

Environmental Sciences and Technology

Energy development, production, and use can induce major environmental and health problems, such as fish kills and respiratory disease. To better understand these problems and develop solutions in response to DOE's concerns, ORNL takes an interdisciplinary approach by integrating a broad spectrum of disciplinary foundations (biology, chemistry, computational sciences, ecology, engineering, geology, geochemistry, geophysics, hydrology, physics, toxicology, and social sciences). Our work, which is anchored in a strong fundamental research program, extends to applications in human health, biotechnology, environmental protection and remediation, separations science, and studies of global change and sustainable development. Facilities for biotechnology, bioprocessing, and ecological and environmental studies support extensive industrial and educational outreach programs.

In 1997, ORNL played a major role in DOE's 11-lab report on technology opportunities to cut greenhouse gas emissions. ORNL researchers have been using computer modeling to better understand how terrestrial ecosystems influence carbon dioxide concentrations in the atmosphere; they found that, in a growing season during an El Niño Southern Oscillation, terrestrial ecosystems take up 1 to 2 billion tonnes of additional carbon. ORNL researchers have been applying scientific knowledge to help Guatemala address its biodiversity and environmental problems and to raise the standard of living of rain forest residents. ORNL has discovered ways to orient electrically charged spinach leaf proteins, bringing us closer to biomolecular electronic devices based on spinach, not silicon. In environmental technology, we are mapping the effectiveness of bacteria in breaking down chlorinated solvents contaminating soil at an Air Force base.

Strengthening Environmental Management in Guatemala

ORNL is helping Guatemala improve its environmental management and decision-making to protect its biodiversity.



In the Peten region in northern Guatemala lies an enormous rain forest. It is a treasurehouse of biodiversity and the largest carbon sink in the Western Hemisphere north of the Amazon River. Because of Guatemalans' demands for jobs, homes, and farm land, this region has been threatened by deforestation, which can eliminate endangered species of medicinal value and increase global greenhouse gas concentrations. By the late 1980s, it was feared that the region would be completely deforested within three decades if nothing was done.

As a part of its development assistance programs in Guatemala, the U.S. Agency for International Development (USAID) established a Mayan Biosphere Project (MBP) in 1991. The goals were to help preserve the rain forest and raise the standard of living for the region's people, many of whose Mayan ancestors go back 1000 years. USAID asked ORNL to organize and lead the multiyear project through an interagency agreement with DOE. The project involved working with a diverse team of nongovernmental environmental organizations and local groups.

ORNL's Keith Kline was assigned to live in Guatemala City, where he has served as the USAID Mission's environmental officer and leader of the project, with support from other ORNL staff members. Since MBP began operating in 1992, the project has significantly slowed the rate of deforestation in the Peten region and helped its 400,000 residents shift to a lifestyle less destructive of the forest. For example, instead of clearing forests to grow corn and beans, some people collect and sell forest products. Others have improved cultivation practices and introduced agroforestry. As a focus for the effort, the project established a national park to provide effective environmental management in the area.

In 1996, a formal evaluation of all USAID environmental programs worldwide ranked MBP number one in effectiveness. In 1997 the agency's Latin American and Caribbean Bureau ranked it first in performance in the hemisphere. In 1996, USAID

extended MBP for four additional years through March 2000, with a total estimated life-of-project budget of \$50 million.

One aspect of the extension added a new policy component intended to improve the capacities of Guatemalan government agencies (equivalents of the U.S. EPA and National Parks Service) to manage the environment for the long term. Since then, ORNL's Tom Wilbanks, Tim Ensminger, Bob Perlack, and Sherry Wright have traveled frequently to Guatemala to meet two challenges: assisting Guatemalan partner agencies in conducting environmental impact and policy assessments related to the most pressing national controversies and setting up a partnership between ORNL and a Guatemalan counterpart, Fundación Solar, to transfer expertise.

The first of the controversies was provoked by a proposal from a U.S.-based multinational forest products firm. It sought to transport logs from a Guatemalan tree plantation to the Atlantic coast by barge on the scenic Rio Dulce, through the heart of a national park, and to construct a barge terminal at the park's edge. This proposal was heatedly opposed by environmental groups and advocates of ecotourism development. USAID asked ORNL to assist Guatemala's equivalent of the EPA in assessing the environmental impacts of the proposed activity and suggesting alternatives to the proposed action. ORNL's work became not

only a basis for discussions at the highest levels of government but also has been widely recognized as setting a new standard for improving information for environmental decision making in Guatemala. In the end, the Guatemalan president disapproved the proposal, but discussions continue on other alternatives, influenced by ORNL's analysis.

As a part of this assessment, ORNL recommended that the country develop a workable environmental management plan for the Rio Dulce area. In 1997 the Laboratory was asked to help organize and lead an effort to develop such a plan, which would give Guatemalans their first experience with a public participation process.

What makes ORNL's accomplishments different from those of, say, a consulting firm is that our assistance is grounded in knowledge obtained through our research in environmental management, environmental impact assessment, biodiversity protection, global climate change, and energy and environmental institution building. Besides applying this knowledge to foster sustainable development, we are bringing back from Guatemala unanswered research questions that may be added to future research agendas.

The project was funded by USAID through an interagency agreement with DOE.

Tim Ensminger (second from right) is one of several ORNL researchers who assessed the environmental impact of a proposed log barging operation on the Rio Dulce (river shown behind the men on the boat dock and in the photograph on opposite page) as a part of an environmental assessment of the Rio Dulce National Park in Guatemala.



ORNL's Big Role in a Major DOE Study

ORNL played a major role in DOE's 11-lab report on technology opportunities to cut greenhouse gas emissions.

In an address to the United Nations in June 1997, on the occasion of the fifth anniversary of the Rio Conference on the Environment, President Clinton spoke on the need for a vigorous technology research, development, and demonstration (RD&D) program to address the challenge of global warming. He noted that the United States has only 4% of the world's population yet produces more than 20% of its greenhouse gases, largely because the nation relies primarily on fossil fuels to heat, cool, and light buildings, run its factories, and power its vehicles. "In order to reduce greenhouse gases and grow the economy," he said, "we must invest more in the technologies of the future. Government, universities, business, and labor must work together. All these efforts must be sustained over years, indeed decades."

Following this address, President Clinton directed his cabinet to respond to the challenge of reducing greenhouse emissions in the United States. In turn, Energy Secretary of Energy Federico Peña asked ORNL Director Alvin Trivelpiece and Richard Truly, director of the National Renewable Energy Laboratory, to lead a DOE national laboratory effort to identify cost-effective technologies to reduce greenhouse gas emissions. A team of 11 laboratories was mobilized to respond to this request. The result was a two-volume report entitled Technology Opportunities to Reduce U.S. Greenhouse Gas Emissions.

More than 150 persons from all 11 national laboratories participated in the effort,

and at times as many as 300 people across the DOE system were involved. Because of the need to complete the report on a compressed schedule, the report was planned, written, and revised largely through electronic mail submissions, conference telephone calls, and reviews of draft reports that were posted on the World Wide Web. At ORNL some 30 scientists, managers, writers, editors, artists, and electronic publishers were involved in putting together the report.

The report describes technology opportunities "that have significant potential to reduce greenhouse gas emissions" between now and 2030. In its second volume, 47 specific technology pathways are profiled. These technologies fall in three categories: energy efficiency, clean energy, and carbon sequestration (removing carbon from emissions and increasing storage of carbon). DOE is already developing many energy efficiency technologies, such as refrigerators and cars that will be two to three times more efficient than today's models. The report proposes a strategy to improve and increase the use of clean-energy sources that emit little or no carbon, such as natural gas burners, nuclear power plants, renewable energy (e.g., solar and wind power, electricity and fuels from agricultural biomass), and fuel cells that use hydrogen to produce electricity. Carbon emissions could also be reduced by switching transportation fuels from gasoline to biodiesel fuel and ethanol; by distributing electricity more efficiently using superconducting transformers, cables,

and wires; and by removing carbon from fuels before combustion. The third category of technology pathways includes those that would efficiently remove carbon dioxide from combustion emissions before they reach the atmosphere or would increase the rate at which oceans, forests, and soils naturally absorb atmospheric carbon dioxide. Technologies to store carbon deep in the ground or in aquifers over a long time might also be devised.

In the report, the DOE lab directors conclude that (1) by 2030, a vigorous RD&D program could deliver a wide array of cost-effective technologies that together could reduce the nation's carbon emissions by 400 to 800 million tonnes of carbon per year; (2) basic research is needed to advance science and technology enough to reduce U.S. greenhouse gas emissions significantly yet sustain economic growth, partly through side benefits such as improved air quality, reduced U.S. dependence on imported oil, and increased exports of U.S. technologies to help other nations reduce their greenhouse gas emissions; (3) adequate support for an accelerated RD&D program could be double the current levels of funding for development of energy-efficiency technologies; and (4) strategic public-private alliances provide the best approach for developing and deploying most greenhouse gas-reduction technologies.

The report recommends that the United States develop and pursue a detailed, comprehensive technology strategy for reducing greenhouse gas emissions. Implementing such a strategy, the report states, would be an "investment insurance policy," one that "DOE's national laboratories stand ready to champion."

Other DOE national laboratories that contributed to the report were Argonne, Brookhaven, Idaho (INEEL), Lawrence Berkeley, Lawrence Livermore, Los Alamos, Pacific Northwest, Sandia, and the Federal Energy Technology Center.

David Reichle, Marilyn Brown, John Sheffield, and Mike Farrell were the technical co-leaders for the planning and drafting of the DOE report, which was released by Secretary Peña on Earth Day, April 24, 1998 (see http://www.ornl.gov/climate_change).



Why Carbon Storage on Land Varies

ORNL researchers are using computer modeling to better understand the influences of terrestrial ecosystems and climatic variation on atmospheric CO₂ content.

What goes up sometimes comes down. By burning gasoline to power cars and trucks, coal to produce electrical power, and forests to clear land for agriculture, people have altered the earth's atmosphere. Fossil fuel combustion and forest clearing currently inject 8 billion tonnes of carbon per year into the atmosphere, which, combined with the carbon dioxide (CO₂) already naturally present, could speed the onset of global warming.

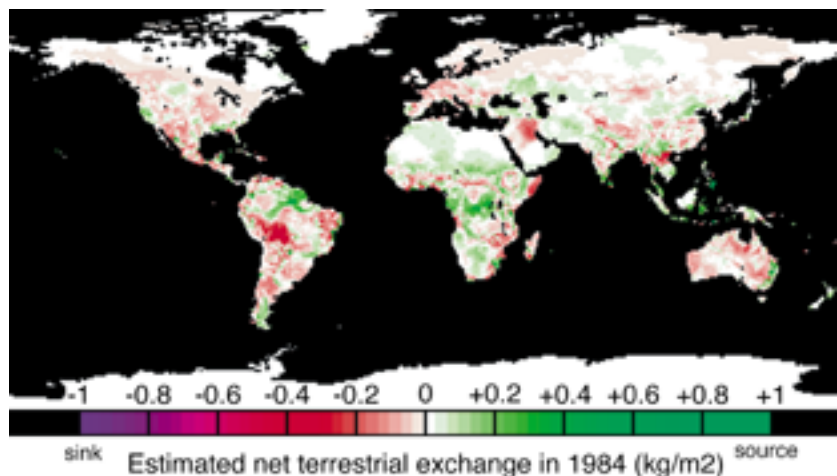
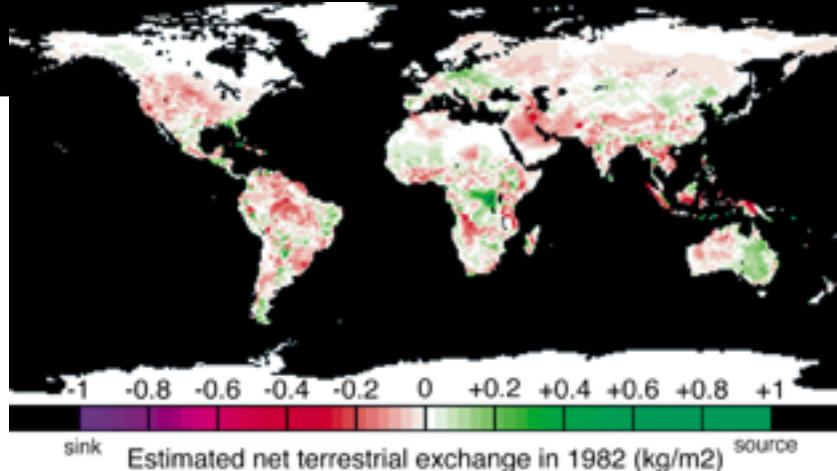
The good news is that not all the carbon added each year stays in the atmosphere. According to computer model estimates, about one-third of this amount is later taken up by the oceans. Another one-sixth (1.5 to 2 billion tonnes) is removed from the atmosphere at least temporarily by the world's terrestrial ecosystems—forests, vegetation, soils, farm crops, and pastures. But terrestrial ecosystems are a source of carbon to the atmosphere as well as a sink for its carbon. Although 15% of all atmospheric carbon, or about 120 billion tonnes, is annually taken up by trees and vegetation for photosynthesis to build plant tissue, about an equal amount is returned to the atmosphere as carbon dioxide from both plant respiration and the decomposition (by bacteria and fungi) of plant litter and soil organic matter. Another small source of carbon from terrestrial ecosystems is forest fires.

Scientists are unable to determine where 0.5 to 1 billion tonnes of carbon goes each year after it enters the atmosphere. They are trying to account for the “missing” sink required to balance this century's global carbon budget. How much of this carbon goes to the ocean and how much is absorbed by

terrestrial ecosystems? It is not now possible to directly observe exchanges between the atmosphere and terrestrial systems at regional, national, or global scales because of the large magnitudes and temporal variations of natural carbon cycle fluxes and the vast amount of carbon stored in vegetation and soil.

What is the fate of the unaccounted-for carbon? To help find out, ORNL researchers led by Wilfred (Mac) Post are using computer modeling to better understand how terrestrial ecosystems influence CO₂ concentrations in the atmosphere. They have discovered that, in the past 100 years, environmental conditions have changed slightly, enabling plant biomass to increase and terrestrial ecosystems to soak up more CO₂. Plants may be growing faster and larger because they are being “fertilized” by increased atmospheric concentrations of CO₂ and increased deposition of air pollutants containing nitrogen, a plant nutrient. Even more significant, the ORNL computer model results show that carbon exchanges between the atmosphere and terrestrial ecosystems are sensitive to climate variations, such as the increase in average global temperature of 0.5°C (1°F) over the past 100 years and the El Niño-Southern Oscillation, the large-scale climatic fluctuation of the tropical Pacific Ocean marked by a warm surface current. In a growing season during an El Niño, terrestrial ecosystems take up 1 to 2 billion tonnes of additional carbon, but much of that extra biomass may decompose and release carbon in succeeding years.

When climate change alone is considered, according to model results, carbon storage in the global terrestrial biosphere



The estimated net ecosystem production (plant biomass growth) changed by 2 billion tonnes of carbon globally between 1982 and 1984 as a result of changing weather patterns produced by the 1982–83 El Niño.

decreased by 1% from 1900 through 1988. However, when a moderate CO₂ fertilization response was added in the model, terrestrial carbon storage increased by 3% because plants took up more carbon for photosynthesis than they released through respiration. In short, terrestrial ecosystems have become more of a carbon sink than a source over the past 100 years. Also, computer model results suggest that climate change combined with CO₂ fertilization increased carbon storage in terrestrial ecosystems enough to account for 55 to 70% of the missing sink from 1900 through 1988.

ORNL's models indicate very large year-to-year variations in net carbon exchange between terrestrial systems and the atmosphere—on the order of 1 to 3 billion tonnes in either direction. Whether the larger fraction of carbon goes up or down in atmosphere–land exchanges depends on large-scale climate fluctuations.

The research was sponsored by DOE's Office of Biological and Environmental Research, Environmental Sciences Division, Carbon Dioxide Research Program.

Spinach Power: Biomolecular Electronics

ORNL has discovered ways to orient electrically charged spinach leaf proteins, bringing us closer to biomolecular electronic devices.

The next generation of optoelectronic devices may be based on spinach, not silicon. Photosynthetic reaction centers from spinach could be used for super-high-resolution video imaging, ultrafast switching, and solar power generation.

Green plant leaves contain two pigment protein complexes that convert light energy into chemical energy (photosynthesis). Both chlorophyll-containing proteins—called Photosystem I (PSI) and Photosystem II (PSII)—use the energy of the sun to make plant tissue. When each of these photosynthetic reaction centers receives a photon of light, charge separation can occur in 10 to 30 picoseconds—100 times faster than a silicon photodiode. If these photosynthetic reaction centers could be lined up perpendicular to a metal surface, current would flow, and biomolecular electronic devices would be possible.

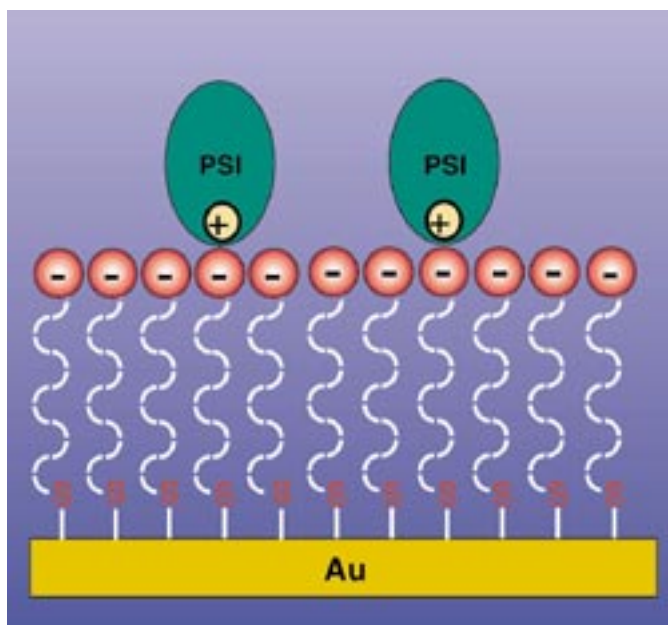
In the past decade, ORNL researchers Eli Greenbaum, James Lee, and Ida Lee came up with a number of significant ideas and findings. First, PSI and PSII can be isolated from spinach leaves. Second, PSI and PSII can be rewired to produce fuels by metallocatalysis and photosynthetic water splitting ($2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$). In plants, the photoenergized electrons are used to form carbohydrates (CH_2O) to build plant tissue. But these electrons (2e^-) can also be made to recombine with the protons (2H^+) to yield hydrogen by metallocatalysis, or the electrons can be put to work as electric current. The group demonstrated that spinach PSI and PSII together can be made to produce both oxygen and hydrogen, a clean fuel.

To generate electrical current, the researchers found they had to provide PSI reaction centers with an electrical contact and a preferred orientation. They learned how to deposit platinum (a good

electrical conductor) on one end of PSI. They showed that platinum anchors PSI to a gold surface and that it does not damage PSI or render it inactive.

The next hurdle was to orient the PSIs so that the same ends point in the same direction. A scanning tunneling microscope (STM) was used to determine the orientation of each PSI because the tunneling current is affected by the preferential direction of the electron flow. PSI will act like a current rectifier under the STM if it is perpendicular to the surface. If a PSI is parallel to the surface, it will act like a semiconductor instead. If all PSIs are perpendicular to the surface, current will flow only if all are pointing in the same direction, but not if half are pointing up and half down.

The initial success at turning a PSI molecule at will came when the group deposited a nanometer layer of platinum atoms on the reducing end of a PSI, which is positively charged. The deposited platinum weakened the electrostatic attraction of that end for a negatively charged gold surface, causing the other positively charged end to be more strongly pulled to the gold surface.



Electrically charged platinumized Photosystem I (PSI) reaction centers from spinach leaves are oriented in the same direction, making possible the development of biomolecular electronic devices. The gold (Au) base is treated with a chemical whose sulfur (S) atoms bind strongly to gold. The negatively charged ends of molecules in this chemical selectively bind to the positively charged free ends of the PSIs. As a result, all PSIs point in the same direction.
Drawing by Ida Lee.

In 1997 the ORNL group found an even better way to achieve preferred orientation of PSIs: chemical treatment of the atomically flat gold surface on a mica substrate. They coated gold surfaces chemically with three different chemicals and reported the results in the October 27, 1997, issue of *Physical Review Letters*. No preferential orientation was observed with 2-dimethylaminoethanethiol. “For mercaptoacetic acid,” they reported, “83% of the PSI reaction centers were parallel to the surface, whereas for 2-mercaptoethanol, 70% were oriented perpendicularly in the ‘up’ position and only 2% were in the ‘down’ position.” Apparently, the sulfur atom in each molecule binds strongly to gold, and the other end selectively binds to the oppositely charged part of a PSI, causing it to point either up, down, or parallel to the surface. Thus, PSI reaction centers can be selectively oriented by chemical modification of a gold surface.

These findings suggest the feasibility of the concept of a “lean clean green machine” that uses sunlight and operates without fossil fuels. Such a machine could meet many DOE mission goals by generating electrical power, producing clean hydrogen fuel, and fixing carbon dioxide on a ruthenium film to produce methane fuel, reducing the atmospheric content of greenhouse gases. It could be a DOE dream machine.

The research was supported by DOE’s Office of Computational and Technology Research, Advanced Energy Projects and Technology Research Division, and DOE’s Office of Basic Energy Sciences, Division of Chemical Sciences.

Intrinsic Bioremediation Across a Plume of Chlorinated Solvents

ORNL researchers are helping define a method for determining whether bacteria at a given site will effectively degrade contaminants such as trichloroethylene.

Chlorinated solvents, including trichloroethylene (TCE), are the most common contaminants in soil and groundwater because they are used as solvents and degreasers in manufacturing, maintenance, and service installations. Elimination or treatment of such contaminants through methods such as pump-and-treat technology and soil removal can be difficult and expensive. Fortunately, soil and groundwater contaminated with TCE often contain bacteria that break it down. In fact, under certain conditions, chlorinated solvents are completely degraded naturally to harmless end products through microbial action, a process known as intrinsic bioremediation. ORNL researchers are participating in a study at Dover Air Force Base (AFB) to help define a method for determining whether in situ biological destruction will occur at a given site. If the conditions for intrinsic bioremediation are present, expensive measures can be avoided.

Bioremediation is possible if the kinds of microorganisms that will destroy the contaminant are already present and if they exist in adequate numbers across the contaminated area, or contaminant plume. In the case of TCE, these organisms are not likely to be present unless contaminants other than TCE are present because the bacteria prefer to feed on the other contaminants. So bioremediation is a very likely possibility if TCE is a contaminant in a landfill or a swamp, and not likely if TCE is simply found in a clean sand environment. In the case of Dover AFB, gasoline is also

present as a contaminant, so it was thought that bacteria that feed on gasoline would be present in adequate numbers to break down most TCE there.

The problem in likely bioremediation sites is to determine whether in situ biological destruction is proceeding at a rate that will degrade the contamination effectively—and uniformly in all directions. To date, little evidence has been obtained regarding the changes in microbial population and activity, or heterogeneity, across subsurface and flowing-sand aquifers. Recent analyses by the ORNL investigators have demonstrated significant differences in rock strata, microbial biomass, and microbial diversity in both the horizontal and vertical directions. Typically, their geostatistical analysis has revealed significant heterogeneity at scales of greater than 1 meter. At these scales, the heterogeneity of the microbial populations is apparently closely tied to the geochemical and physical environment. These changes can be pronounced across regions with differing physical and geochemical properties.

In order to study horizontal subsurface heterogeneity across the TCE plume at the Dover AFB test site, researchers used sonic drilling technologies, proven at uncontaminated sites, in a TCE-contaminated aquifer. Sampling in sand aquifers with ordinary drilling methods is unsatisfactory because sand very rapidly seeps into the sampling

area, and it is consequently impossible to define the exact location of the sample. In “sonic drilling,” a rapidly vibrating drill is inserted into the aquifer. This technique obviates the problems of ordinary methods and allows the researcher to determine exactly the location of the sample. The sampling consists of multiple drillings across a horizontal cross section of the aquifer. The drilling equipment, which is supplied by a subcontractor, can be set up in only a few minutes and takes 10- to 20-ft cores at depths of 50 to 60 ft. The results of these studies will expand the understanding of the heterogeneity of microbial activity and community structure in the subsurface and its impact on the bioremediation process.

The work is sponsored by the U.S. Department of Energy, the U.S. Department of Defense, the U.S. Environmental Protection Agency, and industry, through the Remedial Technology Development Forum.



A member of the project team cuts a sediment core using sonic drilling at Dover Air Force Base. Photograph by Susan M. Pfiffner.