

Exxon Valdez oil no longer a threat?

Almost two decades after the *Exxon Valdez* oil spill, researchers with the National Marine Fisheries Service continue an acrimonious debate with scientists working for ExxonMobil over whether oil that remains from the spill is harming wildlife. In June, the government presented ExxonMobil with a \$92 million plan to address what it argues are continuing problems. In response, the oil giant said that effects to wildlife do not exist.

Altogether, the two sides have published more than 12 research papers in *ES&T* in the past 10 years. The latest is an ExxonMobil-funded study led by toxicologist Robert Huggett with the Michigan-based consulting group White Water Associates. The study, which appears in this issue of *ES&T* (pp 6513–6517), suggests that fish that spend their entire lives living close to shore are not exposed to oil that lies beneath the stony beach.

Both groups of scientists agree that Prince William Sound's waters, beaches, and animals have recovered for the most part. Both groups also agree that *Exxon Valdez* oil lingers below the surface of about 10 kilometers of shoreline. The current controversy centers on whether this oil is harming ducks, sea otters, and other animals that live or feed in the biologically rich lower intertidal zone—the part of the beach that is only exposed during low tide.

In the latest study, Huggett's team collected high cockscomb prickleback fish in 2004 and 2005 from sites with subsurface oil and from unoiled sites. They measured biomarkers for exposure to PAHs in the fish. Statistically, the PAH biomarkers from fish taken from the oiled sites were indistinguishable from those of fish taken from



ROBERT HUGGETT

Nearly two decades after the spill, scientists are debating whether *Exxon Valdez* oil is still harming wildlife.

the unoiled sites. The data indicate pervasive low-level exposure to PAHs from many sources, but the lingering oil is not causing additional exposure, says Huggett.

Publication of the Huggett study comes just a few months after a paper by Jeff Short (*Environ. Sci. Technol.* **2006**, *40*, 3723–3729) and government researchers with the National Marine Fisheries Service. That study estimated that, on the worst-affected beaches of northern Knight Island, foraging sea otters that routinely dig for clams in the lower intertidal zone could encounter oil often enough to slow population growth.

"The oil is there," says Huggett, commenting on the Short paper. "But our research shows that it is not bioavailable to the fish that are an ideal sentinel species, let alone otters," he adds. Huggett's team sampled 11 oiled sites, 4 of which were part of the most recent Short paper.

Short notes that otters and fish are not exposed to lingering oil in

the same way—otters dig down to the oil, whereas fish are exposed if oil gets into the water. He offers scathing criticisms of the Huggett study. Huggett's team used a poorly known, relatively insensitive fish, didn't establish a positive control by evaluating the fish's response to *Exxon Valdez* oil exposure, and didn't go to the worst sites, says Short. "These are all fundamental aspects of a good study, but they left them out. The variability in the biomarker data is so large and the range of values between oiled and unoiled sites is so similar that the study could be reporting unconstrained noise," he adds.

The *Exxon Valdez* oil spill, the largest in U.S. history, flooded Prince William Sound with approximately 38,800 tons of crude oil in 1989, killing hundreds of thousands of birds and marine animals and soiling more than 1200 miles of rocky beach. Under a 1991 settlement, Exxon (now ExxonMobil) was required to pay \$900 million

over 10 years for environmental restoration. But the settlement included a provision that extended other possible fines until 2006.

Last June, the U.S. Department of Justice and the Alaska Department of Law invoked that provision to seek another \$92 million from ExxonMobil to map the larger patches of subsurface oil and then remediate contaminated sites. ExxonMobil was given 90 days to decide whether to cooperate with the government or reject the plan. If the company refuses to comply, the government could go back to court and attempt to force it to pay, according to a Justice Department spokesperson.

Several experts contacted by *ES&T* declined to comment on the ramifications of the new paper, noting that scientific perspectives could be influenced by the longevity, acrimony, and financial stakes involved in the controversy.

But one researcher who has studied these and other intertidal

fish in Prince William Sound says that the Huggett paper is “good work that supports my own conclusions.” As a consultant to the government’s monitoring program, research pathologist Gary Marty looked for signs of PAH exposure in pricklebacks and crescent gunnels, another intertidal-zone fish. Marty notes that pricklebacks do not respond to PAH exposure as readily as crescent gunnels. In 2002, crescent gunnels from oiled sites had biomarker levels that were slightly above background levels in 3 of 4 sites, but pricklebacks had no evidence of exposure. By 2004, even crescent gunnels sampled from sites with lingering oil had no evidence of exposure.

“The oil really is petering out, and it doesn’t look bioavailable at this point,” says Marty. “If the oil isn’t having an effect, then it doesn’t matter how good your study is, you aren’t going to find an effect.”

—REBECCA RENNER

Pesticides lurk in daycare centers

Millions of children get exposed to pesticides while attending daycare, concludes the first nationwide study of insecticide residues in U.S. daycare centers. The study, published in this issue of *ES&T* (pp 6269–6274), found low levels of organophosphate and pyrethroid pesticides. Although the health impacts are unclear, the results raise questions about the risks children face from these chemicals.

“We found at least one pesticide in every daycare center,” says lead author Nicolle Tulve, a research scientist with the U.S. EPA’s National Exposure Research Laboratory. Tulve says that the concentrations were quite low. She did not comment on whether these

concentrations might be harmful but notes that no health advisories or national standards currently exist for such exposures.

For the study, researchers selected 168 daycare centers across the U.S. At each site, a technician wiped samples from indoor surfaces, such as floors and tables, and collected soil from outdoor play areas. The manager of each facility was also questioned about cleaning and pest-management practices. Researchers tested for 39 pesticides, and 63% of the centers reported applying up to 10 different insecticides. Organophosphate and pyrethroid pesticides cropped up most often, and three of the four centers with the most pesti-

News Briefs

Dioxins from Dow

A study released by scientists with the University of Michigan finds that people who live near a Dow Chemical plant in Midland, Mich., have an average of 32 parts per trillion of dioxins in their blood. This level is 28% higher than the average level of dioxins measured in residents from a county only 100 miles away. The U.S. National Research Council recently concluded that dioxins are likely carcinogenic. Increased blood concentrations of dioxins were associated with eating fish caught in waters that had been contaminated by Dow or with working at Dow’s plant from 1940 to 1959. The study was funded in part by Dow under an agreement with the state of Michigan. For more information, go to www.sph.umich.edu/dioxin.

Air conditioning will warm the planet

As global temperatures increase, researchers calculate that Americans will turn down the thermostat. Researchers pinned an economic model to a global circulation model that ran from 2003 to 2025, with a minimum temperature rise of 1.2 °C. In response, American energy consumption shot up by 1.09 quadrillion British thermal units. Experts project that carbon emissions from heating will drop by 4.9 teragrams (Tg) by 2010. However, overall emissions will peak at 9.4 Tg in 2023. “The results reveal the intricate energy-economy structure that must be considered in projecting consequences of climate warming for energy, economics, and fossil-fuel carbon emissions,” they write in a paper in *Geophysical Research Letters* (2006, doi 10.1029/2006GL026652).



USCPSC

cides detected were in the South, where warm weather brings out the bugs.

This study provides a teaching opportunity in terms of training childcare workers to manage pests in the safest way possible, says Lynn Goldman, who is a professor of applied health at Johns Hopkins University and a former EPA official in charge of the agency's pesticide program.

"These chemicals should be avoided around children, and if needed, bait traps, which do not leave residues on the floors and surfaces, are preferable, as long as they are kept out of the reach of children," she says.

Goldman says that she was disappointed that the agency did not use the results to characterize how much exposure to pesticides children face. "These data are interesting but [could] be far more meaningful," she says.

Paul Lioy, the deputy director of the Environmental and Occupational Health Sciences Institute at Rutgers University, agrees. He says that aggregating the total exposures could help to identify individuals with sensitivity to these chemicals.

In the past decade, more and more states have started regulating pesticides in daycare facilities. In 2000, Massachusetts passed a

law requiring all schools to submit integrated pest-management plans to limit children's contact with pesticides. And New York legislators recently introduced a bill to prohibit pesticide applications in daycare centers during business hours. Meanwhile, California is considering a bill to require daycare owners to notify parents when they are treating for pests.

However, Lioy also notes that pesticides are not all bad. These chemicals kill roaches, which can cause allergies in some children. Prudence, he says, dictates wise use of insecticides and complete pest-management plans.

—PAUL D. THACKER

Following mercury in a pristine park

Evidence that links atmospheric mercury to methylmercury in fish is mounting in the scientific literature. In a paper published in this issue of *ES&T* (pp 6261–6268), researchers strongly identify atmospheric deposition as the source of mercury contaminating fish living in Voyageurs National Park. The study comes just weeks after

another paper (*Environ. Sci. Technol.* **2006**, *40*, 5992–6000) reported similar conclusions from the Experimental Lakes Area in northern Ontario, Canada.

Voyageurs National Park, in northern Minnesota, is a relatively pristine region with no point sources for mercury. Two of the park's lakes, however, contain fish

with some of the highest mercury concentrations in the state, and the federal government posted fish consumption advisories in the mid-1990s.

To determine the source of mercury in Voyageurs National Park and how it ends up in fish, a team of researchers led by Jim Wiener of the University of Wisconsin–La Crosse measured mercury in bedrock and soils, and they statistically modeled lake and wetland functions. To study the food chain, the team analyzed 1-year-old yellow perch, which are eaten by loons and larger fish. One of the perch's predators, the northern pike, was also tested; those data will be published later.

The team found negligible geologic sources of mercury in 17 of the area's lakes and in the stream or groundwater catchments that feed them; however, sediment cores record that airborne mercury accounted for two-thirds of total mercury accumulated after 1900. The researchers concluded that atmospheric deposition from anthropogenic activities dominates the contemporary source of mercury pollution.

Atmospheric mercury deposition appears to be the only factor in the ecosystem that doesn't vary spatially, Wiener points out, refer-



Mark Sandheinrich of the University of Wisconsin–La Crosse samples fish from Peary Lake (shown here) and other lakes in Voyageurs National Park that contain high levels of methylmercury.

LELAND GRIM, VOYAGEURS NATIONAL PARK RESOURCES MANAGEMENT DIVISION

ring to data from the Mercury Deposition Network. Between lakes, mercury levels in the perch varied 5-fold, whereas levels in the pike varied 10-fold. Such variations, the team says, are caused by differences in wetland and lake behavior.

For example, total organic carbon served as an indicator of wetland output into the lakes. The team documented wetlands exporting methylmercury—the form of mercury that bioaccumulates in fish—along with the organic matter. That export rate differed among disparate watersheds but was highly correlated with the methylmercury concentrations in lakes and fish.

“My overall impression,” says Ed Swain of the Minnesota Pollution Control Agency, which provided financial support for the research, is that the new work “confirms in a single study a lot of our modern understanding of mercury.” Although many of the team’s conclusions have long been suspected and some have been published in bits and pieces (e.g., as results from METAALICUS), “no one had put it all together before.”

“It’s a neat demonstration of

the fact that a lot of our mercury problems in North America are in areas that are pretty pristine,” adds Drew Bodaly, project leader of the Penobscot River Mercury Study in Maine and a former researcher with the federal Fisheries and Oceans Canada.

The results solidly point to atmospheric mercury as the source of mercury in fish, Bodaly says. In the past, variability in mercury levels in both lakes and fish across a region has been used as an argument against atmospheric sources for mercury. Swain suggests that the variation among watersheds shows that each aquatic system processes mercury from the atmosphere in a unique way but with direct relationships to changes in mercury levels. “The implication is that if you lowered the mercury inputs . . . in each lake, the contamination levels would go down,” he says.

Bodaly also points to the continued effects of acid precipitation, which influences pH and sulfate levels. In the team’s models, the lower-pH, higher-sulfate lakes tended to have fish with higher mercury levels, he notes. “As a factor, [acid rain] hasn’t gone away.”

—NAOMI LUBICK

Lichens: Ready environmental sensors

Robust forests almost always contain healthy lichens, which are part fungi and part algae or bacteria. But the occurrence of these plantlike symbiotes is not the only indicator of ecosystem health: they also incorporate metals and other airborne pollutants. New research confirms that lichens can also be used to document the origin of PAHs, a finding that boosts their value as monitors of air pollution.

In a study published in this issue of *ES&T* (pp 6384–6391), Cristina Nerín of the University of Zaragoza (Spain) and colleagues show that lichens are equivalent to air-monitoring devices for measuring PAHs. The researchers ex-

amined lichens on both sides of the Somport tunnel, which crosses the Pyrenees Mountains, connecting France and Spain. The team also measured 16 PAHs inside and outside the tunnel with traditional air-monitoring devices.

Concentrations ranged from 6.79 to 23.3 micrograms per gram ($\mu\text{g/g}$) in the particulates outside the tunnel and 18.3 to 265.2 $\mu\text{g/g}$ inside; the lichens recorded concentrations of 0.91–1.92 $\mu\text{g/g}$. The results, Nerín says, show that lichens trap PAHs in a representative way. “The data obtained suggest that the main source of the PAHs found in the lichens and particles was road traffic,” she says.

News Briefs

California confronts climate change

Depending on what you read, climate change will either enhance or detract from economic growth in California. First, the bad news. The governor’s California Climate Change Center released a summary of 17 studies that examined how climate change will affect the state. With sea level expected to rise 22–35 inches by the end of the century, the authors of *Our Changing Climate: Assessing the Risks to California* warn that the state faces more coastal flooding, beach erosion, and loss of wetlands.



This rise in sea level could also exacerbate flooding in the San Francisco Bay region, where spring floods are expected to become larger as rainfall increases in the Sierra Nevada Mountains in response to climate change. “The potential impacts of global warming are unmistakable,” says Linda Adams, California’s secretary for environmental protection. Go to climatechange.ca.gov/biennial_reports/2006report to view the report.

Now, the good news. California’s attempts to regulate carbon emissions could provide a boon to business. A recent report by researchers at the University of California, Berkeley (UCB) finds that capping carbon emissions could boost the state’s economy by \$60 billion while creating 17,000 jobs. The economists predict that innovation and efficiency improvements will save consumers money and allow them to redirect it to in-state goods and services. In response, a group of UCB professors signed a letter urging the governor and state leaders to move forward with actions to limit climate change. The group called emissions caps a “potent strategy.” To view the UCB study, go to <http://calclimate.berkeley.edu>.



COURTESY OF CRISTINA NERIN

To measure PAHs, researchers sampled shield lichens (*Parmelia sulcata*) growing on both sides of the Somport tunnel linking Spain and France.

The team found that naphthalene dominated on the Spanish side. Heavier PAHs were more common on the wetter French side, where scientists expected to see the heavier compounds because they are washed out onto

the landscape in rainstorms. From these samples, the researchers also determined ratios of the different PAHs to predict the compounds' origins.

Lichens trapped PAHs from mostly pyrogenic sources—cars

and home heating systems—whereas particles in the tunnel could be fingerprinted to vehicle petroleum.

The new method looks promising, says Linda Geiser, an ecologist with the U.S. Forest Service's Pacific Northwest Region Air Resource Management Program.

The results confirm that lichens, mosses, and other bioindicators can give snapshots of pollutant concentrations and their potential ecosystem effects, she says, something that many people may not be aware of. They are also “a lot less expensive than putting out an instrument that you have to run for a year,” she adds.

Still, Geiser says she will continue to rely on both instrumentation and biological monitoring. “That would be the best way to do it,” even though analytical methods for lichens have improved over the past decade, she comments. “It's difficult trying to separate out organic compounds from an organic organism.”

—NAOMI LUBICK

Surprising release of metals from CO₂ storage

Injecting CO₂ deep within the earth remains one of the more promising methods of getting rid of the greenhouse gas. So far, rocks, composed of porous sandstone filled with salty water many hundreds of meters below the surface, are the main storage-site candidates. Multiyear projects in such settings, from the North Sea to Canada, are generating encouraging results.

But preliminary geochemical data from the first U.S. project to inject CO₂ into such a formation, which is located near Houston, Texas, offer a cautionary note on CO₂ storage. They indicate that because CO₂ makes the deep groundwater more acidic, metals in the sandstone get released. The results were reported in the journal *Geology* in July (2006, doi 10.1130/G22357.1)

by the project's geochemist, Yousif Kharaka of the U.S. Geological Survey, and his colleagues.

“We observed rapid dissolution of calcite and mobilization of large amounts of iron and other metals as a result of [a] major drop of pH from 6.4 to 3,” Kharaka says. “These data are not a snag for CO₂ storage in continental sedimentary basins,” he contends. However, the data do strongly suggest that CO₂ injection wells should use acid-resistant cements and that abandoned wells should be avoided or monitored carefully.

“These former oil and gas wells were never engineered to last for a long time,” says Susan Hovorka, a geologist at the Texas Bureau of Economic Geology and the project's principal investigator. She adds that another reason

to avoid old wells is that most are shallow, because deeper is generally considered better for CO₂ sequestration.

The release of metals identified by Kharaka represents “a new element of risk, because it shows the potential for reactive chemistry that could be of concern,” says geologist Julio Friedmann at the Lawrence Livermore National Laboratory. “But these new results are not likely to present a substantial complication to underground storage,” he adds. This is because metal-bearing oxides and hydroxides usually make up less than 1% of saline aquifers and such aquifers have kept saline brines isolated over 100-million-year geological timescales.

Compared with the Weyburn project in Canada and the Sleipner West project, which has been online since 1996 in the Norwegian North Sea, the U.S. project is a rel-

ative newcomer. Initiated in 2004, the U.S. Department of Energy-funded project is known as Frio, after the rock formation where the gas is stored. Researchers compressed the first batch of 1600 tons of CO₂ into a supercritical fluid, heated it to about 16 °C, and pumped it into a 24-meter-thick sandstone layer roughly 1 mile below the surface.

Scientists already have enough information to be confident in the ability of some rock formations to hold CO₂ for a long time, says Hovorka. "But we need clear guidelines to tell a good place from a bad place," she says. "We want some indicators, and the data from Frio are part of that process."

Reactions that dissolve and crystallize minerals are a mixed blessing, says geochemist Ernie Perkins with the Alberta Research Council (Canada). He notes that observations at Weyburn and elsewhere document other, slower reactions that eventually lead to the crystallization of new minerals. Initial dissolution of carbonates in the formation makes it easier to inject CO₂, he says, by clearing

pathways through the rock. Later crystallization reactions can retain CO₂ by enclosing it in new minerals and reducing pore space in the rock, thus preventing the gas from percolating up. But if the crystallization reactions occur while CO₂ is still being pumped into the formation, then they could interfere with the injection by blocking pathways. "The geochemical reactivity of the formation is another criterion in the selection of an appropriate storage site," he says.

Hovorka hopes that the U.S. government will give larger-scale CO₂ storage projects a green light soon. On July 25, the U.S. government-industry alliance known as FutureGen, which aims to build a \$1 billion coal-gasification and CO₂-sequestration project by 2012, short-listed 2 sites in Illinois and 2 in Texas for its final location.

Meanwhile, the scientists at Frio were expected to start the next stage of their investigation in August. They plan to quantify how much CO₂ is dissolved in the water underground and how much is trapped as gas.

—REBECCA RENNER

Soybeans resurface in wood glue

Soy-based glues for wood products were popular until the 1950s, when they were replaced by petroleum products that had longer shelf lives and were more water-resistant. But wood products that use soy glues, which have lower toxic emissions and cheaper production costs than petroleum-based products, could be on the shelves again by the end of this year.

Today's petroleum-based resins use a combination of phenol or urea with formaldehyde, resulting in emissions of volatile organic compounds (VOCs) during the manufacture and use of wood products. The U.S. EPA and the Occupational Safety and Health Administration (OSHA) classify formaldehyde as a possible car-

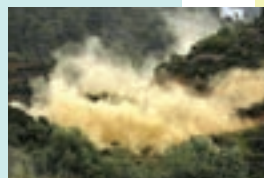
cinogen. OSHA limits workers' exposure to 0.75 parts per million (ppm) over 8 hours, with a short-term limit of 2 ppm over 15 minutes. Currently, no U.S. regulations cover VOCs in nonindustrial indoor air, but indoor formaldehyde levels often reach more than 0.3 ppm, according to EPA. Those levels are high enough to affect human health. The American National Standards Institute requires composite wood materials to emit less than 0.2 ppm.

Some manufacturers voluntarily use proprietary methods to meet these guidelines, says Deland Myers, an Iowa State University food science professor who researches soy-protein products, including soy adhesives. "Using soy protein

News Briefs

Wildfires unleash mercury

Increasing temperatures have led to more fires on the northern tundra, with the potential to release an unexpected cache of mercury into the atmosphere. From the beginning of the Industrial Revolution, atmospheric transport has carried mercury to northern ecosystems, which have incorporated the neurotoxic into vegetation and soils. A team of researchers publishing in *Geophysical Research Letters*



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(2006, doi 10.1029/2005GL025595) quantified the amount of mercury stored in boreal peatlands versus boreal forests, using soil samples. They found that peat soils store 10 times more mercury than forest soils do. The team then estimated on the basis of recent annual burns the acreage that could burn under different climate scenarios. The new results find a 15-fold difference in mercury emissions once peatlands were added.

Pollutants linked to diabetes

People living near hazardous waste sites that contain persistent organic pollutants are more likely to be hospitalized for diabetes. A team from the State University of New York, Albany, gathered hospitalization data from 1993 to 2000 for adults living in different New York zip codes. The researchers corrected for a variety of confounding factors, including class, gender, and age. In results published in August in *Environmental Health Perspectives* (2006, doi 10.1289/ehp.9223), the researchers calculated that residents living near hazardous waste sites were 10% more likely to be hospitalized for diabetes than people residing in "clean" neighborhoods. People living near other kinds of waste sites had slightly lower rates of hospitalization for the disease, which has a prevalence of more than 5% in U.S. adults.



FOREST PRODUCTS LABORATORY

Soy adhesives could reduce the formaldehyde emissions from engineered wood products that are used to construct homes and make furniture.

is another avenue to doing that," he says. Soy-based glues could be "lower-cost, and they are bio-based. . . . I would assume that an adhesive that's more bio-based would probably be something that can be recycled a lot easier."

Because it is a byproduct of soybean oil production, soybean meal is a renewable and low-cost commodity, says Frank Trocino, CEO of Heartland Resource Technologies, an adhesives company that has consulted with Myers in the past.

Depending on the cost of phenol and the amount of it replaced by soy flour, manufacturers of composite wood products could save 10–40% of their costs by making the switch.

Heartland's soy adhesive combines phenol formaldehyde resins and soy flour in a 1:1 ratio. The company is working with researchers at the U.S. Department of Agriculture's Forest Products Laboratory to make resins that are more than 65% soy flour. Since the product still contains phenol formaldehyde, it retains its water resistance.

"The biggest problem with soy in the past was water resistance," says Trocino. He says that the new glue is water-resistant enough to be used outdoors. Trocino has now licensed the technology to an adhesives manufacturer and a wood-products company.

According to Philip Bibeau, executive director of the Wood Products Manufacturers Assoc., some pressure exists in California to reduce VOC emissions from wood products, but it is not enough to

create a large demand for soy-based glues. Such resins are "starting to become more of a need for people looking for green types of products, [but] that demand is a very small percentage of the marketplace," he says. "It's not like people are contacting us and saying, 'Please help me find a soy-based supplier for adhesives.'"

But Trocino believes otherwise, saying that tighter national emissions guidelines may pique the interest of wood-products companies. The World Health Organization (WHO) has tougher rules on formaldehyde exposure than EPA and OSHA do; it recommends an exposure limit of 0.05 ppm. In 2004, WHO went one step further and classified the gas as a known carcinogen. The move "created a lot of stir in the industry, and now everyone's looking at [reducing] formaldehyde," Trocino says. He suggests that if the U.S. lowers its emissions standards, wood-products manufacturers could consider using soy-based adhesives to meet them.

—PRACHI PATEL-PREDD

Sunny forecast for hybrid lighting

With 5 full-scale pilot systems installed and 20 more expected in a few months, hybrid solar lighting is moving quickly toward commercialization in the U.S., according to researchers who developed the technology at Oak Ridge National Laboratory (ORNL). Ten times more efficient than today's most affordable solar cells, hybrid solar lighting uses a rooftop satellite dish to track and collect sunlight. These captured rays then get routed from the roof through a bundle of optical fibers to illuminate 1000 square feet (ft²) of interior room and floor space below. Preliminary field data show energy savings of 70% in the afternoon when electricity is in peak demand. Researchers say the units are projected to save about \$1/ft² annually in energy and maintenance costs. Sunlight Direct, the company that licensed the ORNL technology last year, is targeting retail and office buildings, where as much as 60% of the energy is consumed for lighting. Current hybrid lighting systems cost about \$12/ft², but with some design and engineering changes, "we hope to get that down to less than \$4 over the next year," says Duncan Earl, an ORNL researcher and Sunlight Direct's chief technology officer.

— KRIS CHRISTEN



OAK RIDGE NATIONAL LABORATORY