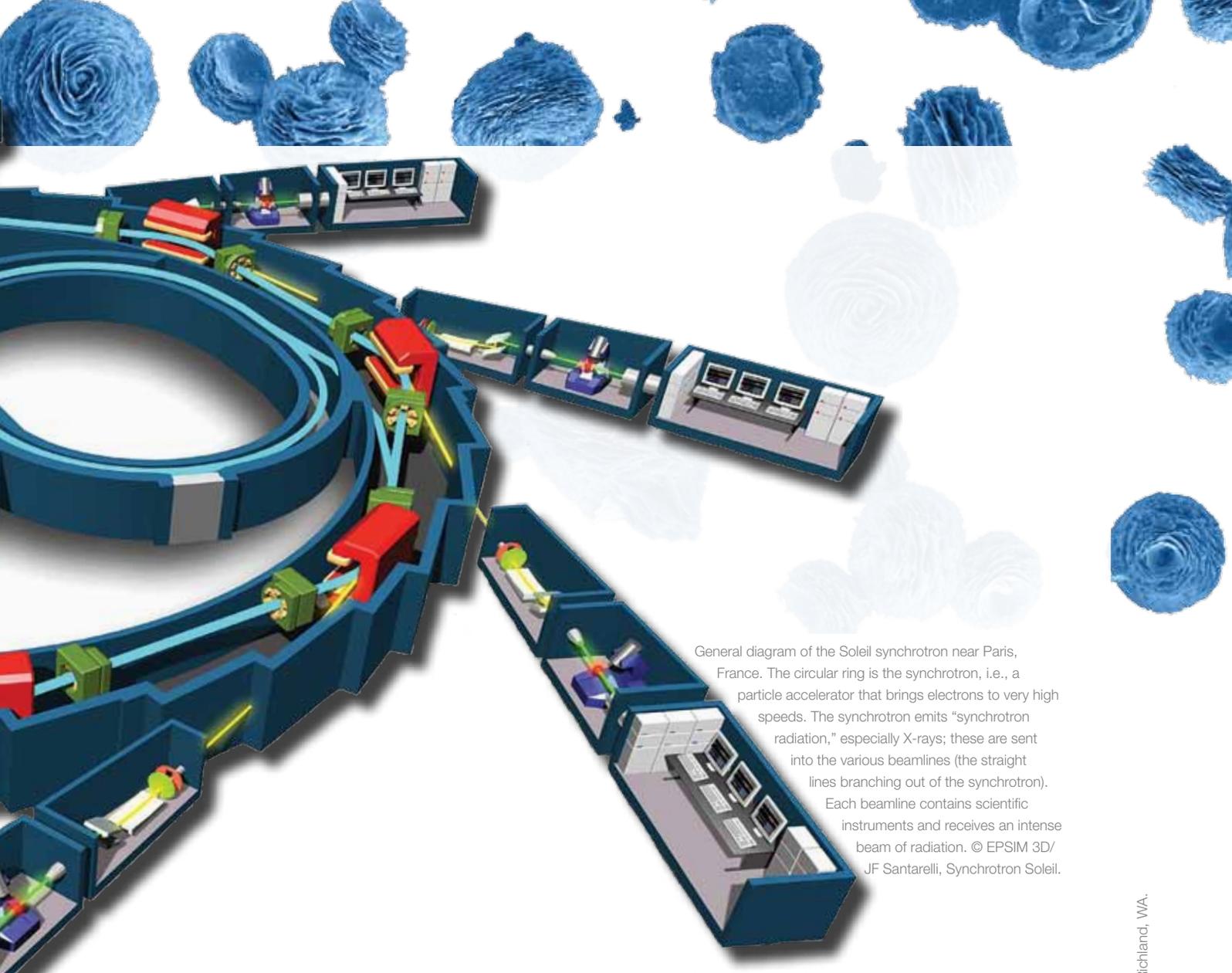


Advanced
Spectroscopy
in soil
biogeochemical
research

by Madeline Fisher



General diagram of the Soleil synchrotron near Paris, France. The circular ring is the synchrotron, i.e., a particle accelerator that brings electrons to very high speeds. The synchrotron emits “synchrotron radiation,” especially X-rays; these are sent into the various beamlines (the straight lines branching out of the synchrotron). Each beamline contains scientific instruments and receives an intense beam of radiation. © EPSIM 3D/JF Santarelli, Synchrotron Soleil.

In the late 1840s, British scientists H.S. Thompson and J.T. Way conducted a series of classic experiments.

Wanting to know why some soluble fertilizers remained in soil even after heavy rains, the pair leached solutions of ions, such as ammonium sulfate, through soil columns and collected what came out the other end. To their surprise, sulfate and other anions passed through while cations like ammonium and potassium did not. Instead, new cations such as calcium appeared in the effluent. Somehow in passing through the soil, the original cations had been swapped for others.

Their discovery of the cation exchange capacity (CEC) of soils spurred many efforts to discover how the process worked. “Scientists were actually dissolving the soil to try to see how it was changing as they put

these chemicals through,” says Dean Hesterberg, a North Carolina State University soil chemist and SSSA and ASA Fellow. But the mechanism would remain mysterious for nearly a century. Finally, a new technique adopted from physics, X-ray diffraction, revealed the crystalline nature of minerals in soil and the ionic substitutions taking place within the crystals that explained CEC. Once the process was cracked, practical approaches for managing CEC-related soil problems soon followed.

Hesterberg likes this story, he says, because it offers an important lesson from the history of soil science: Major advances in the field have often been linked to analytical developments

in the pure sciences. Following this tradition, he and other soil chemists around the world are now wielding a suite of highly advanced spectroscopic techniques, also deeply rooted in physics. The methods were highlighted in a special series of papers in the May–June 2011 issue of the *Journal of Environmental Quality* (see www.soils.org/publications/jeq/tocs/40/3).

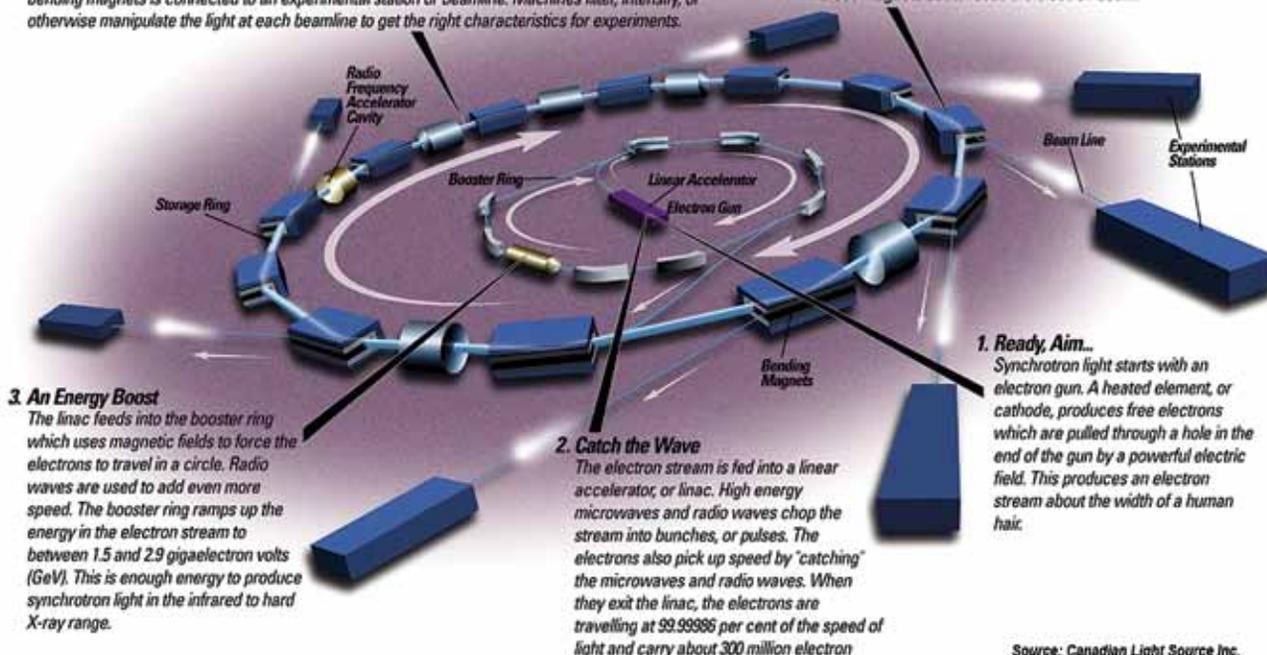
As in all spectroscopy, the techniques shine light on a sample, and the sample’s properties are inferred from the spectra produced when the sample absorbs light of specific wavelengths. In this case, though, the “light” is electromagnetic radiation of exceptional brilliance and quality that’s generated by high-energy particle accelerators, known as synchrotrons, at places such as Brookhaven National Laboratory. This means the

How a Synchrotron Works

4. Storage Ring

The booster ring feeds electrons into the storage ring, a many-sided donut-shaped tube. The tube is maintained under vacuum, as free as possible of air or other stray atoms that could deflect the electron beam. Computer-controlled magnets keep the beam absolutely true.

Synchrotron light is produced when the bending magnets deflect the electron beam; each set of bending magnets is connected to an experimental station or beamline. Machines filter, intensify, or otherwise manipulate the light at each beamline to get the right characteristics for experiments.



3. An Energy Boost

The linac feeds into the booster ring which uses magnetic fields to force the electrons to travel in a circle. Radio waves are used to add even more speed. The booster ring ramps up the energy in the electron stream to between 1.5 and 2.9 gigaelectron volts (GeV). This is enough energy to produce synchrotron light in the infrared to hard X-ray range.

2. Catch the Wave

The electron stream is fed into a linear accelerator, or linac. High energy microwaves and radio waves chop the stream into bunches, or pulses. The electrons also pick up speed by "catching" the microwaves and radio waves. When they exit the linac, the electrons are travelling at 99.99986 per cent of the speed of light and carry about 300 million electron

5. Focusing the Beam

Keeping the electron beam absolutely true is vital when the material you're studying is measured in billionths of a metre. This precise control is accomplished with computer-controlled quadrupole (four pole) and sextupole (six pole) magnets. Small adjustments with these magnets act to focus the electron beam.

1. Ready, Aim...

Synchrotron light starts with an electron gun. A heated element, or cathode, produces free electrons which are pulled through a hole in the end of the gun by a powerful electric field. This produces an electron stream about the width of a human hair.

Source: Canadian Light Source Inc.

methods aren't routine, of course, says University of Delaware soil chemist Don Sparks, an SSSA and ASA Fellow. But then the data they provide aren't commonplace either.

"You're obviously not going to be running thousands of samples," he says. "But what I would say is these techniques provide unique information about soils that is very difficult to get any other way."

For one, synchrotron radiation-based (SR-based) methods let scientists "see" the exact form chemicals take in soil, rather than having to infer those forms, or species, from macroscopic evidence. This includes an element's oxidation state, the solids and dissolved species it's associated with, and its distribution in space—all of which determine its behavior, mobility, and toxicity. Moreover, the methods don't require any process-

ing or altering of samples, allowing them to be examined in natural states, including wet samples and "living" soils influenced by microorganisms and plant roots.

But what truly distinguishes the techniques is their ability to resolve soil details at micro- and even nanoscales. Soil scientists are deeply familiar with the variability of soils at field and other macro-scales; these tools are now revealing that soil complexity extends to the tiniest scales, as well. "One of the things you immediately recognize when you do these studies is the heterogeneity," Sparks says. "Often you can have different chemical species within a matter of a few microns."

The heterogeneity can in fact be overwhelming, leading some to question the data's value, Hesterberg says. "People will say, 'Well, what you're

doing is very interesting scientifically, but how can the information be used?'" It can be challenging, he admits, to relate the data to real-world problems, although soil chemists are making many important inroads here. For his part, though, Hesterberg is mostly looking ahead.

"We continue to place increasing demands on soils, and they play a lot of roles that are sometimes competing in food and fiber production, waste disposal, carbon storage, water quality protection, and so on," he says. "Because of these demands, I believe we're going to need to manage soils more and more precisely in the coming decades. And for that reason, we seek to understand soil with a higher degree of precision."

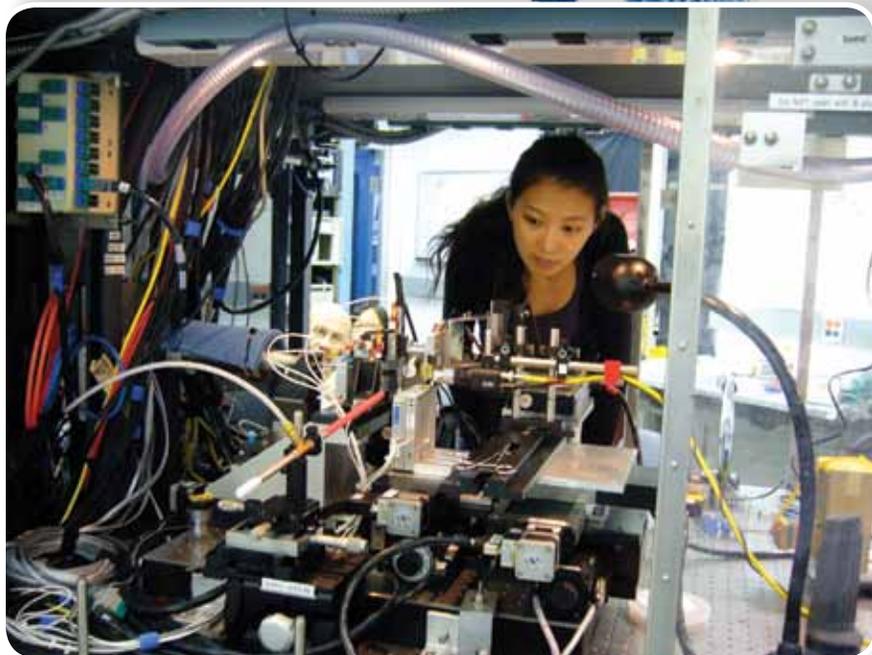
'Waste' Product Proves Useful in Soil Research

Inside the circular ring of a synchrotron, fluctuating magnetic and electric fields accelerate electrons to near the speed of light. The first instruments were built so physicists could study the electrons' behavior under these conditions. Soon, however, a "waste" product of the electrons' movement was observed: extremely bright synchrotron radiation. Although it was originally considered a nuisance that sapped energy from circulating electron beams and confounded calculations, researchers quickly learned to use focused beams of the light to probe the structure of materials.

At first, material scientists, engineers, and chemists were the main users of synchrotron facilities. Then biologists and environmental and soil scientists began to arrive, and one of the first was Sparks. When he and his colleagues began using synchrotron techniques in the early 1990s, they sought to discover how trace metals were bound to different soil surfaces in lab experiments, so that they could better predict the metals' fate and mobility in the environment. Were they held on clay minerals mainly through electrostatic forces, for example, making them relatively easy to dislodge? Or was a chemical bond involved, or even a highly stable surface precipitate?

"Before then, the information we could get was sort of indirect. It didn't give us the real 'smoking gun,' if you will, as to how chromium, for example, was bound to a metal oxide or a clay mineral," Sparks says, "So these techniques were extremely useful."

At the time, though, the techniques didn't permit investigations of actual soil—they were just too complex. Then a number of new techniques employing "micro-focused" SR beams came along that let scientists hone in on finer details. With them, Sparks' group could collect whole soil samples from zinc-contaminated sites,



Yu-Ting Liu checks a sample in an X-ray microscope at the Advanced Photon Source, a national synchrotron X-ray research facility at the Argonne National Laboratory, while Juergen Thieme (left) and Fiona Kizewski (right) look on in the background. Liu and Kizewski are former students of Dean Hesterberg at North Carolina State University. *Photo courtesy of Dean Hesterberg.*

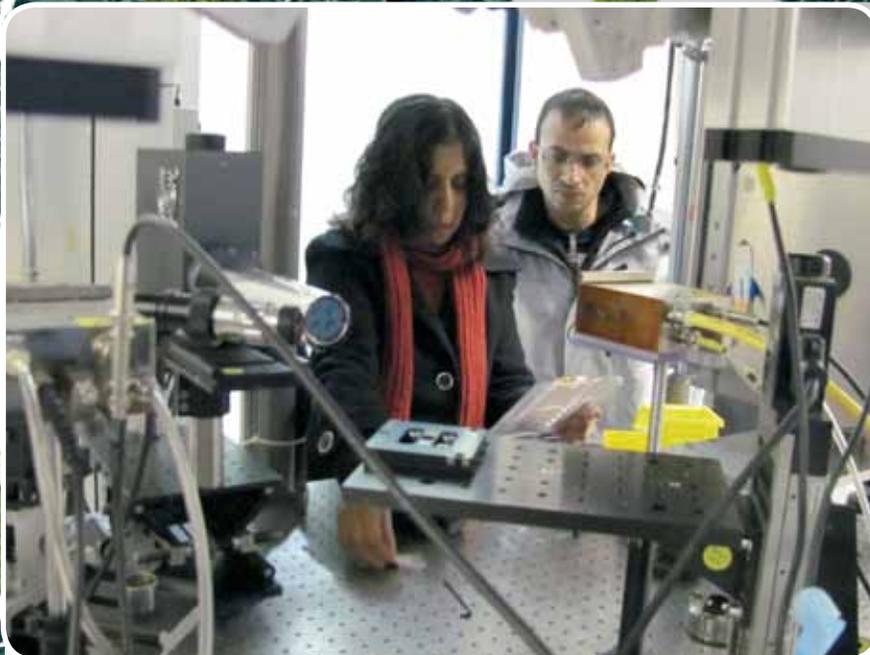
for instance, and resolve all the zinc species present, including their various oxidation states and associations with organic matter or clays. "We could get very precise information," Sparks says, "and the advantage is that once you have that information, it enables you to make wise decisions about remediation."

Their work on zinc and nickel has shown, for example, that the metals aren't likely to be released from contaminated soils, so long as pH is higher than 6.5. That's because exceptionally stable surface precipitates develop under alkaline conditions that keep zinc and nickel tied up. "What we learned is if the pH is high enough, you can basically stabilize them such that you don't have to worry about them being very mobile," Sparks says.

Of course, the old standby, lab-based X-ray diffraction, can also achieve "direct speciation" of the chemical forms in soil; this is how cation exchange was finally explained.

But elements must be crystalline and present at concentrations of roughly 10,000 ppm or more for X-ray diffraction to work, says SSSA and ASA member Ganga Hettiarachchi, a soil chemist at Kansas State University. SR-based techniques such as X-ray absorption spectroscopy, in contrast, don't depend on crystallinity. Plus they can detect chemicals at concentrations as low as 10 ppm, suiting them perfectly to analyses of trace metal contaminants and micronutrients. "The sensitivity is very good," Hettiarachchi says. "It lets us do things that weren't possible before."

What she often addresses with the methods are agronomic and environmental questions that arise from field observations. Before coming to Kansas State, for example, Hettiarachchi was a researcher in South Australia—the country's wheat-growing region—where soils can contain up to 70% calcium carbonate. When nutrients are added in granular forms to these soils, plants can't take much of anything up.



Ganga Hettiarachchi, Kansas State University, shows graduate student Raju Khatiwada how to mount the sample holder with soil samples on the xyz stage of a beamline at the Advanced Photon Source, a national synchrotron X-ray research facility at the Argonne National Laboratory.

But a series of field and greenhouse experiments showed that liquid nutrient sources were more bioavailable. The findings sparked research by Hettiarachchi and her colleagues to find out why.

In a study published in January–February 2008 issue of the *Soil Science Society of America Journal*, the team combined SR-based methods with other tools, such as scanning electron microscopy (SEM), to examine the fates of zinc and manganese added to highly calcareous soils as either liquids or granules. The granules, the researchers observed, took up water immediately when added and began to dissolve, suggesting the micronutrients were being released. However, calcium-laden water rushed into the granules so quickly that most of the zinc never made it out, Hettiarachchi says. Instead, SR-techniques indicated that zinc had precipitated in insoluble forms right inside the granules, while manganese was found just outside—rendering them both unavailable to plant roots. Manganese and zinc

from liquid sources diffused further away, on the other hand, because the same process didn't occur, and they remained more soluble and bioavailable as a result.

The results demonstrate the power of SR-based research to provide information on mechanisms, which scientists can then use to design even more efficient fertilizers and better predict the soil conditions where they will boost productivity, Hettiarachchi says. She and her students recently took a similar approach to phosphorus. Deep banding is known from research plots to increase phosphorus availability over surface broadcasting in some no-till systems, and the chemical reactions responsible for the difference were the focus of their SR-based research. As it often does, her group also compared the spectroscopy results with those from “bulk” chemical extraction methods that are traditionally used to predict phosphorus availability.

“We all don't have that much accessibility to synchrotron tech-

niques,” Hettiarachchi says. “But if we have strong relationships between the advanced techniques and these traditional wet chemical extractions that we can do pretty much anywhere, then we can predict plant-available phosphorus more accurately and confidently.”

Not a Replacement for Traditional Techniques

This brings up a critical point, Hesterberg says. For all the novel insights they offer, SR-based techniques will never replace traditional soil-testing techniques when it comes to practical management of soil. The methods are too specialized, for one. But more importantly, Hesterberg says, “the science of soil testing is very refined, and it supports agriculture very well,” especially since the results have been directly correlated with an easily measured outcome: crop yield.

But where SR-based techniques shine is when outcomes—especially long term—aren't as straightforward, such as in environmental contamination, he adds. “These types of questions, where the impacts are more difficult to measure directly, require a more precise understanding of the behavior of soil chemicals.”

Much of today's knowledge of soil chemistry, he explains, comes from simple systems, such as experiments with pure, isolated elements or ones involving just two or three soil components, as well as general theories like kinetics and thermodynamics. But thermodynamics is most predictive when systems are at equilibrium—which soils decidedly are not. “They're always changing. They're always in a state of flux,” Hesterberg says. His group has seen calcium phosphates persisting in acidic soils, for instance, even though thermodynamics predicts they shouldn't be there.

SR-based methods have also revealed vast numbers of microsites in soil, which Hesterberg likens to a

Their Brilliant Careers: Student Experiences at Synchrotron Light Sources

by Kate Sadowski

Synchrotron research isn't just ideal for exploring natural materials such as soils, plants, and particulates, says University of Delaware soil chemist Don Sparks. It's also ideal for fostering the explorations and development of young scientists.

"It provides a key learning experience," says Sparks, who helped pioneer the use of synchrotron-based techniques in environmental chemistry two decades ago, "and a top selling point when students graduate and head into the job market."

He should know. Under his mentorship, graduate students and postdocs frequently travel to synchrotrons around the country and the world, and today 24 of his former group members continue to conduct research at synchrotron facilities on four continents.

One of them is SSSA member Jen Seiter, who works as a research physical scientist with the U.S. Army Corps of Engineers at the Engineer Research and Development Center in Vicksburg, MS.

"As a former member of Dr. Sparks' research group, I was privileged to travel to Brookhaven, Argonne, and Lawrence-Berkeley National Laboratories, and today I conduct environmental research using the skill set I developed there," she says. "I am very grateful to have a stable and exciting job doing exactly what I was trained to do."

University of Delaware alumnus Ryan Tappero agrees that the synchrotron research he did as a graduate student was very influential in his career. "I gained valuable experience and made important contacts that ultimately influenced my decision to pursue a career at a synchrotron facility at a national laboratory," he says. He now works as a beamline scientist at Brookhaven National Laboratory.

Meanwhile, current University of Delaware doctoral candidate and SSSA, CSSA, and ASA member Matt Siebecker is studying metal sequestration in soils and has used both the National Synchrotron Light Source at Brookhaven and the Stanford Synchrotron Radiation Laboratory for his work. Not only is synchrotron light an indispensable part of his research, he says, but having the chance to work at national labs has really opened his eyes to a larger world of science, as these facilities draw scientists from a vast array of fields.

"When I came to [the University of Delaware] in 2007, I hadn't really done a whole lot of research. I didn't know what types of instruments and techniques were out there," he says. "But Dr. Sparks has done a lot of great



Shannon Carter and Matt Siebecker are two graduate students at the University of Delaware who have benefited from using the synchrotron at the Brookhaven National Laboratory.

research and has been able to help us get time at these national labs. This allows his students to learn some of the advanced techniques that are available and apply them to their research."

Yet another member of Sparks' research group, Shannon Carter, has used the synchrotron at Brookhaven National Lab to determine the species and distribution of metals and metalloids associated with particulate matter emitted from poultry houses. Her goal is to understand whether metals such as arsenic and copper in the particulates could pose health risks to workers who breathe them in—making it crucial to know the metals' exact form.

Working at Brookhaven, she says, is intense: Scientists collect data around the clock, and experiments take an unusual amount of planning because if they get messed up, there isn't time usually for do-overs. But synchrotron research is also rewarding. And while it is specialized, performing it doesn't require any special prior experience or knowledge.

"I come from a biology background," Carter says. "When I joined the group, I didn't know anything about synchrotron spectroscopy. Now I'm comfortable using a couple of different applications. Micro-X-ray fluorescent mapping, for example, provides detailed maps of elemental distribution and association in natural systems."

K. Sadowski, University of Delaware



Robert Fischetti, a beamline director at the Advanced Photon Source, a national synchrotron X-ray research facility at the Argonne National Laboratory, adjusts a sample crystal on a beamline. *Photo courtesy of the Argonne National Laboratory.*

series of minuscule chemical reactors, each with its own effect on soil chemicals. The more Hesterberg delves into this micro-complexity, the more convinced he is of its importance to larger-scale processes—and how understanding it could produce a more robust set of soil chemistry principles.

“In my opinion we need to evolve beyond the idea that we can isolate a chemical component in the soil and predict its behavior in isolation because it may be influenced by all the micro-heterogeneity of whatever environment it’s in,” he says. “So maybe we should look at developing our science around that concept.”

Some of that micro-heterogeneity is surely produced by organisms, yet few studies have so far examined their direct impacts on soil chemistry, says USEPA environmental chemist and SSSA member Doug Beak. So when he and his colleagues used synchrotron techniques to study cobalt speciation, they performed experiments both with and without living plant roots. In soil alone, most of the cobalt remained as Co(II), the team found,

and was associated with manganese oxide and then iron oxide as the soils aged, in agreement with macroscopic work. When rice roots were present, though, the results were quite unexpected: Most of the cobalt ended up in precipitates and was no longer seen associated with iron oxide at all. The lesson? “Caution needs to be taken, I think, when making conclusions based on experiments that don’t incorporate biologic components of soil,” Beak says. The study appeared in the May–June 2011 issue of the *Journal of Environmental Quality*.

Accessibility, Cost of Synchrotron Research

Perhaps the biggest lesson is that “a whole number of studies could benefit from these techniques,” says ASA and SSSA member Kirk Scheckel, a USEPA environmental chemist who earned his Ph.D. with Sparks and collaborates frequently with Hettiarachchi and Beak. But there are a number of myths about SR-based research to dispel first. Many people assume that

“it’s so highly specialized that it must be super expensive and available only to select individuals,” Scheckel says. “And that’s really not the case.”

Any scientist, in fact, can gain access to a synchrotron facility by writing a proposal, which is then judged in a competitive process. Successful efforts usually net three or four days of research time at places like the Advanced Photon Source in Chicago, where scientists can potentially analyze 20 samples per day, Scheckel says. The facilities are free to use (U.S. synchrotrons are supported by tax dollars), and researchers get ample help from beamline staff. There are travel and lodging expenses. But when the costs are broken down, they typically amount to tens of dollars per sample, Scheckel says, comparable to what specialized analyses, like SEM, would run at a commercial lab.

Sparks adds that his graduate students and postdocs have always logged significant time at synchrotron facilities—getting training that he believes not only helps advance soil science, but also helps them advance in their careers. “Many of my former students have been placed in research positions, and I think one of the reasons is that they’ve been exposed to these methods,” he says.

At the same time, researchers who perform SR research know that as intriguing as their field is—and how much they hope it intrigues others—in the end, it’s just one tiny part of the whole heterogeneous world of soil science.

“If society had to wait for us, as soil chemists, to get answers to complex problems, we couldn’t move forward in soils, we couldn’t do all the wonderful things that other scientists are giving us the ability to do,” Hesterberg says. “We’re just looking at soils at another level—trying to forge the way to better solutions and rise to the challenges ahead.”

M. Fisher, lead writer for CSA News magazine