first of its kind to separate out the relative impact of wet and dry deposition on green plants and to permit measurement of the net response to an isolated pollution stress.

An innovative system for the measurement of gaseous uptake by field-grown vegetation represents a major advance in determining the effect of short-term fluctuations in pollutant concentrations on plant response. New, fast-response instrumentation developed at ORNL is permitting staff scientists to study changes in fish blood chemistry as a function of rapid changes in water chemistry that occur during storm events.

Finally, new techniques in information management (see box) are being developed to permit the aggregation of many diverse forms of data and models to support the synthesis and analysis of the ecological consequences of atmospheric deposition. The multipurpose, multidisciplinary nature of ORNL, in combination with a commitment to excellence in research and to answering the long-term "big picture" questions, has made the Laboratory a key contributor in tackling the complex problems associated with this important national issue.

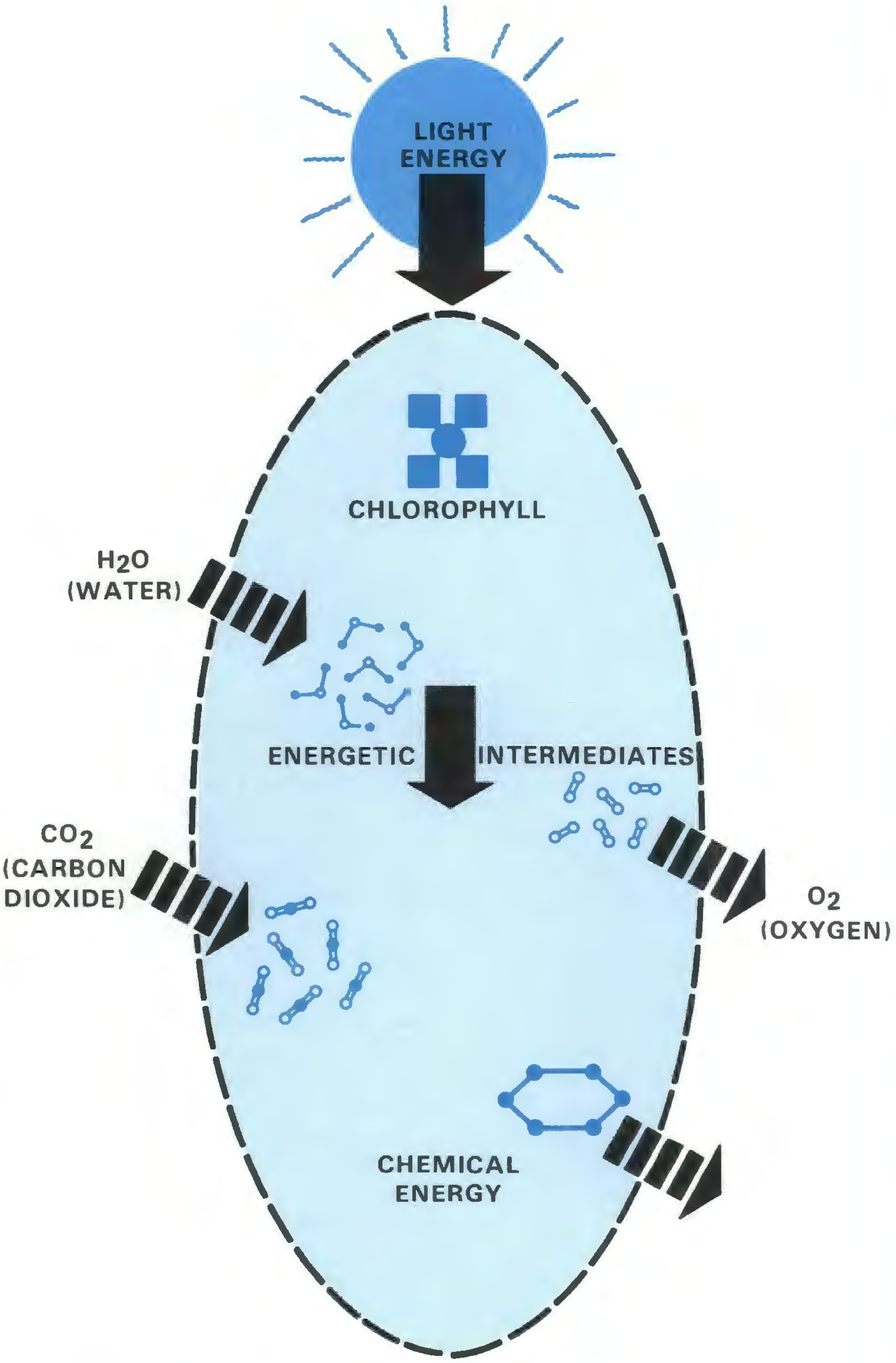


Elias Greenbaum is a group leader in ORNL's Chemical Technology Division. His research responsibilities are physical and chemical problems in photosynthesis and their application to energy and the environment. He has a Ph.D. degree in experimental physics from Columbia University and has recently been elected a Fellow of the American Physical Society. The research described in this article was supported by the Department of Energy, the Gas Research Institute, and the Solar Energy Research Institute. Here, Greenbaum and, behind him, Mark E. Reeves (left) and James E. Thompson work in the experimental facility used at ORNL to study photosynthetic water splitting.

Photosynthetic Water Splitting

By ELIAS GREENBAUM

Photosynthesis is the biological process in which visible light energy is converted into stored chemical energy. This stored energy, in the form of food, biomass, and fossil fuels, has allowed the development of the animal kingdom as well as modern civilization. Photosynthesis is a self-replicating process that can synthesize energy-rich biomolecules such as carbohydrates, proteins, lipids, and nucleic acids (the key constituents of living matter) from renewable inorganic resources such as water, mineral salts, and atmospheric carbon dioxide as the sole carbon source. A key reaction



In normal plant photosynthesis energy-rich, carbon-based biomolecules are synthesized from water, carbon dioxide, and mineral salts. Sunlight provides the energy to drive the synthesis.

in this synthesis is one of the most intriguing challenges at the frontier of photosynthesis research: water splitting.

This water-splitting reaction may be summarized by the simple equation:

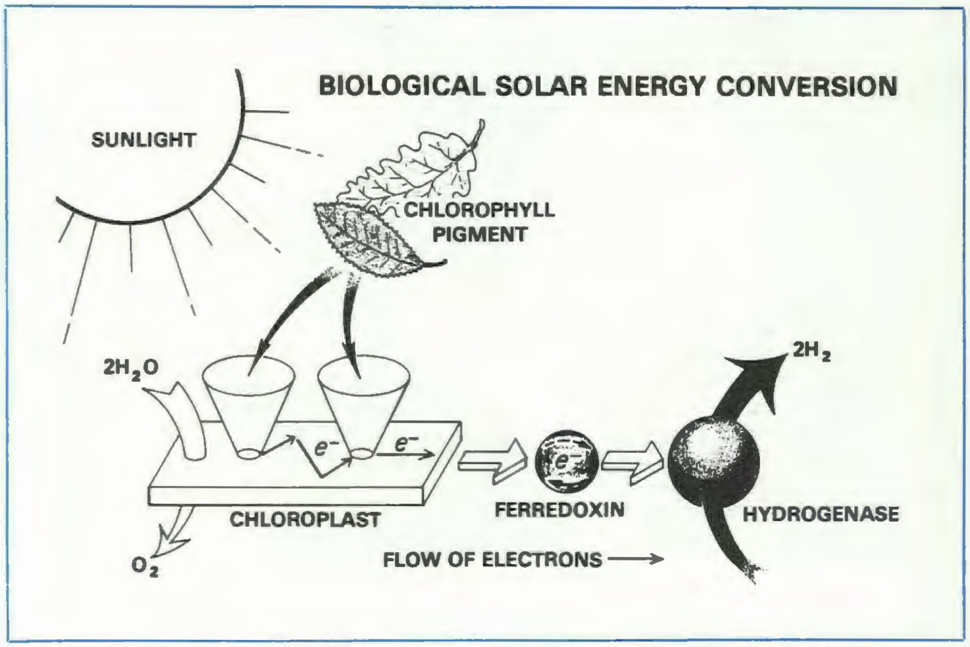
$$2H_2O \xrightarrow{light} O_2 + 4H^+ + 4e^-$$

When water is split photosynthetically, molecular oxygen is produced along with protons (H^+) and electrons (e^-). In normal photosynthesis a second light reaction further elevates the energy level of the electrons so that they may enter the biosynthetic pathway for the production of energy-rich carbon-based molecules. The path of inorganic carbon in this process was first elucidated by Nobel laureate Melvin Calvin and his collaborators. In this article, however, I will discuss a novel photosynthetic pathway in which the flow of electrons is used to produce molecular hydrogen as the energy-rich photoproduct. In this pathway the second light reaction is used to reduce protons as follows:

$$4e^- + 4H^+ \xrightarrow{light} 2H_2$$

The overall reaction, therefore, is the photo-induced cleavage of water into its elemental constituents: hydrogen and oxygen. This reaction can be carried out in a number of ways. For example, we can use living systems composed of green algae or cyanobacteria or a nonliving system composed of isolated chloroplasts, ferredoxin, and hydrogenase. (Chloroplasts are the photochemical factories of photosynthesis. Hydrogenase is the special biocatalyst, or enzyme, that catalyzes the production of molecular hydrogen. Ferredoxin is an electron relay that connects electron flow from the chloroplasts to the hydrogenase.)

Photosynthesis is currently believed to utilize two light reactions, reactions that are linked



Sunlight is used to drive photosynthetic reactions that split water into oxygen and hydrogen. The sunlight is captured by the chlorophyll pigment and funneled to the reaction centers of photosynthesis. Oxygen is produced in the chloroplasts. Ferredoxin, a molecular shuttle, transports electrons from the chloroplasts to the hydrogenase, the enzyme that catalyzes the production of hydrogen. Hydrogen produced in this manner is of interest because it is solar energy stored as a gaseous fuel. Such a fuel can be converted to electricity at high efficiency when desired by chemically reacting it in a fuel cell. Hydrogen can also be used as a feedstock for chemicals and can be substituted for liquid fuels to drive engines, in, for example, automobiles and jet aircraft.

in series by an electron transport chain. The light reaction associated with hydrogen evolution (and carbon dioxide reduction) is called Photosystem I; the light reaction associated with water splitting and oxygen evolution is called Photosystem II. Photosystem I is fairly well understood, but the molecular structure and function of Photosystem II remain a challenging scientific problem, both from a thermodynamic and a chemical-mechanistic point of view. For example, we know from thermodynamic tables that a fairly powerful oxidizing potential (>0.8 V with respect to the normal hydrogen electrode pH = 7) has to be generated to oxidize water to oxygen. In plants and algae, however, this reaction takes place in a molecular architectural structure that is made up of reduced biomolecules. The actual water-splitting reaction therefore occurs in a specialized and protective microenvironment, the structure of which is still unknown, although strong evidence exists to indicate that manganese is an essential cofactor in the water-splitting reaction.

Oxygen Evolution

The molecular mechanism of oxygen evolution is a challenging problem as well. As mentioned earlier, four electrons have to be removed from two molecules of water to evolve one molecule of oxygen. From Einstein's Law of Photochemical Equivalence, we know that one photon will eject one electron. Therefore, a minimum of four photons must be absorbed in a Photosystem II water-splitting reaction center to evolve a molecule of oxygen. These four photons eject electrons from donor to acceptor molecules. The positive charges left behind on the donor molecules are the oxidizing equivalents that oxidize water (i.e., produce oxygen from water).

The best theoretical model for the mechanism of oxygen evolution in photosynthesis is the one developed by the late Bessel Kok and his coworkers at Martin Marietta Laboratories. Kok based his model on results from experiments performed by Pierre Joliot and his coworkers at the Institut de Biologie Physico-Chimique as well as on subsequent collaborative research by himself and Joliot at Martin Marietta Laboratories. His model is based on the characteristic pattern of oxygen yields when photosynthetic preparations are illuminated by brief saturating flashes of light from xenon flash lamps. In his model Kok postulates that oxygen evolution consists of a linear sequence of photon absorption and electron removal. He further postulates that an electron carrier exists in multiple metastable oxidation-reduction states, with each photo-induced state being more oxidized than its predecessor by one oxidizing equivalent. According to Kok, when four oxidizing equivalents have accumulated, water is split, and oxygen is produced. The electron carrier simultaneously cycles to its

Using light and algae or nonliving systems, ORNL scientists have photosynthetically split water into oxygen and hydrogen, a clean fuel and chemical feedstock.

initial position in the "clock" sequence.

Energy conversion by the photochemical machinery of photosynthesis is analogous to energy conversion by silicon photovoltaic cells. The first excited singlet state of chlorophyll (700 nm, 1.8 eV) corresponds to the band-gap of the semiconductor, and the biological electron carriers and biocatalysts provide an external conductive pathway by which the energy is conserved. One such pathway, the focus of this article, is the simultaneous photoproduction of molecular hydrogen and oxygen. Photosynthesis research in the Chemical Technology Division of Oak Ridge National Laboratory—which I have performed in collaboration with Jonathan Woodward, Mark E. Reeves, Joseph P. Eubanks, and James E. Thompson—focuses on the energetics and molecular mechanisms of light energy conversion by photosynthesis.

ORNL's Algae Studies

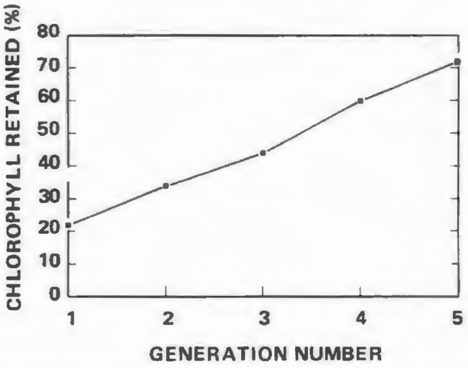
In using microalgae for the biophotolysis of water, an important consideration is the long-term stability and endurance of these organisms during their prolonged periods of simultaneous hydrogen and oxygen production. Reeves and I have performed the first experiments that demonstrate the long-term stability of green algae as they produce hydrogen and oxygen. We found that using visible light irradiation in an oxygen-free environment produces algal variants with enhanced capabilities for splitting water and producing hydrogen. We have also discovered that certain microscopic green algae are extremely rugged organisms for experiments in biophotolysis. For example, in working with the wild-type green alga *Chlamydomonas reinhardtii*, we found that hydrogen and oxygen can be produced simultaneously in a light-driven reaction for hundreds of hours. If these algae are used as the inoculum for algal growth in a new culture medium, a second generation of algae is produced that can be used in a new round of experiments for hydrogen and oxygen production. We have repeated these types of experiments through five cycles consisting of hydrogen and oxygen production alternated with normal periods of photosynthesis.

Mark Reeves (left) checks a cuvette that holds algae, which is exposed to light from the xenon flash lamp up front. Jim Thompson checks the power source that supplies electricity to the lamp. The two researchers have used this apparatus to measure photosynthetic unit sizes for hydrogen and oxygen production from living algae.

The simultaneous photoproduction of hydrogen and oxygen represents a severe physiological stress for the organisms. This stress is manifested in two ways: (1) by the quantitative loss of chlorophyll at the end of each interval of irradiation and (2) by the absolute rates of light-driven hydrogen and oxygen production. We have discovered that the physiological requirements for the simultaneous photoproduction of hydrogen and oxygen serve as selection or adaptation pressures for the survival of algal variants that can better sustain the photoreactions as measured by retention of chlorophyll in the algal sample at the end of each 150-h interval. In this instance, the pressures are the anaerobic (an almost oxygen-free) atmosphere and irradiation that allow a subpopulation of the algae to survive better than the other subpopulations. We have also demonstrated that significant increases in the integrated yields of hydrogen can be obtained by this technique of alternating anaerobiosis and hydrogen production with normal photosynthetic culturing. For example, one strain of *Chlamydomonas*, after 32 h of anaerobiosis and irradiation, exhibited a 320% increase in hydrogen yield in third-cycle cells over that of first-cycle cells.

Nonliving Systems

Another approach to photosynthetic water splitting is



Chlorophyll retention versus generation number for* Chlamydomonas reinhardtii *137c(+). These data demonstrate that alternating hydrogen production with periods of normal photosynthesis is a method for selecting subpopulations of algae with increasing durability of chlorophyll photopigment.

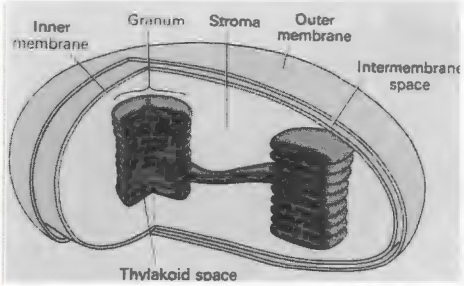
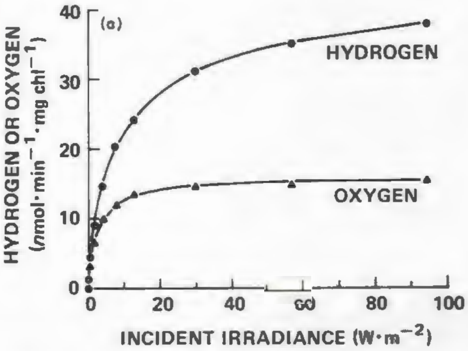


Diagram of chloroplast with its labeled components. The differences in the analytical shapes of the light saturation curves of the simultaneous photoproduction of hydrogen and oxygen may be related to the heterogeneous distribution of the reaction centers of photosynthesis in the photosynthetic membranes. (©1972 by Wadsworth Publishing Company, Inc.)



The first measurements of the light-saturation curves of the simultaneous photosynthetic production of hydrogen and oxygen. The analytical shapes of the light-saturation curves of photosynthesis contain a considerable amount of kinetic and mechanistic information on the overall photoprocesses.

the use of reconstituted in vitro systems, such as the one composed of isolated spinach chloroplasts, ferredoxin, and hydrogenase. Stabilizing the water-splitting reaction center in this extracted nonliving system is a challenging and important biochemical problem. Upon extraction from photosynthetic tissues, the water-splitting reaction and oxygen evolution are among the first physiological functions to be lost. We have begun to make progress in stabilizing nonliving systems to retain these useful functions. Using techniques of stabilization and immobilization of extracted organelles and enzymes, Woodward has performed the first measurements of the simultaneous photoproduction of hydrogen and oxygen in an immobilized nonliving system. Because immobilization techniques frequently lead to greater stability of extracted biological components, we are optimistic that greater improvements in yields and stability can be made using this approach.

Another key factor in biological energy production is net conversion efficiency. Conversion efficiency is a thermodynamic concept, which represents the amount of chemical energy stored in molecular hydrogen divided by the energy of the equivalent solar radiation needed to produce the hydrogen. Thompson has measured the absolute efficiencies of converting light energy into hydrogen in several microalgae using an original experimental technique that involves entrapping algae on filter paper in a precisely known circular geometry. These filter paper–entrapped algae are then put in a specially constructed chamber with a window of optically flat front surface and irradiated in a direction perpendicular to the plane of the algae. Oxygen and hydrogen are produced in the interior of the algal cells. These gases diffuse from the solid-liquid matrix of the algae into the surrounding gas phase, where they are swept out of the reaction chamber and into gas-phase sensors located downstream from the algae.

Photosynthesis is a light-dependent process. It is linear with light at low intensities but saturates at higher intensities—that is, the rate of photosynthesis levels off as the light intensities exceed a maximum limit. Photobiological hydrogen evolution behaves similarly. Conversion efficiencies of 2 to 3% are observed in the linear, low-intensity portion of the light saturation curve. These values decrease steadily with higher light intensity because of photosynthetic saturation, which occurs because the rate of excitation of the reaction centers exceeds the ability of the biochemical electron transport system to process the excitations (i.e., split water and produce energy-rich molecules). In principle, however, a strategy could be employed to sustain higher efficiencies with increasing light intensity. This strategy, first suggested by Kok, would use mutant algae with a smaller photosynthetic unit size. The photosynthetic unit size is the ratio of the number of light-harvesting antenna chlorophyll molecules to the specialized chlorophyll reaction center at which the primary photochemistry of photosynthesis occurs. Decreasing the number of antenna molecules relative to the number of reaction centers helps reduce this kinetic imbalance at higher light intensities. This strategy is being investigated at ORNL.

Perry Eubanks (left) and Jonathan Woodward discuss data on the biophotolysis of water.

In addition to stability and efficiency in photosynthetic water splitting, another factor of interest is the nature of the algae and the source of water. Working in collaboration with Robert R. L. Guillard of the Bigelow Laboratory for Ocean Sciences, we have discovered species of marine microalgae that are capable of sustained simultaneous photoproduction of hydrogen and oxygen where seawater serves as the primary substrate for water splitting. Marine algae are particularly appealing from a practical point of view because essentially all of the nutrients for culturing the algae already exist in seawater and because the water requirements will not compete with freshwater supplies for direct human consumption and agricultural applications.

Inherent in the light saturation curve of photosynthesis is a considerable amount of kinetic and mechanistic information on the overall process. Eubanks has recently performed the first measurements of the light saturation curves of the simultaneous photoproduction of hydrogen and oxygen. The key result of these experiments is that the analytical shapes of the hydrogen and oxygen curves are not the same. That is, the hydrogen curve is not related to the oxygen curve by a simple factor of 2 as would be expected from the reaction $2H_2O \rightarrow 2H_2 + O_2$. These results are intriguing because they imply a partial uncoupling of the two light reactions of photosynthesis. The question of coupling and location of the light reactions is another frontier research problem in photosynthesis. Our results on the simultaneous photoproduction of molecular hydrogen and oxygen are consistent with current thinking that the physical separation between the light reactions of photosynthesis is larger than had previously been thought and that the reactions are partitioned according to the morphological structure of the photosynthetic membranes.

The key goals of photosynthetic water-splitting research in the Chemical Technology Division are a deeper knowledge and understanding of the physics and chemistry of the light reactions of photosynthesis and the application of this knowledge to a practical chemical engineering process for the eventual production of renewable fuels and chemical feedstocks. Through further study and research, we will surely achieve these goals.

BOOKS

"For those of us in the nuclear field, this book represents 'preaching to the choir,' but good preaching it is nonetheless."

Before It's Too Late: A Scientist's Case for Nuclear Energy, *Bernard L. Cohen, Plenum Press, New York (1984). Reviewed by Ernest G. Silver, editor of* Nuclear Safety.

Those of us on the staff at ORNL who remember Bernie Cohen (now professor of physics and director of the Scaife Nuclear Physics Laboratory at the University of Pittsburgh) from his days in the Electronuclear (now Physics) Division in the 1950s and who have followed his career of nuclear advocacy in the years since will not be surprised that this book is a hard-hitting statement of the pronuclear position. It will also be no surprise to Cohen's ORNL colleagues that his arguments are cogent, his scientific foundation solid, and his knowledge of the nuclear energy field encyclopedic.

The other side of the coin with respect to such a book of frank advocacy, strongly felt and strongly expressed, is that it contains many uncompromising attacks on those whom Cohen believes to be antinuclear. These attacks are made not only on the antinukes' arguments and conclusions—refutations that are entirely proper and desirable in such a book—but also on the motives and intellectual honesty of the "antis" and especially of the news media. Although I agree with much of what Cohen says in this regard, I feel it reduces the effectiveness of his work by lowering his standards.

One example will demonstrate this point. Cohen discusses a segment of the CBS "60 Minutes" television program on the Soviet Union's Kyshtym radioactive waste accident. The segment featured comments by Zorin Medvedev, a scientist who fled the Soviet Union, and antinuclear activist Ralph Nader. In Cohen's view, the CBS selection of material deliberately suppressed the fact that an Oak Ridge study, which the "60 Minutes" reporters learned about in interviews with ORNL researchers, showed that the conditions in the United States were so different that no Kyshtym-type event could possibly occur in this country. Nevertheless, Cohen writes that Nader, "who obviously had no information on this incident, spouted off about how the affair illustrates the great dangers of radioactive waste." Cohen then goes on to say:

> I am certain that failure to convey the answer of the scientific studies to this key question [i.e., "Could it happen here?"] was not an oversight by the TV crew but a purposeful attempt to conceal that information from the American public. Instead they gave . . . Ralph Nader's implied answer that is scientifically indefensible. There was no other reason to have Nader on the show . . . . His only interest in the situation was to make politically inspired propaganda, and CBS-TV offered him this free opportunity to do so.

I deplore that sort of rhetoric and wish it had been softened by letting the facts and arguments speak for themselves.

Having said that, however, let me say also that I loved the book. It is an invaluable reference to almost every aspect of the nuclear debate and should be an indispensable tool for those who engage in it. Not all of the book will be easy going for lay readers averse to graphs and quantitative discussions, but the author does try to make his subject comprehensible to that readership and has succeeded at least to the point where, with a certain amount of effort and perseverance, it may be understood.

After an introduction that suggests reasons for public unease with radiation (including some preliminary swipes against John Gofman, Ernest Sternglass, and Helen Caldicott—three major *bêtes noires* in his bestiary of antinukes), Cohen deals with the nature of ionizing radiation, explaining what is known about its dangers compared with other insults to

"Because the public does not agree that the risk of a catastrophic meltdown is low, Cohen discusses why the public perceptions are so distorted and finds that the news media are most at fault."

the body. His discussion of the relative magnitudes of various radiation sources and their risks is excellent. He treats with special attention the Mancuso study and other studies that tend to impute a much-higher-than-official estimate of the risks of low-level radiation.

Next comes a discussion of core meltdowns in which Cohen discusses the Three Mile Island event at length and examines the magnitude of the risks posed by major reactor accidents. He concludes that meltdowns are improbable events (none has happened yet) and that if any were to occur, most would have no effect on the public at all; but he concedes that the "average" meltdown might cause "only" 400 fatalities and $100 million in off-site property damage. Because the public clearly does not appear to agree with the conclusion that the risk of a catastrophic meltdown is very low, Cohen discusses why the public perceptions are so distorted and again finds, not surprisingly, that the news media are most at fault.

Cohen then cogently discusses the nature of risk, how it may be quantified, and what consideration of various risks can reveal. Using the readily understood concept of loss of life expectancy as a way to compare different risks results in some very graphic (in both senses of the word) comparisons.

The single issue to which Cohen devotes the most space is nuclear waste, both high and low level, and the risk it imposes. His treatment includes pathways of radionuclides from disposal sites to the biosphere and especially to people (I cherish the section heading "Probability for an atom in the ground to enter a human stomach"); waste transport questions; and, most interesting of all, the "philosophical" issue of how to weight the far-distant-future impacts of present activities. In all of it he makes very good sense.

The next major issue Cohen covers is the coupling—by the news media and in the public's mind—between production of bomb-grade plutonium and civilian breeder reactors. Not surprisingly, he finds that the coupling is very weak, that reactor-fuel plutonium makes poor explosives, that plutonium would not make an attractive terrorist weapon, and that therefore the risk of terrorist diversion of breeder-produced plutonium to hold society hostage is very small.

Last, Cohen turns to the problem of the economics of nuclear energy and its competitors. Although admittedly writing as a nonexpert in this area, Cohen makes a convincing case that much of the recent cost increase is not intrinsic to nuclear energy and its inherent risks. Instead, he attributes rising costs to "regulatory ratchetting"—that is, the ever-tighter regulation of nuclear power plants to reduce hypothetical risks ever lower, at rapidly escalating cost per (hypothetical) life saved. Cohen calls this cost problem the "Achilles heel" of nuclear power and admits that under present circumstances the ordering of new plants by utilities is practically excluded. Nevertheless, his comparison shows that coal-generated electricity from new plants is increasing in cost almost as fast as nuclear electricity. And in his final set of arguments, he demolishes the hope for really cheap and clean solar electricity as a practical alternative.

As I stated at the outset, this book is flawed, at least to my taste, by Cohen's excessively strident attack on his opponents; nevertheless, it very clearly presents, in a manner suitable for intelligent lay persons, the scientific factors bearing on the nuclear debate. For those of us in the nuclear field, this book represents "preaching to the choir," but good preaching it is nonetheless.

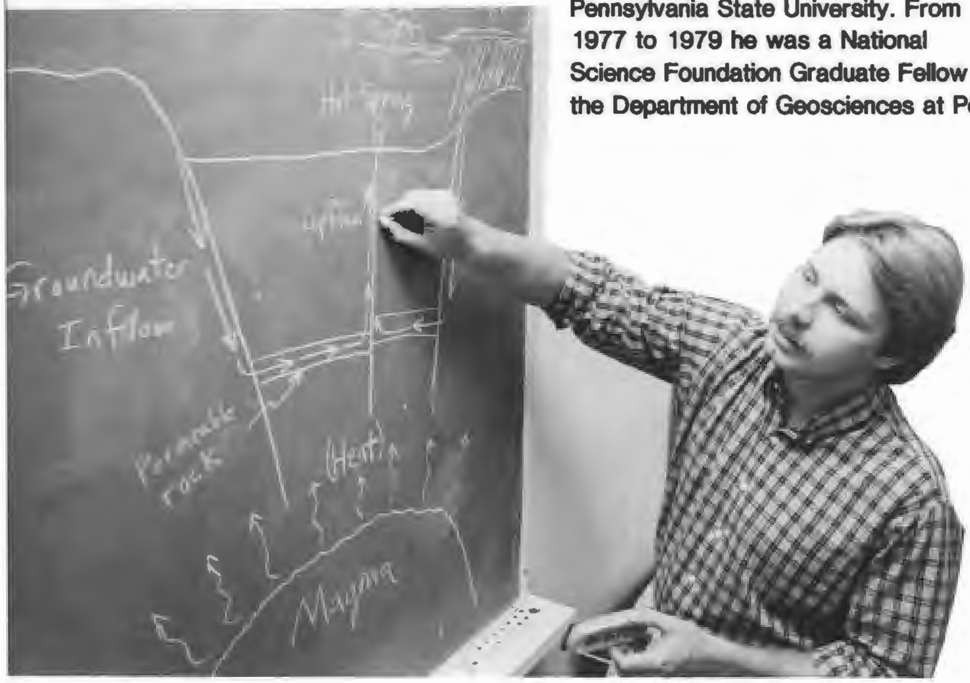
Mount St. Helens in Washington during the May 18, 1980, eruption.

Simulating Processes Within The Earth:

Experimental Geochemistry at ORNL

By DAVID COLE

Whether viewed globally or on a local scale, the earth is a dynamic and evolving chemical system. The recent volcanic eruption of Mount St. Helens in Washington and the discovery of seafloor hot spring vents at 21° N on the East Pacific Rise have focused attention on this fact. To appreciate fully the earth and its origin, one must understand the chemical processes that form rocks and minerals. However, direct observation is severely restricted; many of the major chemical



David R. Cole is a geochemist in the ORNL Chemistry Division. He was born in Cooperstown, New York, and was raised in Lake George, New York. In 1980 he obtained a Ph.D. degree in geochemistry and mineralogy from Pennsylvania State University. From 1977 to 1979 he was a National Science Foundation Graduate Fellow in the Department of Geosciences at Penn State. Before joining the Chemistry Division as a research scientist in July 1982, Cole was a research geochemist with the Earth Science Laboratory of the University of Utah Research Institute in Salt Lake City, a laboratory supported by the Department of Energy. During his stay in Utah he helped develop quantitative models of stable isotope and chemical behavior in geothermal and ore deposit systems in the western United States. Since coming to ORNL, Cole has been theoretically evaluating the mechanisms and rates of stable isotope exchange between minerals and aqueous solutions at elevated temperatures and pressures. In addition, he and Ed Drummond have been modeling the transport and depositional mechanisms of metals, such as gold and silver, in geothermal brines. Here, he shows his schematic of a geothermal system with a magma chamber as a heat source.

processes and events occur at great depths or took place in the prehistoric past. In fact, given present technological capabilities (drilling depths to about 6.4 km, or 4 miles), only about 0.3% of the volume of the earth is readily accessible to sampling or direct observation. Therefore, an understanding of the chemical processes operating within the earth is heavily dependent on the ability to simulate, through experimental or theoretical means, deep-earth conditions currently inaccessible to study.

Analogue studies of simplified geological systems, or experiments that model the natural systems, have been the focus of the geosciences research program in the Chemistry Division of Oak Ridge National Laboratory for the past six years. The principal objective of the program, which is funded by the Division of Engineering, Mathematical and Geosciences in the Office of Basic Energy Sciences of the Department of Energy, is to provide basic geochemical information on high-temperature processes in aqueous and molten-silicate chemical systems responsible for the distribution of of elements in the earth's crust. To do this the program conducts experimental studies over ranges of temperature, pressure, and composition appropriate for depths to 20 km (12 miles, with a temperature and pressure of 1200°C and 4000 bars, respectively).

These experimental geochemical studies can be divided into two broad categories, hydrothermal (hot water) and silicate melt (molten rock) geochemistry. In both classifications we are interested in volatile components, such as water, carbon dioxide, and sulfur dioxide, and their role in the formation of crustal rocks over a wide range of temperatures and pressures. ORNL hydrothermal geochemical research emphasizes the role of aqueous fluids in transporting and depositing the dissolved minerals that form rocks; this research includes studies of mineral dissolution and the chemical form and stability (the temperature, pressure, and composition range over which they occur) of the dissolved constituents up to 600°C and 200 MPa (2000 bars). The current experimental work on silicate melt systems focuses on the mineral stabilities, mineral growth

Geochemists at ORNL are using unique devices to simulate in a very short time the chemical processes that form rocks and minerals. The basic research may help solve problems affecting geothermal power, nuclear waste isolation, and exploration for ores and natural gas.

Hot springs and geysers not only release heat from the earth but also deposit minerals. Examples are Echinus Geyser at Norris Basin (left), the hot springs at Firehole River (center), and Mammoth Hot Springs (right), all at Yellowstone National Park.

rates, and element distributions over temperatures ranging from 600 to 1400°C and pressures to 500 MPa (5000 bars or 72,500 psi) under controlled partial pressures of oxygen.

Together, these generic studies provide insight into problems associated with volcanic processes, mineral resource exploration, enhanced techniques for oil and ore recovery, nuclear waste isolation, geothermal energy, development of ceramic structural materials, and energy transfer in magmatic-hydrothermal systems. The following discussion highlights a portion of the research conducted in these broad areas.

Hydrothermal Geochemistry

Without realizing it, many of us perform a simple hydrothermal experiment every day in our kitchens. Each time we put a teapot of water on the burner to boil, we simulate the physical and chemical processes in many hot spring geysers throughout the world. We observe a vapor (or steam) plume at the spout and mineral deposition at the bottom and sides of the pot. Anyone who has been to Yellowstone National Park and seen the vapor plume of the Old Faithful geyser rising from an orifice surrounded by mineral deposits realizes the similarity of the geyser to boiling water in a teapot.

Natural hydrothermal solutions are hot (>100°C) aqueous fluids ranging from dilute solutions of a single solute in water to complex systems containing high concentrations of more than ten dissolved species. These solutions play an important role in several geochemical and technological processes, for example, hydrothermal formation of mineral deposits, hydrothermal crystal growth and materials synthesis, and high-temperature industrial electrochemical processes. Hot aqueous solutions and mineral deposition can also corrode and clog pipes, respectively, leading to inefficient heat transfer in geothermal power systems and reduced operating capacity in water desalination systems, boilers, power plants, and cooling systems of nuclear reactors. To understand the complex behavior of various types of hydrothermal solutions, a large number of experimental investigations have been carried out to determine the thermodynamic properties of pure water and of aqueous solutions over wide ranges of temperature and pressure.

Based on previous hydrothermal rock-water experiments, we know that during the interaction of rocks and aqueous solutions at high temperature, certain minerals dissolve, while others precipitate, depending on the chemical form and concentration of the elements in solution. During mineral dissolution and precipitation, the porosities (percentage of void space) and permeabilities (ability of rock to transmit fluids) of the rocks can change dramatically, as can the aqueous chemistry. One can easily conclude that if this phenomenon occurs in geothermal systems or petroleum source rocks, the transport of hot fluids, whether water rich or petroleum rich, is directly affected. Because geologic exploration for geothermal systems, petroleum, and even ore deposits relies heavily on information gleaned from fluid chemistry, a complete understanding of the properties of aqueous solutions and their effects on minerals is crucial to the development of sound exploration models.

Significant contributions to these areas have been and are continuing to be made by ORNL researchers in the High Temperature/High Pressure Aqueous Group of the Chemistry

Division. The pioneering work on high-temperature properties of aqueous solutions by Charlie Baes, Dick Busey, Howard Holmes, Milt Lietzke, Bill Marshall, Bob Mesmer, and Fred Sweeton has been used extensively by geochemists in their studies of natural systems. The ORNL geochemistry program is, in fact, an outgrowth of earlier experimental work by members of this group. Currently, hydrothermal geochemistry research conducted by Ed Drummond, Dave Wesolowski, Marshall, me, and others has evolved to a substantial program that complements and to some degree augments the efforts of the Aqueous Group.

The ORNL hydrothermal geochemistry program is divided into two categories, experimental and modeling. The experimental effort uses the group's unique facilities, including *gold-cell pressure vessels* capable of studying corrosive systems at temperatures and pressures up to 600°C and 200 MPa (2000 bars), respectively; *titanium reaction vessels* for measuring mineral solubilities up to 300°C and 20 MPa; *conductance cells* for studies up to 800°C and 400 MPa (4000 bars); and *hydrogen electrode emf (electromotive force) cells* to measure pH-dependent mineral solubilities up to 300°C and 50 MPa. These unique facilities are being used to examine acid dissociation, hydrolysis (reaction of the elements with water) of metal ions, formation of chemical species in supercritical aqueous fluids and chloride brines, solubilities of minerals, and formation of methane by thermal decomposition of hydrocarbons. The modeling research is centered on examining complex high-temperature multicomponent fluid-mineral equilibria, and the rates of stable isotope exchange between minerals and fluids at elevated temperatures.

Origins of Natural Gas. How natural gas (methane) migrates from the deeper source rocks of sedimentary basins to reservoir rocks has long been a matter of speculation. One hypothesis is that acetate (CH_3COO^-), a common constituent in oil field brines, migrates in solution to the reservoir and then decomposes to carbon dioxide (CO_2) and methane (CH_4). This hypothesis would be valid if acetate decomposes at a rate slower than its rate of migration with water from sedimentary basins to reservoir rocks.

In an effort to understand the kinetics (rate and mechanism) of the thermal decarboxylation (removal of COO^- group) of acetate and the role of catalysis in forming carbon dioxide and methane, Drummond and Don Palmer have conducted a series of hydrothermal experiments to measure the decomposition rates of acetate in the presence of a variety of materials including gold, titanium, stainless steel, silica, magnetite (Fe_3O_4), and montmorillonite (a clay mineral). The rates of acetate decomposition varied greatly, depending on the catalytic substrate. Methane and carbon dioxide were the predominant reaction products of these experiments; however, mass spectrometric analysis revealed that hydrocarbons constitute as much as 40 mol % of the carbon in the reaction products, depending on the catalyst. Gold, titanium, and pure montmorillonite were the least active catalysts, whereas stainless steel, silica, and magnetite showed marked catalytic effects.

These results have important mechanistic implications for the process of natural gas migration because acetate is available in significant quantities and is highly mobile in the waters expelled during compaction of basin sediments. The appropriate physical, chemical, and geological constraints for acetate migration and decomposition were considered and integrated in a computer model that couples basin subsidence, compaction, and fluid flow parameters with chemical constraints dictated by the experimental kinetic data. This analysis suggests that a significant geological and chemical "window" exists wherein acetate is sufficiently stable to survive the thermal regime (90–130°C) of a sedimentary basin long enough to migrate out of the source rocks, and yet is sufficiently reactive to decarboxylate to form a natural gas deposit within the time frame imposed by the age of the basin sediments (10 million to 100 million years).

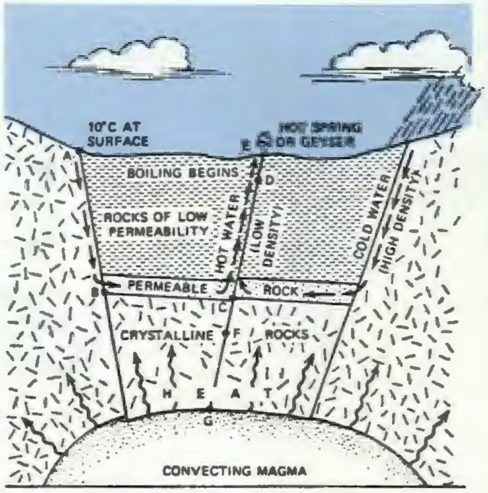
In addition to the implications for natural gas deposits, these results indicate that acetate might be a mobile precursor for the components of petroleum and can survive moderate hydrothermal temperatures (100–300°C) long enough to act as a complexing agent for metals, thereby promoting the mobility of these commodities in some ore-forming systems. Preliminary experiments at 250°C indicate that significant concentrations of gold and iron occur in solution containing acetate and acetic acid (CH_3COOH).

The outcome of these experiments may influence the strategy of exploring for sediment-hosted gold deposits such as those found in the Basin and Range physiographic province of the United States. Currently, the importance of organic matter in transporting or localizing gold in these environments is not well understood. If organic transport of gold proves to be a viable process, then the current exploration strategy may shift emphasis toward examining areas where rocks either are organic rich or exhibit signs of significant organic matter decomposition.

Mineral Solubilities and Cation Hydrolysis. The concentration of any given element occurring in an aqueous solution has an upper limit, or maximum solubility, that is fixed by the least soluble mineral form of that element under the prevailing physical and chemical conditions. This limiting solubility is a function of temperature, pressure, and the concentration of other solutes present. Supersaturation (concentration in excess of the maximum solubility) is sometimes attained in natural solutions—usually owing to environmental changes taking place during movement of water—but a supersaturated solution is unstable and tends to return to equilibrium, however slowly, by precipitation of one or more minerals. A detailed understanding of the equilibrium solubilities of minerals and the rates of dissolution and precipitation is required to evaluate quantitatively the transport and depositional mechanisms of important rock-forming elements in natural geothermal solutions and waters encountered in high-level nuclear waste repository sites.

Changes in porosity and permeability caused by mineral dissolution or precipitation not only affect the transport of hot fluids and subsequent heat transfer in geothermal systems but also may correspond to modifications in the channelways along which radionuclide-bearing waters can migrate from a nuclear waste repository to potable groundwater aquifers. To better understand these processes, ORNL researchers are conducting mineral solubility and cation hydrolysis studies using the Laboratory's unique high-temperature hydrogen electrode concentration cell.

Recent experiments have demonstrated the feasibility of measuring mineral solubilities in a hydrogen electrode cell. This technique is being used to measure the solubility of hydrolyzed magnesium, or brucite [$Mg(OH)_2$], by Drummond, Baes, and Paul Brown of the University of Wollongong, Australia.



Schematic model of convective flow in a hydrothermal system showing effect of variations in permeability of the region on the flow and showing surface discharge of the total flow.

A series of potentiometric titrations in the hydrogen electrode cell were carried out to measure brucite solubility and the hydrolysis (addition of hydroxides to the metal ion) of magnesium in aqueous sodium chloride solutions in temperatures ranging from 60 to 200°C. The results of the experiments indicate that the formation of negatively charged species, such as $Mg(OH)_3^-$, was negligible in the experiments and that the titration data can be explained solely in terms of the Mg^{2+} and $Mg(OH)^+$ aqueous species. The experimental solubilities agree remarkably well with earlier estimates made by Baes and Mesmer on the basis of empirical correlations with hydrolysis data from other elements. More importantly, these experiments demonstrated for the first time that mineral solubilities at elevated temperatures can be measured directly by monitoring the proton concentration in the hydrogen electrode cell.

Using the same apparatus, Wesolowski, Drummond, Mesmer, and Professor H. Ohmoto of Pennsylvania State University measured the formation constants

Dave Wesolowski (left) and Ed Drummond insert a Hastelloy pressure vessel in a stainless steel housing containing a furnace. Inside is a gold bag. This gold-cell pressure vessel is used for metal and mineral solubility experiments.

for protonated ("proton added") mononuclear and polynuclear forms of aqueous tungstate (WO_4^{2-}) in sodium chloride solutions. Tungstate concentrations ranged from 90 to about 2000 parts per million (ppm), and the temperature and pH ranges were from 95 to 290°C and from 2 to 8, respectively. The experimental data suggest that WO_4^{2-} and HWO_4^- species account for most of the tungsten in natural hydrothermal solutions. These results were combined with existing solubility data on scheelite ($CaWO_4$, a calcium-containing mineral found in tungsten ore deposits) to describe the chemical mobility of tungsten in crustal fluids. This work suggests (1) that typical tungsten ore fluids in equilibrium with scheelite can carry about 10 ppm tungsten as HWO_4^- at all temperatures and (2) that cooling is less important than a decrease in the solution acidity in localizing tungsten in the crust.

In related studies using the conductance apparatus, Marshall; Arvin Quist of ORNL; John Frantz of the Geophysical Laboratory, Carnegie Institution of Washington; and others, have measured electrical conductances of chloride salts (NaCl, KCl, $CaCl_2$, $MgCl_2$), acids (HCl), and other electrolytes (conducting fluid in which the flow of current is accompanied by movement of ions) in dilute aqueous solution at temperatures up to 800°C and pressures up to 400 MPa (4000 bars). The primary goal in measuring electrical conductances in these solutions as a function of temperature and pressure is the determination of the ionization constants (equilibrium proportionation between the ions and the molecules that are not ionized in solution) of the salts and acids. This work has demonstrated a straight line relation of limiting equivalent conductance (conductance at infinite dilution) to solution density for all the electrolytes studied.

Constant temperature plots of the logarithm of the ionization constants versus the logarithm of solution density also produce straight lines for the salts and acids. Most importantly, the simplicity of the observed ionization behavior of these electrolytes at temperatures above 300°C provides a basis from which reliable estimates can be made of ionization constants in regions of temperature and pressure not easily measured by experiment.

Combining this knowledge with information on mineral solubilities, one can then quantitatively predict the consequences of fluid-rock interaction such as the sequence and amounts of minerals deposited in geothermal systems. Variations in fluid chemistry monitored in hot springs and shallow wells and changes in mineralogy are used by exploration geologists to target deep geothermal drill holes. By integrating the field data with computer models using the experimental measurements, geologists can more accurately assess the potential of an area for geothermal energy.

Transport and Deposition of Metals in Geothermal Systems. Many shallow gold-silver ore deposits are probably "fossil equivalents" of high-temperature geothermal systems like Broadlands, New Zealand, and Steamboat Springs, Nevada. The evidence strongly suggests that the fossil and active systems are similar in their rare chemical elements (gold, silver, arsenic, antimony, lead, zinc, and mercury), ranges of temperature and pressure, fluid compositions, isotope relationships, and mineralogy of ore and altered host rocks. These similarities have prompted many geothermal companies to adopt the same exploration strategy to find economic geothermal systems as that used by mining companies in gold-silver prospecting—namely to look for specific trace elements (gold, silver, lead, zinc, and mercury) and mineralogical patterns in surface rocks and shallow drill holes.

Our goal is to relate quantitatively the chemical and mineralogical patterns observed in the surface rocks to physical chemical processes occurring at depth in order to more readily discriminate between geothermal systems having great energy potential from those that do not. However, fundamental questions still remain unanswered regarding the mechanisms (e.g., boiling, mixing, and cooling) responsible for transporting (solubilizing) and depositing gold, silver, lead, zinc, mercury, and other trace metals.

Ed Drummond and I are currently examining through detailed computer calculations the importance of geochemical parameters such as temperature, salinity, pH, hydrogen sulfide (H_2S) and carbon dioxide on trace metal solubilities in geothermal brines. We are also quantifying the role of boiling and fluid mixing as agents of metal localization. We singled out boiling because in the majority of high-temperature geothermal systems, some of the liquid is carried off as steam. The most significant effect of boiling on the chemistry of a geothermal solution is associated with the exsolution (removal from solution) of carbon dioxide and hydrogen sulfide. Carbon dioxide exsolution causes dramatic increases in the solution's pH (lowering the acidity level), whereas hydrogen sulfide loss to the vapor phase causes sulfide minerals such as sphalerite (ZnS) and galena (PbS) to decompose and oxidizes the fluid (usually increasing the oxygen partial pressure).

Through chemical modeling we have demonstrated that significant gold transport, as $Au(HS)_2^-$, can occur at low temperature (<250°C), high total H_2S, and relatively high pH (>5). Conversely, silver concentrations in solution, as $AgCl_2^-$, are highest at high temperature (>250°C), low total H_2S, and low pH (<5). The two distinct populations of silver/gold ratios observed in both geothermal and fossil ore deposit systems can be attributed to these differences in the transport properties of gold and silver.

Under most circumstances, gold and silver concentrations decrease in solution because boiling induces mineralization. In fact, boiling is generally a favorable process for depositing most minerals, including oxides, native metals, sulfides, quartz, and, to a lesser extent, carbonates and sulfates. Interestingly, systems rich in carbon dioxide, although more effective in causing pH changes and subsequent mineralization, also tend to enlarge the areas over which deposition can occur. The reason for this dispersed deposition is that, at higher carbon dioxide concentrations, the total fluid pressure is also higher; thus a pressure drop occurs during boiling over a greater vertical interval, resulting in a "smeared out" or enlarged mineral depositional zone. ORNL research efforts are focused on examining geothermal and fossil hydrothermal systems for evidence of this behavior to validate the chemical models.

Silicate Melt Geochemistry

The most abundant material erupted from volcanoes is some kind of silicate melt. Depending on the composition and pressure, melting temperatures of silicate rocks can range from 800°C to well over 1400°C. Silicate melts have as their fundamental structural units the SiO_4^{4-} tetrahedral group and associated larger cations (positive ions) such as calcium, magnesium, and sodium. At the source of a volcanic eruption, the melt is commonly a mixture of liquid silicate and suspended crystals. There may be significant quantities of gas such as water vapor, carbon dioxide, or sulfur dioxide trapped as bubbles in the melt that are released from the magma to the atmosphere during eruption. Natural molten material of this kind, called magma, consolidates on the surface as lava flows or domes, or it may be ejected explosively into the atmosphere to fall as fragments of crystals and glass. In the depths of the earth beneath centers of active volcanism, bodies of magma exist that may solidify completely without being erupted at the surface. These masses of molten material may have volumes ranging from a fraction of a cubic kilometer to hundreds of cubic kilometers.

The complexity of the physical and chemical behavior exhibited by these melts arises from the presence of numerous chemical components and their interactions over a broad range of temperature, pressure, and oxidation states. Knowledge of natural silicate liquids, or magmas, is based largely on indirect evidence and is primarily confined to their compositional variety. The effort involved in gathering this type of information in field-based studies vastly exceeds the work of making experimental measurements of the physical or thermodynamic properties of magma. Magma, after all, is not the easiest material to study; it is hot and often explosive. Our understanding of magmatic processes must rely on experimental geochemical studies and draw from related fields of materials science and glass technology.

High-temperature and high-pressure equilibrium and kinetic studies of silicate melts, which are chemical analogues of natural magmas, are being conducted by Mike Naney, Sam Swanson (visiting professor from the University of Alaska), and me. We are working to estimate quantitatively the physicochemical conditions responsible for magma genesis (pressure, temperature, volatile solubility, and oxidation-reduction conditions) and to gain insight about the mechanisms (i.e., crystal-liquid fractionation, trace element distributions, and aqueous fluid-melt interactions) that control magma evolution in the earth's crust.

High-temperature experiments are conducted at pressures ranging from 0.1 MPa (1 bar) to 500 MPa (5000 bars) using the unique facilities of ORNL's High Temperature/High Pressure Geosciences Group for studying oxidation-reduction-dependent reactions. These include a hydrogen-service internally heated pressure vessel (to 500 MPa) and two 0.1 MPa gas-mixing furnaces. This equipment allows simulation of a wide spectrum of rock-forming processes, from 1-atm volcanic eruptions with surface temperatures in excess of 1200°C to conditions 20 km (12 miles) below the surface where comparable magmatic temperatures are accompanied by pressures in excess of 400 MPa (4000 bars). They also provide immediate access to the simulated magmatic products, while natural geologic processes require thousands or even millions of years to expose magmatic products on the earth's surface (see box on pages 30–31).

Oxidation-Reduction Studies in Silicate Liquids. One possible indication of potentially violent volcanic eruptions is the oxidation state of the parent magma. Because the magma's oxidation state is not directly measurable, a related chemical phenomenon, such as Fe^{+2} to Fe^{+3} ratios, must be found that can accurately indicate the oxidation state. This need has been emphasized in recently published reports by Richard Sack (Purdue University) and Attila Kilinc (University of Cincinnati), who formulated empirical functions describing the relationship among oxygen partial pressures, Fe^{2+} to Fe^{3+} ratio, temperature, and bulk rock composition. However, previous experimental investigations of the Fe^{2+} to Fe^{3+} ratios in silicate systems have been fraught with problems both in experimental design and in interpretation of data.

Naney and Swanson designed experiments to determine the rates of iron oxidation-reduction reactions for a broad range of silicate liquid compositions at geologically reasonable oxygen partial pressures. Three rock compositions were used: a basalt (silica poor, <52% SiO_2), an andesite (silica intermediate, 52–60% SiO_2), and a rhyolite (silica rich, >65% SiO_2). One-atmosphere experiments conducted at 1243°C and two oxygen partial pressures ($\log PO_2 = -7.83$ and -6.08) indicate that the Fe^{2+} to Fe^{3+} ratios in basalt and andesite melts reach equilibrium in 500 and 1050 min, respectively. In contrast, experiments with a rhyolite did not equilibrate, or even change Fe^{2+} to Fe^{3+} ratios, in experiments lasting up to 5700 min.

These data suggest that the reaction gases (carbon dioxide and carbon monoxide) used in the experimental system are less effective in controlling the oxidation state in the rhyolite melt because of the slow rates of migration (diffusion) of these gases as well as of other chemical components compared with the basaltic and andesitic melts. The results indicate that the Fe^{2+} to Fe^{3+} ratios in rhyolite and other natural silica-rich rocks extruded

Geochemist's Pressure Cooker Reproduces Rock-Forming Conditions

The molten rock that erupts in spectacular displays at Kilauea Volcano in Hawaii or violently at Mount St. Helens in Washington is produced deep within the earth. Researchers in the ORNL Chemistry Division are using a specially designed internally heated pressure vessel to study the properties of such molten rock (magma) under conditions simulating those 16 km (10 miles) below the earth's surface. The equipment currently operates at hydrogen pressures up to 500 MPa (5000 bars) and temperatures up to 1400°C (2550°F). However, after additional pressure-generating capacity is added to the system, the pressure vessel will be capable of operating at 1000 MPa (10,000 bars), simulating conditions to depths of 33 km (20 miles).

Hydrogen is used in this facility to create a reducing atmosphere—that is, it removes oxygen from materials, permitting investigation of oxidation-reduction-dependent reactions that are important in natural magma systems. In the past, use of hydrogen-containing atmospheres to study these reactions was limited and hazardous because hydrogen embrittles steel vessels and thus weakens them. The novel design of ORNL's pressure vessel uses sealing plugs made of a copper-beryllium alloy and a vented liner made of austenitic stainless steel. Because these materials are resistant to embrittlement, hydrogen gas can be used to simulate a deep-crustal reducing atmosphere over wide ranges of pressure and temperature.

ORNL geochemist Mike Naney is using the facility to study oxidation-reduction-dependent processes in silica-

Mike Naney loads the furnace assembly and samples into the internally-heated pressure vessel. The apparatus is capable of heating samples to 1400°C at hydrogen pressures up to 500 MPa. Hydrogen gas is used in this facility to create a reducing atmosphere—that is, to remove oxygen from materials, permitting studies of oxidation-reduction dependent reactions that are important in natural magma systems.

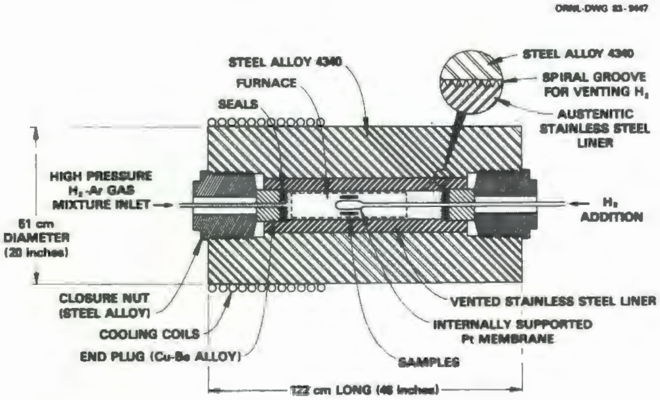
onto the surface can be used as a preeruption "fingerprint" of the oxidation state in the parent magma below the surface. Oxidation state when combined with other chemical parameters (such as water content of the melt) is a measure of the chemical evolution of magmatic systems. Because the violence of a volcanic eruption increases as the magma evolves chemically, oxidation state may be a useful guide to assessing potential volcanic hazards.

Crystallization Studies. To better understand the influence of cooling history on textural development in silicate melts, Naney is investigating the formation of crystals, their growth rates, and their stabilities in silicate liquids and solidified silicate rocks under controlled oxidation-reduction conditions.

Quenching (or fast-cooling) techniques are being used to determine the crystallization behavior and growth rates of olivine (Mg_2SiO_4) at 1 atm as a function of undercooling in two synthetic basalt melts having different viscosities (a measure of the consistency or "stickiness" of the melt). Undercooling is a crystal-growing technique in which a sample is melted completely; cooled a given increment below its melting temperature, say 10, 20, or 40°C; held at that temperature for a certain length of time; and finally quenched. By varying the magnitudes of the cooling interval and the time, Naney has been able to quantify olivine crystallization. He found that increased viscosity of the melt inhibits the formation of olivine crystals. High viscosities are usually attributable to silica-rich melts or melts devoid of volatiles such as water. The initial olivine growth rates are two to three orders of magnitude greater than "average" rates observed for long times and seem to typify classic "diffusion-controlled" growth.

Outlook

The combination of techniques and facilities used in this program to study geologic problems is unique and allows unprecedented experimental control over a wide range of pressure and temperature conditions. This capability offers



Schematic cross section of the internally-heated pressure vessel, which shows its novel design. Austenitic stainless steel and a copper-beryllium alloy are used in the areas exposed to hydrogen gas. These materials were selected because they resist hydrogen embrittlement. If hydrogen should diffuse through the stainless steel liner, the gas is swept out through the spiral groove (inset upper right) to eliminate embrittlement of the load-bearing 4340 alloy steel. The platinum membrane is used to osmotically control the hydrogen content of the hydrogen-argon gas mixture in the pressure vessel. Samples, which are contained in sealed platinum tubes, may consist of powdered rock, water, and gases such as carbon dioxide. Inside the pressure vessel the samples are subjected to pressure and temperature conditions simulating those deep in the earth's crust.

rich melts. Such melts are analogues for the magmas that cool slowly at depth to form granitic rocks. These rocks form the core of many mountain belts and often produce rugged landscapes such as Yosemite Valley in California or the sheer face of Stone Mountain in Georgia. Silicic magmas are typically enriched in economically important metals—uranium, thorium, copper, tin, molybdenum, and tungsten—that may form ore deposits. Magmas of this type are currently targets for DOE's Continental Scientific Drilling Program.

The ORNL equipment is used to produce synthetic magmas, rocks, and minerals under *known* temperature, pressure, and chemical conditions. Materials synthesized under known conditions provide geochemists with references with which to compare natural geologic materials. The experimental products are characterized by the same methods geochemists use in investigating natural rocks and minerals. Among the techniques employed are polarized light microscopy, X-ray diffraction, electron-beam microanalysis, and secondary ion mass spectrometry. By comparing mineral constituents and their chemistries in natural rocks with those in compositionally similar synthetic rocks, geochemists can estimate the pressure and temperature conditions that existed during the formation of the natural material.

the possibility of quantitatively describing, through integrated research, the evolution of geochemical systems from magmatic to ambient conditions. Hence, for the future, it will be technically feasible and scientifically sensible to consider geochemical problems that traverse the boundaries of traditional disciplines in geochemistry (e.g., igneous petrology, metamorphic petrology, and hydrothermal geochemistry) by treating the intensive parameters of geological systems as a continuum. With this approach new perspectives and research tools can be used to address broader scientific questions of both academic and practical importance. Among the problems amenable to this strategy are properties of silicate melts and aqueous geochemical fluids and their role in elemental transport and rock transformations.

ORNL will continue to coordinate experimental investigations of fundamental geochemical problems and thereby accelerate the progress of scientific understanding of large-scale crustal processes. The scientific knowledge gained will have practical benefit for problems associated with underground waste disposal, enhanced oil recovery, petroleum and natural gas exploration, geothermal and magma energy development, and the exploration and extraction of mineral resources.

take a number

By V. R. R. Uppuluri

More on Squares

The successive integers 3, 4, 5 have a curious property. The sum of the squares of the first two numbers equals the square of the third number. Thus $3^2 + 4^2 = 5^2$ $(9 + 16 = 25)$. The only other three successive integers that have this property are $-1, 0; 1$.

The five successive integers 10, 11, 12, 13, 14 also have this property. In their case, the sum of the squares of the first three numbers equals the sum of the squares of the last two numbers. Thus $10^2 + 11^2 + 12^2 = 13^2 + 14^2$ $(100 + 121 + 144 = 169 + 196 = 365)$. Only one other series of five successive integers has this property: $-2, -1, 0; 1, 2$.

One can raise the question about seven successive integers: Are there cases in which the sum of the squares of the first four integers equals the sum of the squares of the last three integers? Only two such sequences exist. These are 21, 22, 23, 24; 25, 26, 27 and $-3, -2, -1, 0; 1, 2, 3$. One can verify that $21^2 + 22^2 + 23^2 + 24^2 = 25^2 + 26^2 + 27^2$ (2020); $(-3)^2 + (-2)^2 + (-1)^2 + (0) = 1^2 + 2^2 + 3^2$ (14).

Convergence by Repetition

Take the number 6. Take its square root and add 6 to the result. Take the square root of this answer and add 6 to it. Continue this process, and soon you will obtain the number 3.

Similarly, take the number 24. Take its cube root and add 24 to the result. Take the cube root of this result and add 24 to it. Continue this process. In a short time, your calculations will converge to 3.

Now, take the number 78. Take its fourth root and add 78 to it. Take the fourth root of this result and add 78 to it. Continue this process, and once more you will quickly converge to 3.

How about fifth roots? If one wants convergence to 3, it can be done by selecting the proper number.

Elaine Zeighami is leader of the Health Effects and Epidemiology Group in ORNL's Health and Safety Research Division (HASRD). She joined HASRD in August 1979 as a research staff member. A native of Perry, Oklahoma, she earned a Ph.D. degree in epidemiology in 1974 from the University of Oklahoma. She spent the next three years teaching and doing research at the medical school at Pahlavi University in Shiraz, Iran. In 1977 she joined the faculty of the University of Pennsylvania. At ORNL her research interests include water chemistry and health effects, cardiovascular diseases, and occupational epidemiology. Here, she points to regions of the United States where ORNL has conducted cardiovascular disease studies. Listening to her are, from right, Hazel Burum (HASRD), who did the clerical and administrative work associated with the study; Max Morris of ORNL's Engineering Physics and Mathematics Division, who did the statistical analysis; and Annetta Watson (HASRD), who is working in the area of drinking water research and dietary calcium studies. This group looked at questions concerning the potential impact on cardiovascular disease risk of drinking water intake of both toxic metals and essential nutrients.

Drinking Water and Cardiovascular Disease

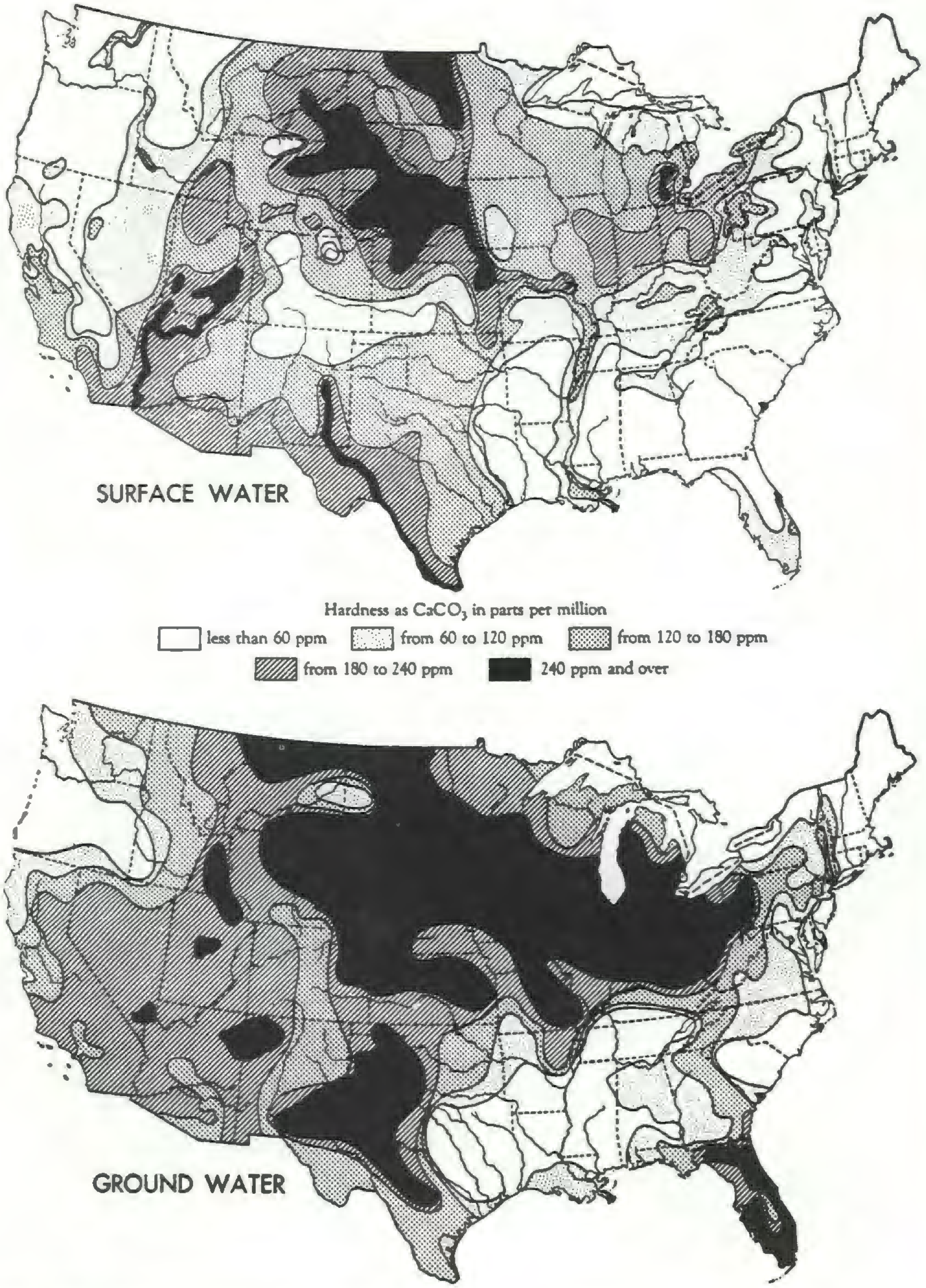
By ELAINE ZEIGHAMI

A one-liter glass of tap water
typically contains
10–50 milligrams (mg) of calcium
5–20 mg magnesium
10–40 mg sodium
1–8 mg potassium
0.2–1.5 mg iron
0.1–0.5 mg zinc
0.01-.25 mg copper
0.2–2 micrograms (μg)
of cadmium
3–7 μg lead
0–1 mg residual chlorine
varying amounts of
chlorinated organics

Diseases of the cardiovascular system account for more than half of the deaths in the United States each year. The most common causes of death are myocardial infarction (heart attack) and cerebrovascular accident (stroke). Men in their forties and fifties face an especially high risk of heart attack. About 46% of all deaths among men from 50 to 59 years old are caused by heart attacks.

Myocardial infarction results from the death of cardiac tissue caused by a decrease or total cutoff of blood supply, and consequently oxygen, to some portion of the heart muscle. A stroke occurs when the oxygen supply is cut off from the brain tissue. In both instances, one common cause (perhaps the most common) is the blockage of an artery by the buildup of atherosclerotic lesions within the artery. These lesions begin as lipid deposits (including cholesterol), which subsequently calcify.

An epidemiological study of Wisconsin farmers indicates that persons with cardiovascular disease drink softer water than persons without the disease.



Water hardness is determined by calcium and magnesium content of the water. Tennessee and most states in the Southeast generally have soft water. The hardest waters in the United States are found in the Great Plains states.

Primary risk factors for heart attack include elevated blood pressure, elevated blood lipids, and smoking. For stroke, elevated blood pressure is the primary risk factor. Most programs to prevent heart attacks and strokes have therefore concentrated on making changes in those "big three" factors, and recent evidence from prevention trials has demonstrated the efficacy of that focus.

These risk factors for cardiovascular diseases depend largely on "personal" lifestyles (e.g., what we individually eat and drink, how we exercise, and how much we smoke); thus these factors are, to some extent, under individual control. Unlike cancer risks, for which considerable evidence exists that environmental exposure to carcinogens plays a role, little is known about the role of environmental exposures in causing cardiovascular diseases. There are, however, several possible such exposures of significance to the human cardiovascular system. Chemicals known to have deleterious effects on the cardiovascular system include carbon disulfide and nitroglycerin, at levels of exposure encountered in the occupational environment. In the general environment, carbon monoxide, lead, and cadmium are all strongly suspected of having harmful effects on the cardiovascular systems of exposed humans. Food and drinking water can both be sources of exposure to some potentially deleterious substances, of which lead and cadmium are examples. In addition, intake levels of some nutrients have been suspected of having either beneficial or harmful effects on the cardiovascular system. These nutrients include calcium, magnesium, sodium, and potassium.

Study of Wisconsin Farmers

The epidemiology research group at Oak Ridge National Laboratory has been looking at questions concerning the potential impact on cardiovascular disease

For analytic purposes, Wisconsin was divided into six regions. Region 2 has the hardest water and was the only region in which there was no evidence that cases (people with cardiovascular disease) had softer water than controls. In all other regions, cases drank softer water than controls.

risk of toxic metals and essential nutrients consumed in drinking water. ORNL staff working with me on the project include Jeanne Calle and Annetta Watson of the Health Effects and Epidemiology Group of the Health and Safety Research Division and Max Morris of the Engineering Physics and Mathematics Division. The University of Wisconsin and the Wisconsin State Hygiene Laboratory have analyzed water samples for the study involving Wisconsin subjects and provided water chemistry expertise. A field office was maintained in Madison, Wisconsin, for the period of the first study.

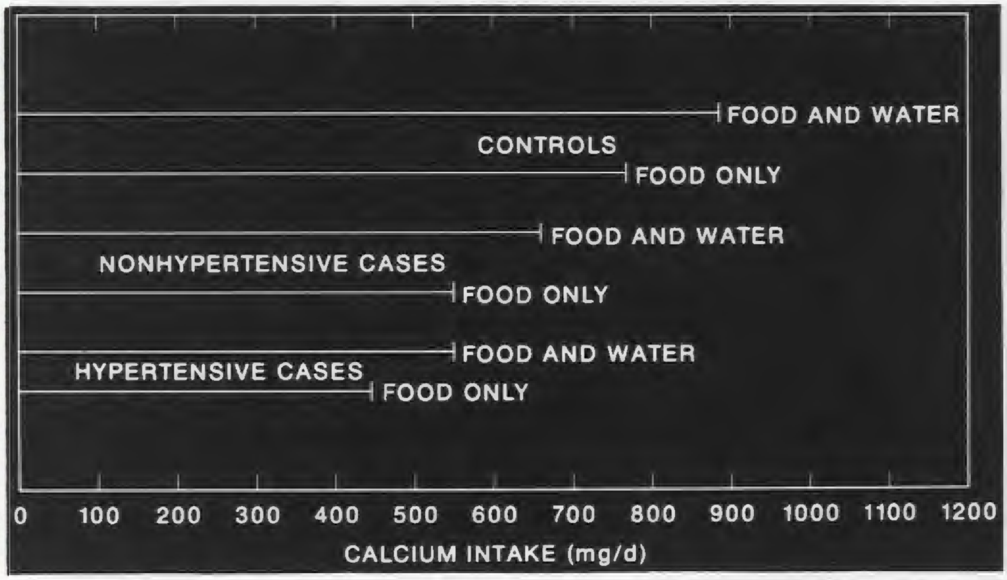
This three-year study has been completed. It examined drinking water intake of inorganic elements among two groups of Wisconsin farmers—white males dying from coronary artery disease (principally heart attack) or stroke and white males having no evidence of disease. All the respondents obtained their drinking water from their own wells. Inorganic elements and compounds were identified and quantified by sampling from the kitchen cold water tap. The inorganics measured included lead, cadmium, iron, nitrate, calcium, magnesium, sodium, copper, and manganese. The pH of the water was also measured because the level of acidity influences corrosivity of the water as it passes through and resides within tanks and pipes of the distribution system.

Lead and cadmium in drinking water arise principally from the leaching of those two elements from pipes and from solder. Other metals, such as iron, may enter drinking water both from geochemical sources and from pipes. Nitrate contaminates groundwater principally by nitrogen fertilizer runoff and by water runoff from manure. Calcium and magnesium, which are essential nutrients, are bulk elements in drinking water. "Hard" water, which is water high in calcium and magnesium, may supply as much as 20% of the average intake of these nutrients.

The study of Wisconsin farmers eventually enrolled 520 cases (persons dying with one of the two conditions) and 854 controls (persons without disease). Controls were drawn from lists maintained by the Wisconsin Department of Agriculture. The number of controls selected in each county represented that county's proportion of farmers in the state. Data obtained from respondents, or their wives, included information concerning their length of residence, use of drinking water, diet, smoking history, and medical history. For cases, a medical history was obtained from their physician. All persons in the study had lived at their residences at least two years.

The data indicated that in comparison with persons without the disease, those with disease more often had a "soft" water supply—that is, water with a lower calcium and magnesium content

ORNL researchers are studying the calcium intake from dairy foods and drinking water of three case groups in a population: (1) those who died from coronary artery disease or stroke and had a physician diagnosis of high blood pressure, or hypertension (hypertensive cases), (2) those who died from coronary artery disease or stroke but had no physician record of hypertension (nonhypertensive cases), and (3) those not known to have cardiovascular disease conditions or hypertension (controls). So far, their findings indicate that persons without cardiovascular disease or hypertension tend to have a higher calcium intake than do diseased cases.



than is typically present in hard water—and were more likely to have measurable lead and cadmium in their drinking water.

Wisconsin was divided into six regions to permit studies of regional variation. Although cases and controls were not identical in regional distribution, the two groups were very similar in region of origin (place of residence). The southern part of the state contains the hardest water, and the two northernmost regions have the softest water. Within all the regions except one, the case group had been drinking softer water than controls.

While a soft water–higher cardiovascular death rate relationship has often been observed on a geographic basis, this study is the first to observe the relationship in a large group of individuals. Because calcium and magnesium levels are so closely related in drinking water, separating the effects of the two was impossible. However, recent evidence obtained by others has indicated that calcium intake may be inversely related to blood pressure—that is, low intake of calcium may increase blood pressure. These recent findings, if confirmed, may provide new leads in the puzzle of the water–cardiovascular disease relationship, which could have enormous implications for the prevention of hypertension (high blood pressure).

As expected, the relationship between low calcium and magnesium intake and increased risk of cardiovascular disease was not strong, with an odds ratio of 1.1 (a 10% change in probability of being a case) associated with a 100 mg/L decrease in water hardness. By contrast, smoking one pack of cigarettes per day changes risk by 50 to 100%. We also estimated calcium intake from dairy products, based on responses to dietary information. The estimated odds ratio for calcium intake from dairy products was nearly identical to the odds ratio for calcium intake from water. Of course, establishing the accuracy of any dietary estimates is difficult.

Lead and cadmium were also more frequently detectable in the water of Wisconsin cases than in that of controls. These elements were almost without exception present at extremely low levels, representing only a small fraction of daily intake of those metals. Only 20–30% of the water samples had detectable levels of either element. At the levels found in this study, lead and cadmium intake from water is less than 1% of the intake from food. The higher levels of those two metals possibly reflect higher levels of corrosive leaching from piping systems delivering water to cases rather than to controls. Levels of these metals were generally higher in the water consumed by older members of the case group; the reason for this age–metal content correlation may be that older people have older homes with piping systems that have corroded extensively over time. These relationships require further delineation before any inferences can be drawn.

Death Rates and Regions

Observations of the relationship of hard water intake to lower death rates from cardiovascular disease were first made about 40 years ago. In several countries, including the United States, soft water areas have higher death rates from cardiovascular disease than do hard water areas. In the United States, certain parts of the Southeast, particularly the lower Atlantic coast, have the highest death rates from cardiovascular disease. Although these areas also tend to have the softest waters in the

GROUP	MEDIAN DAILY DIETARY INTAKE (mg)	CALCIUM LEVEL IN DRINKING WATER (mg/L)		
		10	40	80
		AVERAGE CONTRIBUTION OF DRINKING WATER (%)		
WHITE MALES	778	3	10	21
WHITE FEMALES	526	4	15	30
BLACK MALES	548	4	15	29
BLACK FEMALES	371	5	22	43

ASSUMES AVERAGE INTAKE OF TWO LITERS PER DAY. THE CALCIUM CONCENTRATIONS GIVEN CORRESPOND *ROUGHLY* TO A TOTAL HARDNESS OF ~45 mg/L (CALCIUM = 10 mg/L); ~180 mg/L (CALCIUM = 40 mg/L); AND ~360 mg/L (CALCIUM = 80 mg/L).

An intake of 2L/d of hard water could make a meaningful contribution to total calcium intake for population groups who have inadequate dietary intake, such as black or white females and black males. For people whose water is soft or moderately hard (like water in Oak Ridge), two large glasses of milk each day or calcium supplement tablets may be needed to ensure that they get the recommended level of 800 mg/d of calcium.

country, other characteristics exist that distinguish high-rate regions from low-rate regions of the country. Altitude is one geographic factor that has been suggested as a possible contributor. High-rate areas in the United States tend to be at low altitudes. On the other hand, people who live in the Rocky Mountains, which have the highest altitude in the United States, exhibit the lowest cardiovascular death rates.

The question of a relationship between the high intake of soft water and the high rate of death from cardiovascular disease has always been clouded by the fundamental uncertainty of whether hard water contains beneficial elements or whether soft water contains toxic elements—or conceivably both. Soft water is more corrosive and therefore generally picks up more metals, such as lead and cadmium, in the distribution system. In animals, the effects of high intake of lead and cadmium on the cardiovascular system, particularly blood pressure elevation, are firmly established. For humans, however, intake of these elements through drinking water is, with few exceptions, only a tiny fraction of their intake from other sources, mainly food.

Beneficial elements in hard water are principally calcium and magnesium, although drinking water does contain some essential trace elements, such as zinc and copper. As previously mentioned, recent evidence has lent some support to the hypothesis that low calcium intake is linked to elevated blood pressure in humans. In addition, animal studies have shown that heavy metals, such as lead and cadmium, have an enhanced ability to elevate blood pressure in calcium-deficient rats. Magnesium deficiency also apparently escalates the toxic effects of lead and cadmium in raising blood pressure. In view of these studies, questions about the contribution of hard drinking water to calcium and magnesium nutrition and the impact on the cardiovascular system need to be evaluated.

Drinking Water Treatment

Drinking water in the United States may come either from a public supply or from a private supply. Private supplies are generally well water and are usually not treated. Public supplies are either groundwater or surface water such as a river or lake. Surface water supplies are almost without exception treated with some form of chlorine for disinfection. Groundwater may be treated with chlorine. In drinking water, chlorine combines with organic material to form various chlorinated organic compounds. The principal such compound is chloroform, although other trihalomethanes are also formed.

The principal health-effects concern about chlorinated drinking water has been the possible carcinogenicity of ingested chlorinated organics. The fact that chloroform has been found in some animal studies to be carcinogenic raises questions about the possible cancer-causing effects of chlorine and chlorinated organics at the much lower dose levels ingested by humans.

The consumer of drinking water also ingests residual chlorine in varying amounts, depending on the nature of the treatment. Recently work by Nathaniel Revis, formerly of the ORNL Biology Division and now director of the Oak Ridge Research Institute, and by the Environmental Protection Agency (EPA) has indicated that chlorine ingestion itself may also be a problem. It may affect thyroid function and raise blood pressure and cholesterol levels in rats. This finding has stimulated further interest in studying chlorine ingestion in humans.

In 1985 our group will begin an EPA-sponsored project in several states to examine more closely the relationship between levels of blood pressure and blood lipids in humans and the total intake of chlorine and

Most of the Wisconsin farmers surveyed by the ORNL epidemiological study live and work on dairy farms similar to this one. The farmers were chosen for the study because they have their own wells and consume virtually all their drinking water from one source.

of calcium (from both food and water).

Other Drinking Water Hazards

Pollutant contamination of drinking water is one of the principal environmental concerns of both the present and future. While this concern has tended to center on industrial pollutants in urban drinking water, groundwaters are also a target for pollutants from a variety of sources. In rural areas nitrate contamination of drinking waters caused by runoff from nitrogen fertilizers and manure is a major problem. High nitrate levels in drinking water are established as the cause of methemoglobinemia, a condition caused by the conversion of hemoglobin in the blood to methemoglobin. The condition, which occurs mainly in infants, impairs the ability of the blood to transport oxygen to tissues.

High nitrate levels in drinking water are strongly suspected of causing high abortion rates and possibly congenital malformations in livestock. Recent evidence of high rates of certain types of congenital malformations in humans exposed to high nitrate levels in drinking water has reopened inquiries into the potential effects of nitrate ingestion.

Research performed at ORNL, under the direction of Bob Jolley of the Chemical Technology Division, has helped to identify substances in drinking water that decrease thyroid function. These substances are called goitrogens. Studies at ORNL and elsewhere increasingly suggest that the human thyroid can be adversely affected by chemicals in drinking water such as resorcinol (see "Environmental and Health Impacts of Water Chlorination," pages 44–49).

Pollutants in drinking water could have a variety of effects. Concern centers primarily on carcinogenesis, potential reproductive effects, diseases of the cardiovascular system, and reduced thyroid function. Drinking water is a universal source of nutrients and toxic metals, and even small effects could have a major impact on public health. For this reason, we intend to work with other scientists at ORNL and at other institutions to develop further approaches to understanding the impacts of drinking water on human health. ornl

technical capsules

Neutron and X-Ray Diffraction Studies Shed Light on Structure of Water

Scientists have been studying water for centuries but so far have not come up with a definitive theory of the structure of liquid water. However, they have proposed and developed water models. These models can now be tested by comparing their predicted results with actual measurements of interatomic distances and other structural information obtained by neutron and X-ray diffraction studies at Oak Ridge National Laboratory. Once the models are modified so that their results fit the ORNL data, a realistic statistical mechanical theory of liquid water could be developed. The ORNL X-ray data also may be used for improved medical diagnoses.

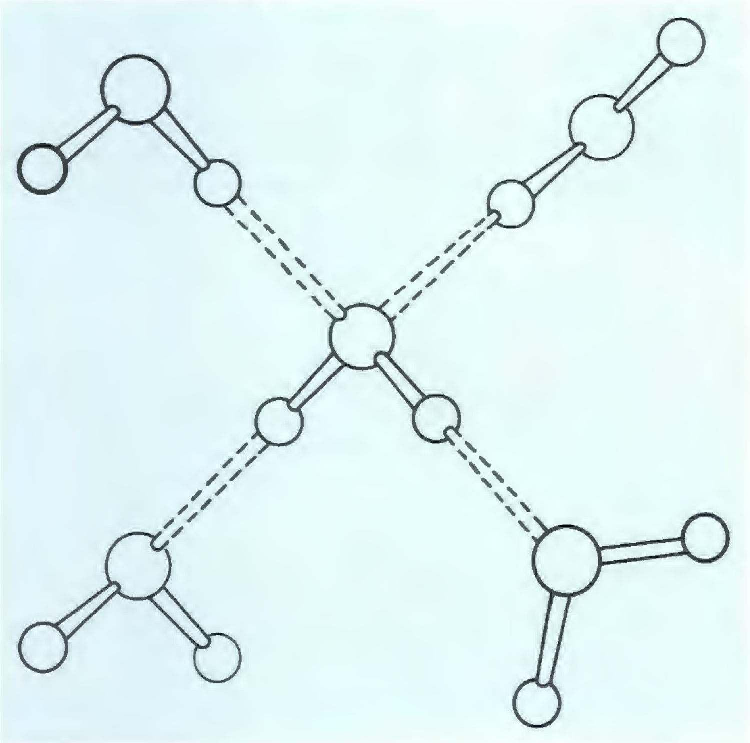
The structure of water and other liquids is not the same as the structure of crystalline solids. Atoms in crystals are arranged in a periodic order that repeats itself throughout the solid. The structure of liquids, however, refers to the relative average location of molecules and distances between specific atoms on molecules. Thus when Al Narten and Bill Thiessen of the ORNL Chemistry Division study the structure of water, they measure interatomic distances—that is, distances between hydrogen atoms on different water molecules and distances between oxygen atoms on different H_2O (water) molecules. A measure of the interatomic distances between oxygen atoms is called the "oxygen atom pair distribution function."

ORNL has a long, distinguished history of work on the structure of liquid water. At the Graphite Reactor in 1946, Ernie Wollan and Cliff Shull made the first measurement of the neutron diffraction pattern of water. In 1966 Narten, Merle Danford, and Henri Levy obtained the oxygen atom pair distribution function from X-ray diffraction. This work confirmed the open tetrahedral arrangement (like the corners of a triangular prism) of the oxygen atoms in water and has provided a crucial test of proposed water models.

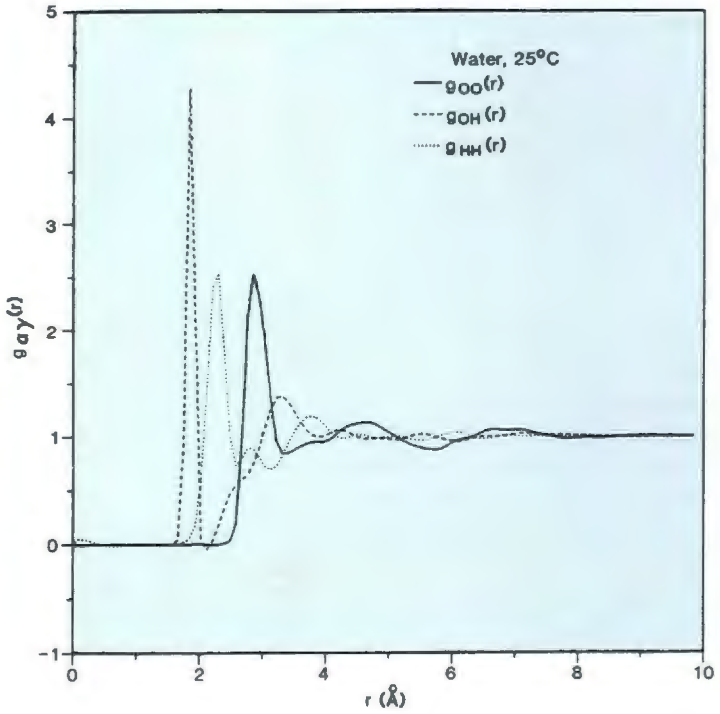
In 1981 Narten and Thiessen completed a long and difficult neutron diffraction study of light- and heavy-water mixtures at ORNL's High Flux Isotope Reactor. This work, which could be carried out only at ORNL's unique facilities, has yielded the O-H and H-H atom pair distribution function not previously known.

"As a result of our work," says Narten, "there are now three distribution functions available for inferring the positional and orientational correlations between water molecules. This structural information will provide a sensitive test of proposed water models and should lead to a realistic statistical mechanical theory of liquid water."

Model for the average orientation of pairs of near-neighbor molecules in liquid water. Large local and instantaneous deviations from this average configuration occur in the liquid.



Intermolecular atom pair distribution functions for liquid water at 25°C.



Because hydrogen atoms have only one electron each and because X rays are scattered from electrons, neutron scattering is the only useful method for locating the positions of hydrogen atoms in crystals and liquids. Levy, in fact, was the first to use neutron scattering to find the positions of hydrogen atoms in single crystals. To find the relative locations of hydrogen atoms in water, Narten and Thiessen used samples prepared with four different mixtures of light (H_2O) and heavy, or deuterated, water (D_2O). Light and heavy water scatter neutrons differently. By intercomparing data obtained for the different mixtures, the researchers made an unambiguous, direct measurement of the O-O, O-H, and H-H interatomic distances and coordination numbers. Narten and Thiessen, in collaboration with L. Blum of the University of Puerto Rico, published their results in the September 10, 1982, issue of *Science*.

The ORNL chemists found that the distance between oxygen and hydrogen within a molecule is 0.96 Å, that the distance between an oxygen atom on a molecule and a hydrogen atom on the nearest molecular neighbor is 1.86 Å, and that the distance between oxygen atoms on adjacent molecules is 2.85 Å. These results, states the *Science* article, "suggest that most water molecules are connected to their nearest neighbors through nearly straight hydrogen bonds."

X-ray diffraction measurements of water made at ORNL have proved useful to radiologists seeking to correct for lowered resolution and contrast in X-ray images of body organs or tumors. This degraded resolution and contrast is caused by X rays scattered away from the primary beam and into the detector by water in the body. By using ORNL X-ray cross-section data, physicists have developed correction methods for taking out the scattered radiation and producing an enhanced image that is less ambiguous than the normal X-ray image. Such enhanced images are especially significant for three-dimensional, low-energy X-ray studies of the lower abdomen, where up to 20% of the primary beam is scattered. The use of the ORNL data for these correction methods was reported in the *Journal of Physical Chemistry* in 1982 and *Medical Physics* in 1983.

Finding the structure of water is still a struggle, but work at ORNL is guiding the theorists in the right direction and helping medical diagnosis as well.

Iodine Hydrolysis: A Key Reaction in Nuclear Accident Scenarios

One of the scientific lessons of the March 28, 1979, accident at the Three Mile Island (TMI) nuclear plant was that the releases of radioactive iodine (^{131}I) to the environment were much lower than anticipated. In fact, less than 0.001% of the iodine that escaped from the ruptured fuel elements could be detected outside the containment building. The amount of iodine released from light water reactors during loss-of-coolant accidents is thus expected to be almost negligible. Because ingestion of ^{131}I can cause cancer of the human thyroid, this is welcome news.

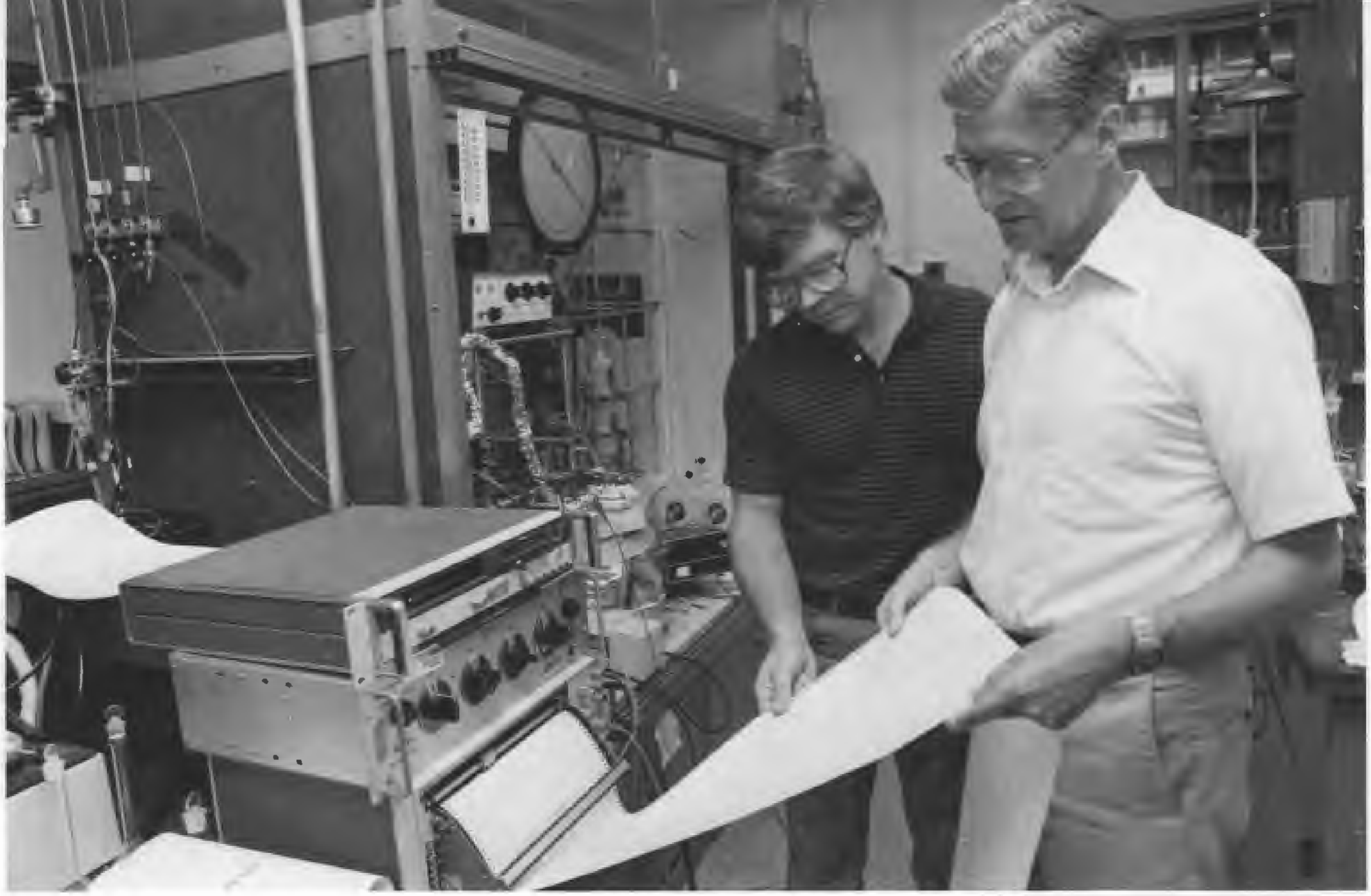
Since the TMI accident, emergency planners, regulators, and scientists have sought to determine whether any condition exists at which volatile ^{131}I might escape in some form to the environment. Emergency planners want to know the anticipated level of iodine release during loss-of-coolant accidents in pressurized-water reactors and boiling-water reactors in order to devise a strategy for its removal and reduce the need to evacuate area populations. Regulators wish to ascertain the volatility of iodine species to assess their impact on the environment. Scientists must try to unravel the reactions that occur during various accident scenarios to be able to predict the amounts and the nature of the iodine species formed.

Four years ago, Dave Campbell and Tony Malinauskas of ORNL's Chemical Technology Division, in collaboration with Bill Stratton of Los Alamos National Laboratory, provided a very plausible explanation for the behavior of iodine at TMI. (See "Iodine and Reactor Accidents," ORNL *Review*, Spring 1982.) They stated that ^{131}I escaped from the fuel as the core temperature rose from 1000 to 2000°C and then combined immediately with the excess cesium (Cs) present in this highly reducing atmosphere to form the iodide salt CsI, rather than persisting as highly volatile elemental ^{131}I. Because CsI is highly soluble in water, it was readily dissolved in the emergency cooling water to form nonvolatile iodide ions, I^-.

If this were the end of the reaction sequence, the radioactive iodide ions released during an accident would remain effectively trapped in the water. However, scientists have been concerned that further oxidation reactions, including those caused by radiation in the reactor, may transform I^- to other more volatile forms, such as molecular iodine (I_2) and the transient hypoiodous acid species (HOI).

Molecular iodine, in particular, is not inert. It reacts with water, or hydrolyzes, by a complex series of interrelated pathways. The key reaction is an oxidation-reduction, or redox, process that converts the potentially volatile I_2 molecule to the nonvolatile ions IO_3^- (the oxidized form) and I^- (the reduced form). This redox process is extremely sensitive to changes in temperature, in the acidity of the water, and in the concentrations of the iodine species involved.

To better understand and quantify some of these processes, research efforts were undertaken within the Chemistry and Chemical Technology divisions of ORNL. (The important questions of the volatility of iodine species and the kinetics of the hydrolysis reaction have been extensively studied in the Chemical



Don Palmer and Dick Ramette read voltages recorded from an electrochemical cell inside a constant-temperature water bath. By recording the voltage differences, they can measure the extent, or equilibrium distribution, of the oxidation-reduction process that results when dissolved molecular iodine reacts with water.

Technology Division by Mac Toth and his colleagues in a program for the U.S. Nuclear Regulatory Commission. These questions are not addressed here.)

To answer the question concerning the stability of iodine in water, physical chemists in the Chemistry Division's High Temperature Aqueous Chemistry Group originated an approach for studying the principal hydrolysis reaction, the formation of iodate (IO_3^-) and iodide (I^-) ions. The method involves splitting the reaction into its two redox partners, the oxidizing half with I_2 and IO_3^- and the reducing half with I_2 and I^-. Together they make up two compartments of an electromotive force (emf) cell. This arrangement constitutes a battery whose potential very accurately indicates the equilibrium distribution of all the species. This general method is often employed at room temperature for other redox systems, but has never been attempted until now on iodine species or at temperatures as high as 210°C.

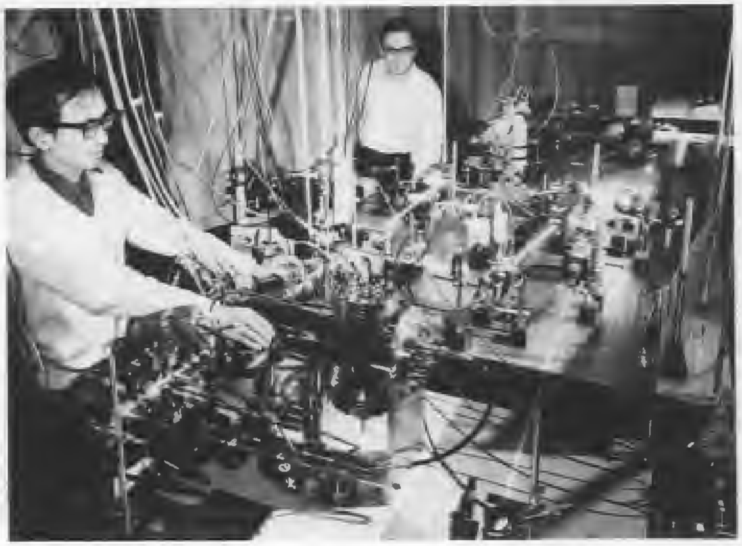
Two physical chemists, Donald Palmer of ORNL and Dick Ramette, a chemistry professor from Carleton College (who is serving as coordinator of the Great Lakes College Program at ORNL), collaborated in developing a unique cell design to implement this technique. The two-compartment cell that they designed allowed iodine to migrate freely between the two redox-partner solutions. Given time, the iodine concentration eventually attains the same value in both solutions. This condition enabled the researchers to make exact measurements of the concentrations of all iodine species present, including the elusive I_2. Because of the low concentrations present, however, better methods of analysis were necessary.

Ramette used his considerable experience with the precise technique of potentiostatic coulometry, a sensitive analytical method for identifying and quantifying reducible species, such as iodine, to meet this need. This approach proved highly successful; from the results, the exact concentrations of iodine and the other major components can now be predicted at conditions similar to those considered in reactor accident scenarios. Besides this relevance to nuclear technology, the results have provided an important contribution to basic solution chemistry. They provide a new verification of the preferred model for predicting temperature variation of thermodynamic quantities.

The transient species HOI has also been considered a possible environmental hazard if released in a nuclear accident. Its existence in solution is known from equilibrium and kinetic observations, but spectral evidence for its existence has been lacking. Palmer has used controlled chemical conditions, with removal of interfering species, to observe a weak ultraviolet band that could be due to HOI. If this proves to be the HOI spectrum, it would be the first reported physical property for the species.

Howard Adler (left) and Weldon Crow developed an enzyme system for growing oxygen-sensitive bacteria quickly and conveniently. This process could aid in the diagnosis and treatment of important human and animal diseases.

Chung-hsuan Chen (left) and Steven Kramer were among the developers of a laser-based detector, which can identify and count single atoms of rare gases, permitting researchers to measure the age of polar ice and determine safe locations for disposal of nuclear wastes.



ORNL Scientists Win Four I•R 100 Awards

Oak Ridge National Laboratory has once again shown itself to be among the leading U.S. research and development (R&D) organizations in originating technological advances having possible commercial applications. An annual competition sponsored by *Research & Development* magazine (formerly *Industrial Research & Development*) yielded five awards for the Martin Marietta Energy Systems, Inc., facilities in Oak Ridge. Four of these were awarded to scientists at the Laboratory for technologies judged to be significant advances or to have market potential.

Anaerobic environments. Howard I. Adler and Weldon D. Crow of the Biology Division were honored for the development of an enzyme system that quickly and conveniently provides a suitable (anoxic) environment for oxygen-sensitive (anaerobic) bacteria, replacing expensive inorganic catalysts containing platinum or paladium. (See Adler's "A Novel Way To Grow Anaerobic Bacteria," ORNL *Review*, Winter 1983.)

Adler says that an almost certain application is in clinical laboratories, where bacteria that produce diseases in animals and humans are grown from tissue samples and tested for sensitivity to antibiotic drugs. The enzyme system could be used to maintain oxygen-free conditions necessary for culturing the oxygen-sensitive bacteria that cause infections. Other possible applications are

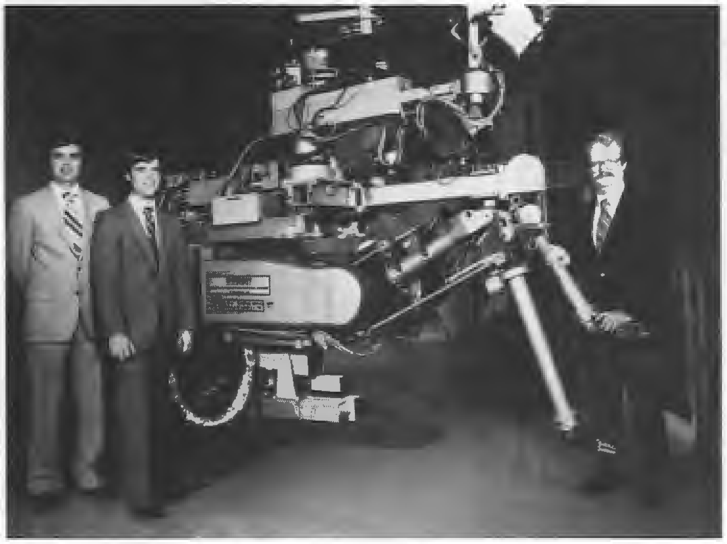
- Municipal waste treatment systems—to promote the growth of anaerobic bacteria used to break down wastes
- Chemical synthesis—to maintain reduced environments in which to synthesize oxygen-sensitive chemicals
- Isolation of biological catalysts (enzymes)—to maintain reduced environments in which to isolate oxygen-sensitive enzymes

The enzyme system is already patented. Adler says that development of a marketable product could go either to a company that would add it to their current product line or to an Oak Ridge company that might be created specifically for marketing the enzyme system. Adler believes that clinical laboratories are a certain market and that municipalities, chemical and biotechnology companies, and R&D laboratories are possible markets.

Single-atom detector. A detector that identifies and counts single atoms of rare gases was developed by G. Samuel Hurst, Marvin G. Payne, Steve L. Allman, and Ronald C. Phillips in the Photophysics Research Group of the Health and Safety Research Division. According to Payne, applications that are "ready to go" deal with basic physics studies. A potential environmental application is the detection of argon-39 in the ocean. Determining argon-39 content permits scientists to chart circulation currents and mixing times as a way of determining the uptake by the oceans of carbon dioxide, including that discharged by combustion of fossil fuel.

Another possible use is detection of krypton-81 to estimate how long groundwater has resided in a particular location without mixing with surrounding water sources. In October 1984 the

Paul Satterlee (formerly of ORNL), H. Lee Martin, and Joseph E. Herndon (right) developed the Model M-2 Control System, a sophisticated microprocessor-based control system for an advanced servomanipulator used for remote maintenance of components in industrial environments inaccessible to direct human entry.



Gerald Schulze (left) and Herbert Mook developed an ultrasonically-pulsed neutron time-of-flight spectrometer, which dramatically increases reactor-produced neutron intensity for scattering research.

ORNL researchers used the rare gas counter on the first practical sample: 1 L of groundwater from Switzerland. They counted about 1000 atoms of krypton-81 in the water—equivalent to finding a grain of sand on Coney Island. Information on the krypton-81 content of water can help geochemists determine the age of water in geological sediments. It is also invaluable in finding environmentally safe locations for the disposal of nuclear wastes—that is, underground areas protected from the flow of water, which can leach out isolated radioactive materials.

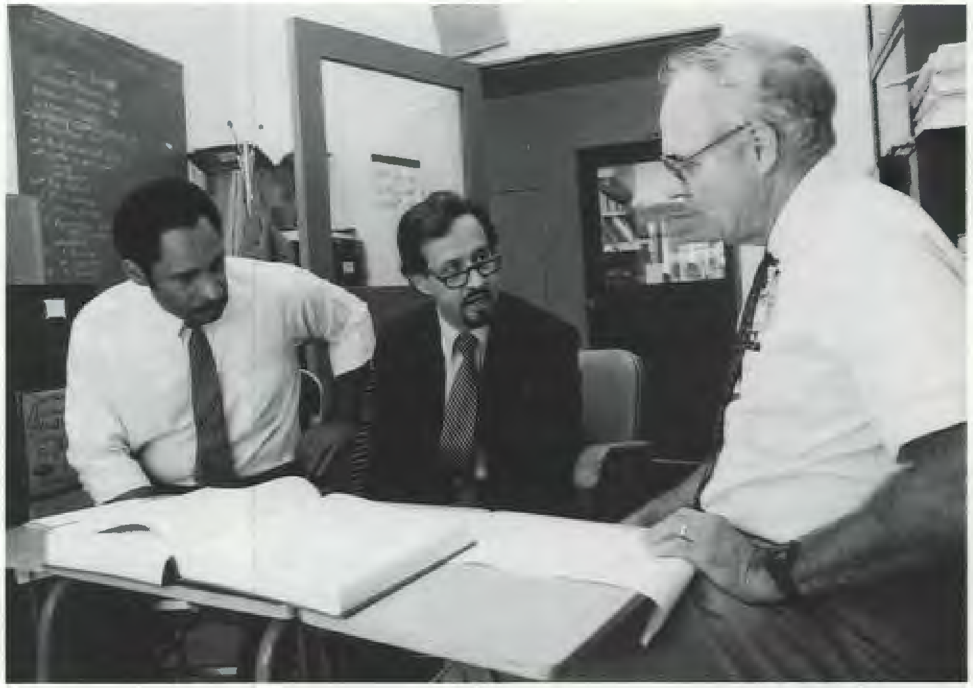
The group will be looking for funding to use the technology to detect the presence of lead atoms in thallium ores as a way of inferring the passage of solar neutrinos through the earth. Solar neutrinos, which provide information about the interiors of stars, are particles created by particle decay in the sun that have virtually no mass and that interact weakly with matter. The solar neutrino study may be funded on an ongoing basis within the next couple of years.

A spin-off company, Atom Sciences of Oak Ridge, holds the patent for the detection system and is pursuing the nuclear waste disposal application.

Servomanipulator digital control system. H. Lee Martin [Instrumentation and Controls (I&C) Division] and Joseph A. Herndon (Fuel Recycle Division) along with Paul E. Satterlee (formerly of ORNL) were honored for their work on a digital control system for an advanced servomanipulator. According to Martin, previously used analogue systems were not amenable to modification and required frequent adjustment to perform acceptably. The digital system is more reliable and provides more information on manipulator operation.

The control system was developed specifically for the Fuel Recycle Division for remotely handling hazardous materials, such as radioactive fuels (uranium and plutonium) removed from spent fuel elements for reuse in new fuel elements fabricated for nuclear reactors. This system was developed in cooperation with Central Research Laboratory (CRL), a commercial operation in Red Wing, Minnesota. CRL owns all patents and licenses connected with the system. Besides its fuel-recycle application, the control system could be used by orbiting space laboratories for satellite repair. "Although the system is currently prohibitively expensive," says Martin, "the next-generation controller, which we are now developing, will be constructed from off-the-shelf components, making it much less expensive."

Ultrasonically pulsed neutron spectrometer. A high-resolution, ultrasonically pulsed neutron time-of-flight spectrometer developed by Herbert A. Mook (Solid State Division) and Gerald K. Schulze (I&C Division) was also an I-R 100 winner. The spectrometer, which greatly increases reactor-produced neutron intensity, is a significant advance that will have a definite impact on neutron-scattering research. Patents have been applied for, but because neutron scattering is exclusively a research field at this time and the number of reactors used for this purpose are few, development of this technology to a marketable system is unlikely.—*Lydia Corrill.*



Bob Jolley (right), Dr. Eduardo Gaitan (center), and Nathaniel Revis, director of Oak Ridge Research Institute (and former staff member of ORNL's Biology Division), discuss chemical spectra produced by the analysis of drinking water samples sent by Dr. Gaitan to Jolley. Dr. Gaitan conferred with Jolley after giving a seminar to ORNL staff members September 4, 1984. Jolley and his colleagues have found in several samples a chemical known to cause thyroid disease.

Environmental and Health Impacts

By CAROLYN KRAUSE

ORNL chemist Bob Jolley was the first to identify potentially hazardous organic compounds formed by adding chlorine to wastewater. He has also led an effort to identify drinking water compounds that cause thyroid disease.

In the early 1970s when Bob Jolley, a chemist at Oak Ridge National Laboratory, began work on his doctoral thesis, he was unknowingly getting a taste of a new career. Since that time, his watchwords have been organics and organizing. He has become an expert on identifying and quantifying organic compounds in water—including potentially hazardous compounds in drinking water—and has been responsible for organizing five international conferences on the health and environmental impacts of water chlorination.

Before Jolley became a doctoral candidate at the University of Tennessee, he had been using liquid chromatography in ORNL's Chemical Technology Division to analyze wastewaters and body fluids for organic materials. For his thesis topic, however, he chose to examine wastewaters for organic compounds that might be formed as a result of the addition of chlorine, which is used to kill disease-causing bacteria. In his 1973 dissertation, Jolley identified and quantified 17 chloroorganics produced during the chlorination of wastewater and suggested that research be done to determine whether these organics pose any health hazards.

In 1974 Jolley was first to publish a paper announcing to the scientific world that chlorinated organics are formed when chlorine is added to wastewater. A few months later, his results were corroborated in a paper published by Bill Glaze, then with North Texas State University and now with the University of Texas at Dallas. The same year, a Dutch scientist, John Rook, announced in a paper that he had found chloroform, a chlorinated organic compound, in drinking water in Holland. At about the same time, Jim Liechtenberg and Tom Bellar at the Cincinnati regional office of the U.S. Environmental Protection Agency (EPA) reported that they

Jolley and Norman Lee used this gas chromotograph-mass spectrometer to identify resorcinol in drinking water samples supplied by Dr. Gaitan. Resorcinol is a goitrogen—that is, it can cause enlargement of the thyroid and lead to health problems.

Lee examines the interior coil of the gas chromatograph as it awaits repair.

# of Water Chlorination

had identified chloroform in chlorinated drinking water in Cincinnati.

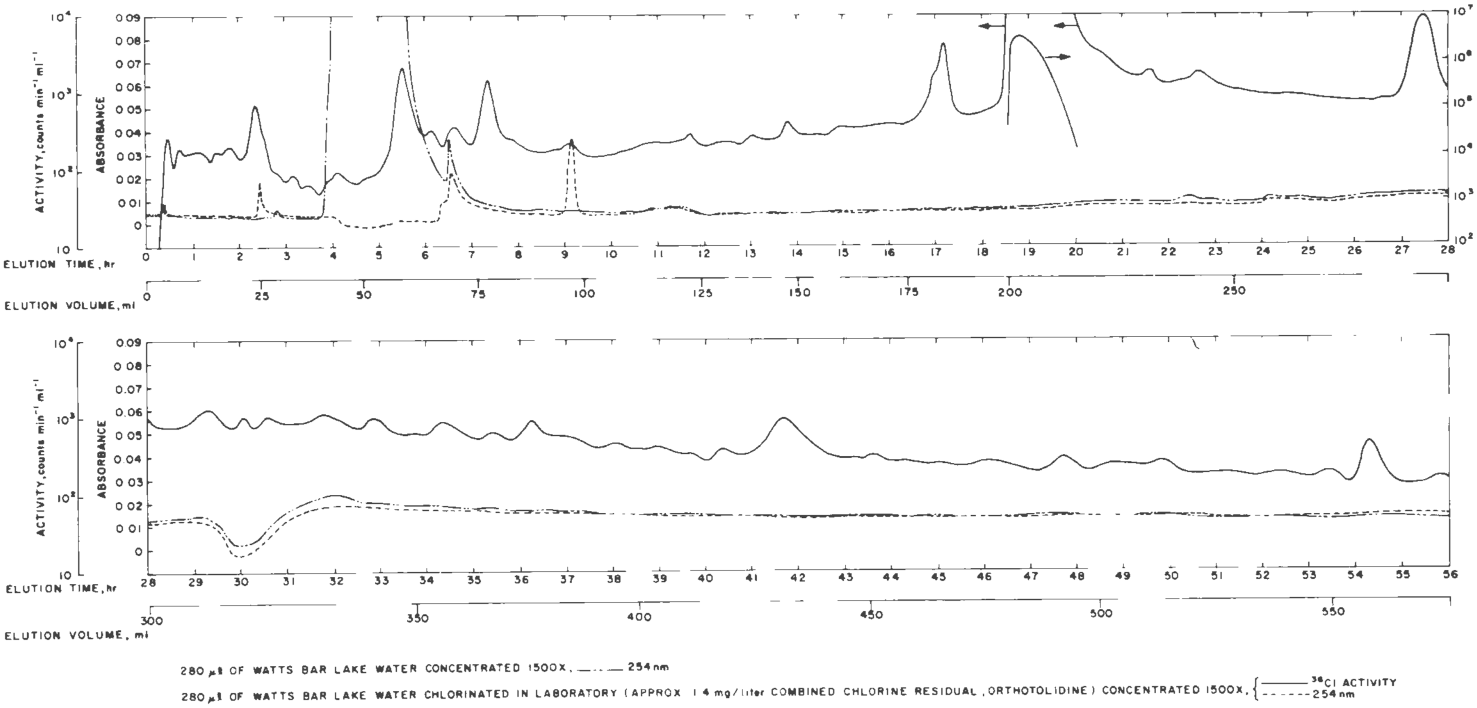
As a result of this flurry of reports about chlorinated organics in water, EPA in 1975 started a national reconnaissance survey to determine the extent to which chlorinated organics were present in drinking water in U.S. cities. The EPA survey showed that chloroform and other trihalomethanes were present in drinking water throughout the nation. This finding was cause for concern because chloroform at high level is known to cause cancer in animals.

Cooling Water Studies

Meanwhile, back in Oak Ridge, Jolley teamed up with Carl Gehrs of ORNL's Environmental Sciences Division (ESD) to examine the environmental effects of chlorinated organics. In 1974 Jolley began obtaining samples of waters used in cooling power plants to determine whether they contained chlorinated organics. Chlorine is routinely added to power plant cooling systems—both once-through systems and recirculating systems with cooling towers—to destroy bacterial slimes and fouling organisms like mussels that reduce the efficiency of electricity generation. Jolley collected samples from the once-through cooling systems at the Kingston Steam Plant on the Clinch River and Memphis's Allen Steam Plant on the Mississippi River and from cooling towers at ORNL's High Flux Isotope Reactor and the Oak Ridge Gaseous Diffusion Plant. Using radio-tagging techniques, he identified more than a dozen different chlorinated organics in these cooling waters.

Gehrs then undertook to determine whether these organics were toxic to water fleas (*Daphnia*). After subjecting the *Daphnia* to different concentrations of organics, Gehrs and later John Trabalka of ESD found that at high concentrations, several of the chloroorganics identified by Jolley killed at least half of the test animals. However, these concentrations were at least 1000 times as high as the measured average concentrations of the chloroorganics released from power plants.

Because of reports that excessive releases of chlorinated effluent to waterways may have killed fish and because of concern about potentially carcinogenic and mutagenic chlorinated organic



Chlorinated cooling water from Watts Bar Lake examined by Jolley and his associates was found to have chlorine-containing organics and constituents that absorb ultraviolet light. At ORNL more than 50 chloroorganics were separated from the chlorinated water using high-resolution ion exchange chromatography. Several of the constituents were identified as chlorophenols, chloropurines, and chloropyrimidines.

chemicals in drinking water, EPA supported studies at ORNL and elsewhere to determine the environmental effects of chlorinating cooling waters and methods of reducing these effects. In 1977 Jack Mattice, then of ESD, and Bud Zittel of the Energy Division coauthored a paper stating that toxicity to water organisms depends on the concentration of chlorine over time. In this work, they proposed a model designed to help power plant operators achieve safe levels of total chlorine residuals. It takes into account site-specific dilution factors and allows higher limits for chlorine discharges (and hence higher chlorination levels) in cases where dilution is extremely rapid. The time-concentration curve developed in this paper was accepted in 1978 by EPA's Region 5 as the method for determining acceptable chlorine discharge limits.

Drinking Water Problem

In 1975 when the EPA survey of chlorinated drinking water was under way, Jolley and Gehrs conceived the idea of organizing an international conference, "Water Chlorination: Environmental Impacts and Health Effects." They wrote to people who had published in the field and invited them to the conference, which was held that fall at ORNL. Several talks dealt with organics in drinking water and possible health effects. One paper, by Al Stevens of the EPA Cincinnati office, pinpointed the precursors of chloroform and other trihalomethanes: humic materials formed naturally by the degradation of plants and aquatic life.

Since then, Jolley has been the driving force behind four other international conferences on water chlorination—held in 1977 in Gatlinburg; in 1979 in Colorado Springs, Colorado; in 1981 at the Asilomar Conference Center in Pacific Grove, California; and in June 1984 at the College of William and Mary in Williamsburg, Virginia. (The number of participants in these conferences grew from 170 in 1975 to 320 in 1979 and 225 in 1984.) In addition, Jolley edited and published proceedings for all five conferences, with assistance for the past two from Vivian Jacobs of the ORNL Information Division.

From his work with conferees and the proceedings, Jolley is much aware of the concern over chlorinated organics in drinking water. In the late 1970s he sampled some drinking water in Oak Ridge and found that it contained about 100 parts per billion (ppb) of chloroform and other trihalomethanes. "The level of chlorinated organics in Oak Ridge's drinking water then was about the same as the average for the

At Oak Ridge's water treatment plant, Hal Williams adjusts the rate of flow of chlorine into the drinking water. Above are "feeders," small pipes that add chlorine to the water as it enters the storage reservoir.

Dan Kearney (left) and Williams check the chlorine storage tanks at the pump station on the Clinch River. Water is chlorinated at the river near Clark Center Recreation Park before being pumped to the treatment plant on top of the hill, where more chlorine is added. Kearney is with the Construction Division of the Department of Energy's Oak Ridge Operations, and Williams is water plant superintendent with Rust Engineering Company.

nation," Jolley says. "EPA later set a limit of 100 ppb for trihalomethanes. That posed problems for cities in places like south Florida whose levels of trihalomethanes approached 300 ppb. They had to use chemical techniques to reduce the organic content of the water."

In 1977 an ORNL biochemist found evidence that a compound detected in drinking water could be a potential health hazard. Bob Cumming of the ORNL Biology Division (who helped Jolley and Gehrs organize the first water chlorination conference and who helped in the planning of each of the others) became interested in the genetic effects of 5-chlorouracil, a chlorinated organic chemical (formed from the chlorination of uracil, which is excreted in urine). First identified in 1973 by Jolley in chlorinated wastewater, this compound was subsequently found in drinking water in 1978 in Great Britain by Brian Crathorne.

Cumming was interested in 5-chlorouracil because it is an analogue of cytosine, a constituent of DNA. He wanted to test whether such an analogue would be incorporated into DNA and possibly cause mutations (genetic changes). If such mutations occurred, the altered genes would make mutated, or foreign, proteins. Cumming fed 5-chlorouracil to mice and found that they incorporated it into their DNA as determined by sperm DNA analysis. But he was unable to detect any sign of mutations.

Says Jolley, "Cumming's finding that 5-chlorouracil is incorporated into DNA suggests that the compound may have subtle health effects, and scientists should look for them. And the fact that Craythorn found 5-chlorouracil in drinking water in Great Britain suggests scientists should search for it in drinking water elsewhere, too."

Have any links been established between incidence of cancer and the concentration of chlorinated organics in drinking water? According to Jolley, several scientists have persuasive evidence that such a link exists. Donna Cragle, an epidemiologist formerly with the University of North Carolina and now with Oak Ridge Associated Universities, presented a paper at the 1984 Water Chlorination Conference suggesting that consumption of chlorinated drinking water is significantly associated with colon cancer among older white residents of North Carolina.

Also at the recent Water Chlorination Conference, K. P. Cantor of the National Cancer Institute reported that the relative risk of bladder cancer for a nonsmoker is higher if the person drinks chlorinated surface water instead of nonchlorinated groundwater. To someone who drinks the groundwater, the relative risk is 1.0; to someone who drinks the chlorinated surface water, the relative risk rises from 1.4 for <20 years of use to 3.1 for >60 years of use. Relative risk is defined as the rate of incidence of disease in the exposed population divided by the relative risk of disease in the unexposed. If the number is greater than 1, the exposed population has a higher incidence of disease than the unexposed.

In a talk given August 3, 1984,

Sleuthing for Drinking Water Compounds That Impair Thyroid Function

In the 1960s Dr. Eduardo Gaitan, a Colombian endocrinologist and practicing physician, was perplexed by a medical problem that he saw in many of his patients in western Colombia. He could not understand why so many children suffered from goiter, an enlargement of the thyroid gland that can lead to impaired function of the gland and, at the worst, to lethargy and mental retardation. He noticed that even after nationwide preventive treatment with iodine, the incidence of goiter among his patients remained high. Eventually, his curiosity impelled him to undertake a classic epidemiological study.

Dr. Gaitan focused his attention on the Colombian village of Candelaria. His 1964 survey of schoolchildren showed that many had thyroid problems, with 11% of the children in the southern half of the village and 23% in the northern portion having goiter. It occurred to him that an environmental cause might explain why proportionally more children in the northern part than in the southern section had thyroid problems. He began to suspect that the drinking water of the two groups was different.

When Dr. Gaitan checked the sources of drinking water, he learned that the town drew its water from two unchlorinated wells. The water in one well came from an aquifer surrounded by sedimentary rock, while the water in the other originated in an igneous rock formation. The differences in the underlying rock suggested to the doctor that water from one well, but not from the other, contained compounds called goitrogens, which caused goiter or potential thyroid disease in some of Candelaria's children. Goitrogens inhibit the ability of the thyroid to use iodine to make thyroid hormones, which control the overall metabolic rate in the body. Through interviews with the children about their health conditions and places of residence, he gathered evidence that strongly suggested a link between the children's thyroid disease and drinking water from the sedimentary rock formation. He published his results in 1969.

This 12-year-old Colombian boy has goiter, an enlargement of the thyroid that can be seen by inspecting his neck.

Several years later, Dr. Gaitan became intensely

at ORNL, Richard Bull, director of the Toxicology and Microbiology Division at EPA's Health Effects Research Laboratory in Cincinnati, said that recent research results indicate that chemicals in chlorinated drinking water that were found to cause mutations in bacteria or skin and lung tumors in mice are not limited to the volatile trihalomethanes. Biological activity, he said, can also be induced by nonvolatile chemicals present in water, which include acids, aldehydes, ketones, nitriles, aromatics, alkenes, and alkanes.

Bull said that at EPA research is under way on the potential health effects of not only chlorine but also alternative disinfectants such as chlorine dioxide. Researchers are identifying the chemical by-products of a given disinfectant, which, he said, depend on secondary water characteristics, such as the pH (acidity level) and temperature of the water. "In some cases," Bull noted, "by-products are also formed in the intestinal tract after the chemical has been metabolized."

Is There a Solution?

Jolley is not alarmed by these findings on possible health effects of chlorinated water. "The risk of cancer from drinking chlorinated water," he says, "is considerably less than the risk of early death from drinking unchlorinated water. If drinking water weren't chlorinated or otherwise disinfected, people would likely become ill or die from diseases caused by bacterial pathogens. In interested in pinpointing which chemicals in the Candelarian well water caused goiter in the village children. He read the scientific literature to find out who had been working on identifying organic compounds present in water. He ran across the name of Bob Jolley of Oak Ridge National Laboratory. Dr. Gaitan then contacted Efraim Otero-Ruiz, president of the Colombian National Science Foundation. In 1976 Otero-Ruiz visited Jolley at ORNL and asked him if he were willing to analyze some water samples from Candelaria. Jolley said yes and thus began his long collaboration with Dr. Gaitan. About the time that the samples were shipped to Jolley, he received a letter from Dr. Gaitan informing him that the doctor was moving to the United States to take a position at the University of Alabama in Birmingham.

Jolley and Jim Thompson of the Chemical Technology Division (CTD) analyzed the samples using high-pressure liquid chromatography. They found humic materials (decayed organic matter) in the water but did not turn up any known goitrogens. Jolley suggested that Dr. Gaitan send him more samples of the water, including concentrates, as well as activated carbon filters used to remove the organic constituents from the well water.

In 1981 Dr. Gaitan sent Jolley concentrates and filters from Candelaria. Jolley froze the samples until he could make time to investigate them. In 1982 he and Norman Lee of CTD used different solvents to extract a variety of organic compounds from the filters and concentrates. Then they ran the extracts through a CTD gas chromatography–mass spectrometry system. In their analysis of the methylene chloride solvent, they hit the jackpot: They found evidence of resorcinol, a naturally occurring goitrogen known to be extremely potent.

Today Dr. Gaitan is a permanent resident of the United States, works as chief of the Endocrinology Section of the Veterans Administration Medical Center at the University of Mississippi, and continues to collaborate with Jolley. The doctor now is investigating whether drinking water in two Kentucky counties is responsible for an unusually high incidence of goiter in children there. He has collected ten water samples that are being analyzed at ORNL by several different techniques. Funds from the University of Mississippi are supporting the analyses, which are being performed by Jolley and Kevin Felker of the Chemical Technology Division; Michelle Buchanan, Cecil Higgins, and Jerry Uhlrich of the Analytical Chemistry Division; and Ben Benjamin and Emily Douglas of the Chemistry Division. Preliminary results indicate that 2,4-dihydroxy acetophenone, whose structure is similar to that of resorcinol, is present in one sample of Kentucky drinking water.

"The likelihood that goitrogens are present in drinking water may be greater than is commonly realized," Jolley says. "Leachate from Chattanooga shale is known to be goitrogenic, and several water supplies in Alabama are suspected of containing goitrogens. Also, goiter in American children is not an uncommon disease. In California, for instance, 7% of the school children have goiter. In U.S. hospitals 1% of all operations are related to thyroid problems.

"If we can establish that drinking water can be linked to many cases of goiter," Jolley adds, "we will have uncovered a public health problem of worldwide significance. Such a finding would imply that more attention should be paid to removing organic materials from water as well as disinfecting it to make it fit to drink."

Third World communities where water is untreated, many people succumb to gastrointestinal diseases and typhoid fever, and many babies and young children die from diarrheal diseases."

Would it be preferable for U.S. cities to treat their water with ozone as many cities in continental Europe do? Jolley thinks not, considering the current state of knowledge. He says that ozone, an active chemical compound consisting of three atoms of oxygen, can react with constituents of water to form oxidized organics and aldehydes that are known to cause mutations. But, Jolley observes, Americans can learn a lesson from the Europeans about how to make treated drinking water as clean and safe as possible.

"European cities," he says, "operate on the principle that water should be of high quality before it is disinfected and piped to people for drinking. The Europeans achieve this quality by using filtration and other means to remove the organic material before treating the water.

"In the United States," he adds, "we frequently get our drinking water by treating surface water with chlorine without removing the organic material first. Considering the possible health costs of drinking water laden with organics, the investment to improve the drinking water source by using techniques such as bank filtration would be worthwhile. The resulting high-quality source water will make the drinking water product cleaner and safer for all."

Near a pond at the east end of the ORNL complex, Dick Ketelle (left) and Francois Pin demonstrate what Ketelle calls "high-tech water witching"—using an instrument consisting of a black box, cable, and hula hoop-size coil to determine where groundwater is likely to be located. By taking electrical conductivity measurements of the ground below, the two researchers can determine where monitoring wells should be placed to test groundwater quality. (See box on pages 52–53.)

Groundwater Pollution:

What Are the Environmental and Legal Problems?

Half of the drinking water in the United States comes from groundwater, which is subsurface water that occurs beneath a water table in soils or rocks or in geologic formations called aquifers. Many residents who drink water from wells assume that they are drawing pristine, high-quality, unpolluted water from the earth. Unfortunately evidence that some aquifers have been contaminated by synthetic organic chemicals discharged by industrial and agricultural operations continues to increase. Some of these chemicals are known to cause cancer and nerve disorders in animals. Although the long-term health impacts on humans of low-level exposure to these chemicals are unknown, the American public has expressed concern. Concerned citizens are pressing legislators to enact laws to require monitoring and protection of groundwater and reclamation of polluted aquifers to ensure that all sources of drinking water are clean and safe.

The extent of known groundwater pollution, knowledge of health effects, and attempts to deal with the problem are documented in *Groundwater Pollution: Environmental and Legal Problems*, a 1984 American Association for the Advancement of Science Selected Symposium book. The book, a compilation of papers by five experts on the groundwater problem, was edited by Curtis Travis and Elizabeth Etnier. Travis is editor of the journal *Risk Analysis* and director of the Office of Risk Analysis of the Health and Safety Research Division of Oak Ridge National Laboratory; Etnier now works in the Information Research and Analysis Section of the ORNL Information Division.

In their introduction, Travis and Etnier provide several examples of groundwater pollution and possible contamination of drinking water that aroused public concern:

- A 1975 survey of 80 chlorinated water supplies from aquifers throughout the United States found widespread contamination by such potentially toxic organics as trihalomethanes, carbon tetrachloride, and 1,2-dichloroethane.
- In 1979 a Massachusetts state commission reported that the drinking water supplies in one-third of the state's communities were chemically contaminated and that private and public wells were closed or restricted in 22 towns.
- In January 1980, 37 public wells that supplied water to more than 400,000 people in 13 cities in the San Gabriel Valley of California were closed because of trichloroethylene contamination.

- Analysis of samples of drinking water drawn in 1981 from 1000 wells in New Jersey showed that the water contained 56 toxic substances, including 47 chlorinated hydrocarbons and 9 heavy metals—arsenic, beryllium, cadmium, copper, chromium, nickel, lead, selenium, and zinc.

Pesticide Pollution

The case of the toxic pesticide aldicarb (sold under the trade name Temik®) illustrates the "insidious nature of chemical contamination of the nation's drinking water supplies," say Travis and Etnier. The pesticide, used to kill insects and other pests that attack potatoes, cotton, and sugar beets, is a nerve poison that is fatal to humans in high doses. Nevertheless, the manufacturer and users of the pesticide believed that its toxic residues would break down into nontoxic chemicals before reaching groundwater.

In August 1979 scientists sampled nearly 8000 wells in the potato-farming area of Long Island, where aldicarb was being widely used. They found that nearly 30% of the sampled wells showed contamination by aldicarb, with 15% exceeding the New York State Department of Health guideline of seven parts per billion (ppb). As a result of these findings, Long Island in 1980 banned Temik® for agricultural use. The ban will not solve the problem entirely: A Cornell University study estimates that Temik® in Long Island drinking water could persist at concentrations above the state's limit for 100 to 140 years.

A book edited by two ORNL researchers discusses the implications of groundwater pollution caused by human discharges of synthetic chemicals. ORNL scientists' attempts to monitor and prevent deteriorating groundwater quality are explored.

Temik® was also banned in Florida in 1983 shortly after it was detected in at least eight wells at concentrations as high as 315 ppb, 30 times the safety limit (10 ppb) recommended for drinking water by the U.S. Environmental Protection Agency (EPA). One reason for the ban is concern that three of the state's major potato-growing counties lie above the the Floridian Aquifer, from which 42% of the state residents take their drinking water.

How widespread is the problem of groundwater pollution? David E. Burmaster, former staff member of the President's Council on Environmental Quality and now an associate with Industrial Economics, Inc., in Cambridge, Massachusetts, says that during the past ten years synthetic organic chemicals have been detected in drinking water wells in virtually every state.

The abundance of synthetic organic chemicals and their improper disposal in the past 25 years are largely responsible for today's groundwater pollution problem. Travis and Etnier report that annual production of industrial and agricultural chemicals in the United States quadrupled between 1960 and 1980 and that only 10% of the more than 3.5×10^{10} kg of hazardous chemical wastes generated by chemical production are disposed of in an environmentally safe manner.

Since 1960 most of the chemical wastes have been discharged to surface waters or left exposed to rainwater. Runoff from rain and snow melts dissolves chemicals and seeps into the ground, eventually finding its way to aquifers. In fact, 25% of all precipitation ends up as groundwater. Chemicals in the surface water enter the sediments and seep into subsurface areas, eventually ending up in groundwater.

Groundwater can itself pick up contamination by moving into underground areas where waste chemicals have been buried. The movement of groundwater is of concern also because that is the route by which contaminated water reaches public and private wells. Groundwater movement ranges from 1 to 500 m/year; thus it can be detained for only a few years or for tens of thousands of years. If the detention time is long, centuries might pass before a polluted aquifer could flush itself of contaminants. However, as Robert Cleary, professor of geoscience at the University of Sao Paulo, points out, groundwater flow patterns are difficult to describe and predict accurately because of the extensive fieldwork and digital computer models required for the task.

Health Effects Unclear

The health effects of contaminated groundwater are poorly understood, according to Robert Harris, codirector of the Hazardous Waste Research Program at Princeton University's Center for Energy and Environmental Studies. One reason is that where human health problems of unusual proportions exist, proving that contaminated drinking water caused them is difficult.

Consider the cancer cases of Woburn, Massachusetts. In 1979 a red flag was raised when the Centers for Disease Control in Atlanta learned that six Woburn

Electromagnetic Terrain Conductivity Surveys Tell Where Best To Monitor Groundwater Quality

Public and institutional concern about the failure to protect groundwater from contamination and to reclaim polluted aquifers has risen sharply in recent years. At the same time, increasingly sophisticated groundwater studies and the associated technology are helping researchers and regulators accurately evaluate groundwater quality. However, because the cost of performing high-quality studies of groundwater is great, investigators must develop techniques that will enable strategic placement of monitoring wells and groundwater tests. One approach is to use surface geophysical techniques; they can provide rapid and economic characterization of subsurface conditions and can locate the best sites for groundwater testing.

ORNL researchers Richard H. Ketelle of the ORNL Energy Division and Francois G. Pin of the Engineering Physics and Mathematics Division have been using a surface geophysical technique for studies of migration of hazardous wastes into groundwater on the Oak Ridge Reservation and in Wyoming. The technique, called electromagnetic terrain conductivity mapping, has been used for many years as a mineral prospecting tool. The mapping technique uses special equipment, including two coils, to measure the apparent electrical conductivity of subsurface materials over varying depths, from near the surface to depths exceeding 50 m.

In this technique a Geonics EM 34-3 instrument uses a 63-cm-diam transmitting coil to generate a primary electromagnetic field, which induces current flow in conductive materials, such as water and dissolved solids, within the area of influence. A 63-cm receiver coil detects and measures the secondary electromagnetic field that results from the subsurface current flow.

According to Ketelle, "An electromagnetic conductivity greater than that of a similar 'background' area may indicate the presence of more subsurface water, or pore fluid, which can indicate groundwater flow paths; more dissolved solids, such as soluble waste materials; or both."

The instrument's depth of influence can be varied by changing the separation of the coils, which are held aboveground at distances of 10, 20, or 40 m apart. The greater the separation, the deeper the measurements. By using different coil separations, multiple depth measurements are made over the same traverse route, yielding a three-dimensional map of conductivity.

The ORNL scientists used the technique to map potential groundwater flow paths in a portion of the proposed Central Waste Disposal Facility site on West Chestnut Ridge. With the technique they characterized flow paths controlled by dissolution of the dolomite

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children living in a six-block area had developed leukemia. This finding triggered a study of cancer mortality in Woburn, which showed that the town had a death rate higher than the national average for leukemia and kidney cancer. The culprit for the excess cancers was believed to be toxic waste disposal sites containing hide-tanning chemicals and pesticides produced in Woburn between 1850 and 1920. Researchers in 1979 had found no evidence that cancer victims were exposed to toxic substances in drinking water at levels high enough to cause cancer. However, according to Travis, "A recent study by the Harvard School of Public Health has found a positive statistical association between exposure to these substances and childhood leukemia."

Harris says there is generally insufficient information to link public health impacts to chemical contamination of groundwater. The Office of Technology Assessment (headed by Jack Gibbons, formerly of ORNL) reports that 3 million chemical compounds are used in the United States and that 3000 new chemicals are added each year. Unfortunately health-effects data exists for only a small number of chemicals, and most of this data comes from animal studies. "Despite these problems," says Travis, "several very recent studies indicate that organics in drinking water may be a ticking time bomb."

Pollution Solutions?

Is there a technical fix for groundwater pollution? David Miller, author of *Report to Congress on Waste Disposal Practices and Their Effects on Groundwater*, argues that the best protection for groundwater is to prevent it from ever becoming contaminated. This protection can be ensured only by banning disposal of toxic wastes near aquifers whose waters are still pristine. Miller says that measures exist to treat groundwater to reduce its concentration of chemical contaminants and to help it recover from the intrusion of hazardous wastes. Remedial actions include pumping the water from the aquifer over a 25-year period, bedrock. Groundwater tends to flow through areas of the dolomite where it has created cavities by dissolving the rock, forming beds of wet clay (which are more conductive than solid bedrock). Performance of a fluorescein dye tracer test in the same area confirmed the general flow path, indicated by the electromagnetic conductivity study. This information was used in the pathways analysis for the site and helped the ORNL researchers identify the best areas for locating groundwater monitoring devices.

Because terrain conductivity may be strongly influenced by the electrical conductivity of pore fluids, the technique is useful for locating seepage plumes containing electrolytic fluids, such as acids, which are found in some hazardous wastes. The ORNL researchers mapped the migration of electrolytic fluids in the vicinity of the S-3 ponds at the Oak Ridge Y-12 Plant, using the technique in conjunction with a preliminary evaluation of the hydrogeology of Bear Creek Valley.

Infiltrating fluids are known to travel through fractures and bedding planes in weathered shale bedrock. Ketelle and Pin's terrain mapping confirmed that the shale bedrock structure in Bear Creek Valley controls the direction of the migrating fluids. They also found that the elongated plume parallels the geologic strike, or outcrop trend—that is, the compass orientation of the bedrock controls the flow path of the seepage plume. The results of their electromagnetic mapping correlated well with measurements of electrical conductivity (specific conductance) in groundwater taken from wells in the study area. Ketelle and Pin's results were used in planning the layout of treatment facilities for use in closeout activities at the S-3 ponds to minimize disturbance of soils in the plume area.

Ketelle and other ORNL staff members are using the electromagnetic method at selected uranium mill tailings management areas in Wyoming for the Uranium Recovery Field Office of the U.S. Nuclear Regulatory Commission (NRC). They are demonstrating the effectiveness of this technique for NRC, which may use it to monitor seepage of fluids out of tailings ponds. The terrain conductivity surveys are being correlated with groundwater pH (acidity level), specific conductance, and available subsurface data.

"Electromagnetic terrain conductivity is just one of many surface geophysical techniques available," says Ketelle. "It has broad applicability in groundwater studies, as we've shown by a variety of applications in various geological settings. Now, we hope to refine our interpretive methods and depth resolution to further enhance the technique's versatility. It could be used by industry and regulators to select the best sites for monitoring groundwater quality."

detoxifying it, and reinjecting it into the ground. However, he adds, these measures are rarely completely successful.

Because of growing public and congressional concern over groundwater pollution, EPA in 1982 proposed a national groundwater policy. This policy would give state and local governments a lead role in developing and implementing means of protecting groundwater.

Classifying groundwaters by quality is "the first step in establishing any groundwater quality program," says James T. B. Tripp, counsel for the Environmental Defense Fund (EDF) and director of EDF's Eastern Water Resources and Land Use Program. Tripp recommends classifying aquifers according to whether they have (1) pristine, unpolluted water, (2) contaminated water that can be made potable with reasonable treatment, or (3) water so contaminated and so isolated that it is unusable. Following classification, Tripp says, land use restrictions should be imposed to prevent contamination of pristine or potentially potable sources and to permit waste disposal only near unusable groundwater sources.

"Groundwater," concludes Burmaster, "is easily contaminated, especially by certain volatile organic chemicals which readily penetrate the normal protective mechanisms. Once contaminated by organic chemicals—even in concentrations of a few parts per billion—groundwater can no longer be used for drinking water, unless expensive treatment methods are installed.

"Some former drinking water supplies are so contaminated now that they may never be used again for many generations—if ever. These hydrologic and biological realities are quite sobering. Having spent several years now understanding the intricacies of groundwater management, I am glad to paraphrase the saw, 'An ounce of prevention is worth a *ton* of cure.'"—*Carolyn Krause.*

Diverting Groundwater from Buried Radioactive Waste

Shallow land burial of low-level radioactive waste in the eastern United States was considered a safe practice for more than three decades. However, in the mid-1970s a potential problem was found to exist: Moving groundwater could come in contact with the buried waste, leach radionuclides, and transport them to unrestricted, off-site areas where they might eventually jeopardize private and public water supplies. Water enters waste trenches either by the upward flow of groundwater as the water table rises following a period of heavy precipitation, by lateral subsurface flow of groundwater, or by direct surface infiltration from rainfall and snow melts.

One institution with a direct interest in this problem is Oak Ridge National Laboratory, where low-level radioactive wastes have been sequestered in trenches in six solid waste storage areas (SWSAs). Water has been found to enter and collect in waste trenches at ORNL. In 1976, for example, shortly after the 49-trench area in SWSA No. 6 was closed, Harpal Arora, Dale Huff, and Dave Ward of the ORNL Environmental Sciences Division (ESD) noted that many trenches were holding water much like bathtubs, particularly during the wet winter and spring months. In an attempt to prevent rainwater from infiltrating the cover material and collecting in the trenches after each rainstorm, workers installed a bentonite clay cover in the fall of 1976 to seal the entire 0.44-ha (11-acre) trench area. This sealing operation was expected to result in a gradual draining of water from the underlying trenches.

Despite this attempt, water continues to collect in the underlying trenches at depths fluctuating between 1 and 2 m. The maximum water level occurs in January, February, and March; the minimum, in September and October. Says Ed Davis of ESD: "The seal may be keeping out direct infiltration of rainfall. But after eight years, water levels in the trenches still fluctuate seasonally, suggesting that the seal may be faulty. Another possibility is that subsurface flow from outside the sealed area is contributing to water in the trenches."

Concerned about the possible intrusion of water from below the surface, ORNL researchers, led by Davis and R. G. Stansfield of ESD along with W. D. Barton of the Engineering Division, considered several engineered barriers that could intercept shallow subsurface flow and suppress the fluctuating water table within the 49-trench area. These options included surrounding the site with rock-filled caissons, a slurry wall anchored to bedrock, a drilled pier cutoff wall, or a passive French drain. They selected the French drain, which is a trench lined with filter fabric, backfilled with crushed stone, and covered to the original surface level with the excavated soil. Their decision was based on total design and construction costs, ease of installation, and probability of success.

The design goals of the drainage project were to (1) intercept and divert subsurface flow from uphill slopes before it can enter the waste trenches and (2) lower the water table within the 49-trench area and keep it suppressed during the wet months of the year so that the groundwater is too low to flow laterally into the waste area. Over a 40-day period starting in August 1983, a French drain 252 m long, 1 m wide, and 9 m deep was constructed at a cost of $153,000. The topography of the site required construction of the drain in two sections, which intersect in the northeast corner of the site at a depth of 9 m below the ground surface.

As the design depth of the drain was reached, filter fabric made of nonwoven celanese with openings of up to 0.015 cm was placed on the sidewalls, and crushed stone was poured into the lined excavation to within 0.6 m of the surface. Next, the filter fabric was folded over the crushed stone fill-material, and the remaining 0.6 m of trench was brought to the original grade by backfilling with site soil. No drainage pipe was placed in the bottom of the excavation.

Except for the five days spent excavating sidewall material that slid into the drain during construction, the project proceeded smoothly. In late September 1983 the excavation equipment was removed from the site, and construction began on the two concrete catch basins used to receive flow from the two drain sections. In October the catch basins were completed, and the site was seeded and returned to nearly original conditions.

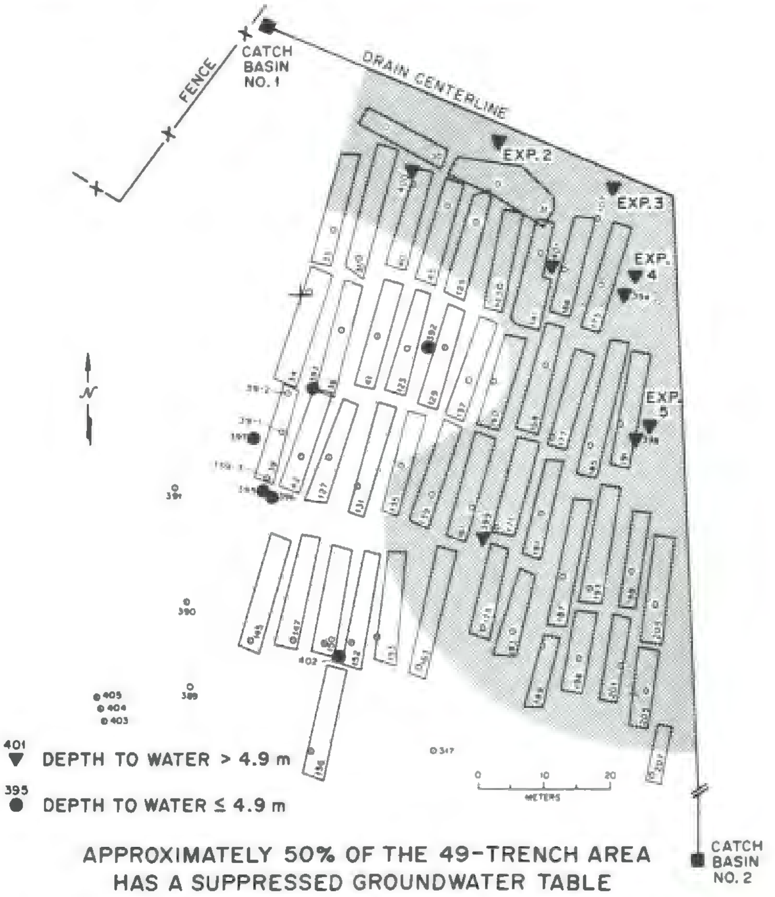
To evaluate the effectiveness of the French drain in SWSA No. 6 during the wet winter months, Davis and Stansfield compared the water table elevation records in the 49-trench area for February 1983 (before drain construction) with those for February 1984 (after construction). Says Davis: "We found a significant postconstruction drop in the water table level, bringing it generally below the lowest portion of the buried waste."

Davis also says that "the water table level was drawn down toward the drain bottom in an area extending about 60 m into the 49-trench area. The site water table no longer mimics the surface topography; instead, it slopes toward the bottom of the drain. As a result, the water table has been lowered about 4 m in the northeast corner of the site, where the two drains intersect. This achievement will be useful in the design construction of other drains in similar geologic media."

The French drain is considered successful in protecting the radioactive waste in the 49-trench area if it suppresses the water table to a depth of at least 4.9 m. At this depth the water table will no longer intersect the bottoms of the waste disposal trenches and cause periodic trench inundation and possible radionuclide migration.

According to Davis, "We found from

A view of the solid waste storage area (SWSA) No. 6 French drain during construction. The 1-m wide excavation is lined with filter fabric, backfilled with crushed stone, and covered to original grade with excavated soil. The drain was found to protect half of the burial site for low-level radioactive waste (and 29 of 49 trenches) from contact with rising groundwater.



Plan view of the SWSA No. 6 French drain showing the extent of groundwater suppression. The drain was completed late in 1983. As a result of this drain, 5 of the 49 trenches have dried out and 24 others are no longer targets for intruding groundwater and for surface water percolating into the ground.

our water elevation survey that the drain suppressed the water table in half of the 49-trench area through the winter of 1984. Thus 29 of the 49 waste disposal trenches were protected from contact with rising groundwater. We also found that monitoring wells more than 60 m away from the center of the drain have not been affected by the drain's drawdown. They continue to show water at less than 4.9 m after rainfall."

From analyses of the data, Davis and Stansfield also identified five waste trenches that were completely drained of intratrench water as a result of the drain's construction. They attribute the drying of these trenches to their close proximity to the drain. "No other trenches in the area dried up so dramatically," says Davis. "In fact, many continued to show a pattern of rising intratrench water levels during November and December 1983 and January 1984 after drain construction. This postconstruction rise in intratrench water levels suggests that the bentonite clay seal is leaking and that the water is entering the trenches as surface infiltration, not as rising groundwater or lateral subsurface flow. We've concluded that the entire bentonite clay sealing procedure should be reevaluated."

The SWSA No. 6 drainage project has demonstrated that a French drain can help control water table fluctuations at waste disposal sites. "If the surface topography is suitable, a drain can discharge to surface water at a lower altitude than the area being protected and thus require no future operation and maintenance costs," Davis says. "The concept of subsurface drainage as demonstrated by this project is actually quite simple, but it could be applied to various water-related problems at waste disposal sites throughout the nation."

awards and appointments

James O. Stiegler has been appointed director of the ORNL Metals and Ceramics Division. **James R. Weir, Jr.,** has been named associate director of the division.

Christine Travaglini has been named director of the ORNL Finance and Materials Division. She is the first woman to be appointed division director at ORNL.

Martin S. Lubell has been appointed to the International Organizing Committee for the Magnet Technology Conferences. This committee has 16 members, who represent the major technology nations, including East Bloc countries and the Peoples Republic of China. Lubell is one of two members from the United States.

Jagdish Narayan has been named a Fellow of the American Association for the Advancement of Science.

Stan A. David and **Chain T. Liu** have been named Fellows of the American Society for Metals. David was recognized for "contributions to understanding of solidification behavior and microstructural characteristics of welds, peritectics, and composites." Liu was cited for "contributions to understanding materials behavior in the solid state, particularly with precious metals, and recognition of the importance of electron-to-atom ratio in production of ductile long-range ordered alloys."

Brian C. Sales and **Lynn A. Boatner** received an award in the Department of Energy's 1984 Materials Science Research Competition for developing lead-iron phosphate glass to store high-level nuclear wastes. For their work in developing ductile nickel aluminides for high-temperature structural use, **Chain T. Liu, Joseph A. Horton,** and **Calvin L. White** also received an award in this competition. Both developments were cited for their "significant implication for energy technology."

Robert J. Gray has been named the 1984 recipient of the Albert Sauveur Achievement Award from the American Society for Metals. He was honored for his "pioneering metallurgical achievements."

David L. Greene and **Patricia S. Hu** have received the Pyke Johnson Award of the National Research Council's Transportation Research Board for their paper "Vehicle Usage in Multi-Vehicle Households and the Price of Gasoline." This award is given each year for the best paper in the area of planning and administration of transportation facilities.

David E. Bartine has been appointed manager of ORNL's new Strategic Defense Initiatives ("Star Wars") Program.

James W. Terry has been appointed manager of institutional planning for ORNL. **William H. Butler** has been named manager for computer planning at ORNL. Both are members of the ORNL Program Planning and Analysis Office.

Eric Hirst has been appointed a member of the Committee on Behavioral and Social Aspects of Energy Consumption, a committee of the National Research Council's Commission on Behavioral and Social Sciences and Education.

John G. Merkle has received the George R. Irwin Medal for 1984 from the American Society for Testing and Materials. The award is given annually to an individual who has made original contributions in the field of fracture mechanics whose applications lead to improved safety of structures.

Curtis C. Travis, editor-in-chief of the journal *Risk Analysis*, has been appointed coordinator for the ORNL Office of Risk Analysis.

Lee Berry has been appointed associate division director for Development and Technology in the ORNL Fusion Energy Division. He is also manager of the ORNL Fusion Energy Development and Technology Program.

Michael J. Saltmarsh has been named head of a newly created Confinement Projects Section in the ORNL Fusion Energy Division.

William R. Laing has been awarded a certificate of appreciation by the American Society for Testing and Materials for editorial excellence in the preparation of standards.

James B. Roberto has been appointed technical assistant to Alex Zucker, Associate Director for Physical Sciences at ORNL.

Peter Lalley has left ORNL to become director of the Institute for Medical Research in Bennington, Vermont.

reader's comment

To the editor:

Betrayers of the Truth, by William Broad and Nicholas Wade, was reviewed rather favorably in issue Number Two of the 1984 *Review*. The book was less favorably reviewed for *Science* in its March 25, 1983, issue (pp. 1417–18) by Marcia Angell, deputy editor of the highly respected *New England Journal of Medicine*. Her criticisms bear repeating here. She points out that the same charge that Broad and Wade level at scientists—namely, falsification of data—can be leveled at these authors, thus undermining or invalidating their principal thesis.

"How frequent is fraud in science?" asks Angell. "After considering the scanty evidence on the subject, Broad and Wade conclude, 'We would expect that for every case of major fraud that comes to light, a hundred or so go undetected. For each major fraud, perhaps a thousand minor fakeries are perpetrated.'" Angell comments, "No basis for these numbers is given. This sort of *calculation by expectation* [italics mine] is surprising in such stern critics."

Broad and Wade have done exactly what they attempt to lay on the scientific community: enlarged their data by factors of 100 or 1000 at the stroke of a pen! Just who is betraying the truth?

Angell goes on: "Perhaps the most serious error in the depiction of science . . . is the implication that scientists do not take into account the possibility of self-deception. This is not so." Broad and Wade decry the impersonal format of the scientific report as a sort of public relations trick ("to give the appearance of objectivity," they say). Angell points out that one reason for that format is "to require the researcher to confront his or her data," as Broad and Wade should know.

Broad and Wade see the responses of the scientific community as inadequate, which Angell concedes. However, she points out that "their tone of outrage is inappropriate and does not allow for the complexities and uncertainties of dealing with a situation as it unfolds, rather than in hindsight. . . . [Also, there are] uncertainties about due process and the legal ramifications of making an accusation of fraud."

She concludes, "It would be a pity if the scientific community allowed the misconceptions [and, I might add, the exaggerated 'evidence'] in [this] book to deflect it from the important point that we must take fraud seriously and continue our efforts to develop methods for dealing with it effectively."

Waldo E. Cohn, senior biochemist, retired
Consultant in Biology Division.

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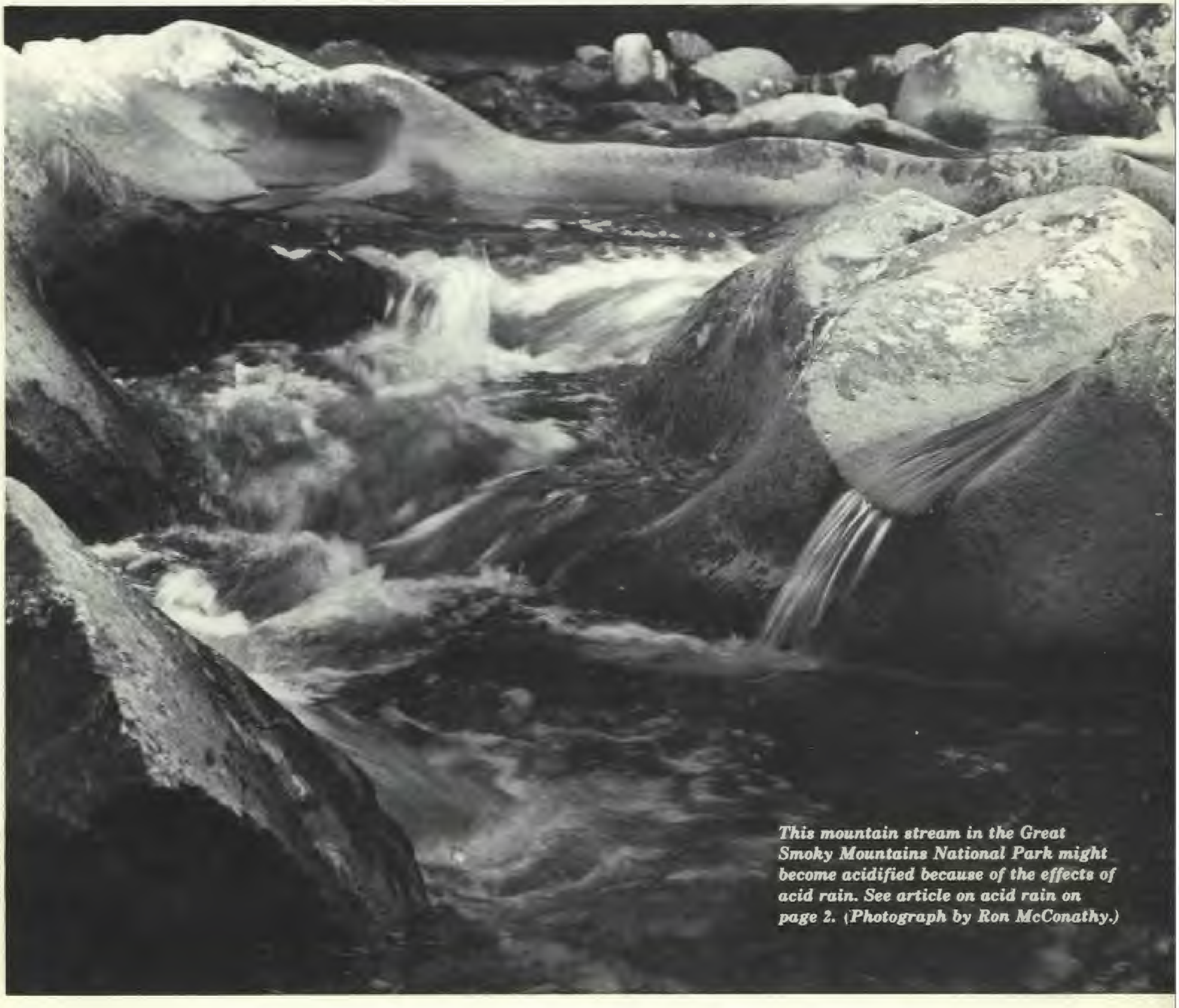

This mountain stream in the Great Smoky Mountains National Park might become acidified because of the effects of acid rain. See article on acid rain on page 2. (Photograph by Ron McConathy.)