Superfund Scoop
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THE NEWSLETTER OF THE UNC SUPERFUND BASIC RESEARCH PROGRAM

Team finds new ways to keep NAPLs at bay

Non-soluble chemicals at Superfund sites pose special challenges. A UNC SBRP research team is developing new techniques to remediate these stubborn hazards.

Stainless steel columns in an interdisciplinary SBRP lab hold soil samples from a former manufactured gas plant in Salisbury, NC. Casey Miller's group is using the samples to study physiochemical remediation techniques, such as the use of chemical oxidation and enhanced flushing techniques, while Michael Aitken's SBRP research team studies bioremediation techniques.

CHEMICALS THAT DON'T MIX WITH WATER POSE A SPECIAL challenge to the people charged with cleaning up Superfund and other contaminated sites. Since flushing these chemicals out of the ground using water isn't a viable option, new techniques must be developed to remove the contaminants and reduce their risk to the environment and human health.

That's where a research group led by UNC-Chapel Hill Superfund Basic Research Program (SBRP) Investigator Cass (Casey) T. Miller comes in. Miller's team is focused on finding more effective ways to remediate chemicals called NAPLs (short for non-aqueous phase liquids, and pronounced "napples"). NAPLs are liquids that don't mix with water – if you pour them into the same jar, they separate. NAPLs such as chlorinated solvents are commonly used as dry cleaning agents and degreasers.

"NAPLs are found at most of our nation's Superfund sites, and these chemicals have known or suspected health effects, including links to cancer," Miller, a professor of environmental sciences and engineering, explains. "They get trapped in the ground, and they are difficult to remove.

continued>>

The UNC SBRP brings together a diverse group of more than 70 biomedical researchers, engineers, chemists, statisticians, experts in conventional and bioremediation, environmental modelers and students. Together, we are achieving the program's goal to advance society's understanding of the human health and environmental risks associated with hazardous waste and to develop new environmental strategies and technologies for the cleanup of Superfund sites, thereby minimizing human and environmental risk.

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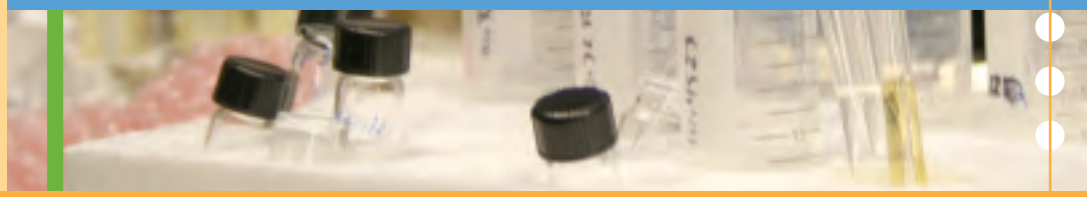
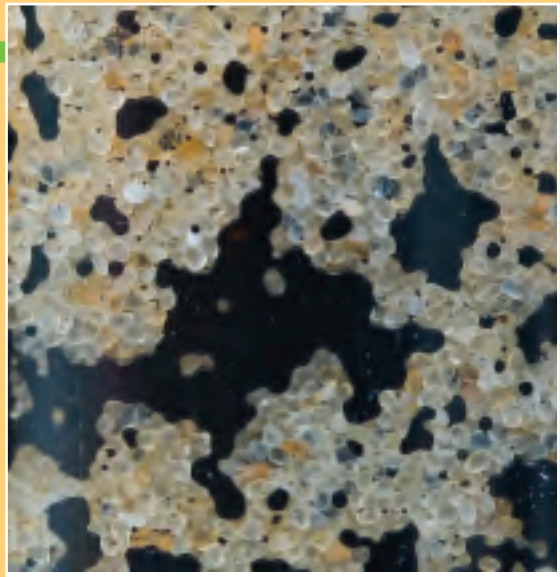
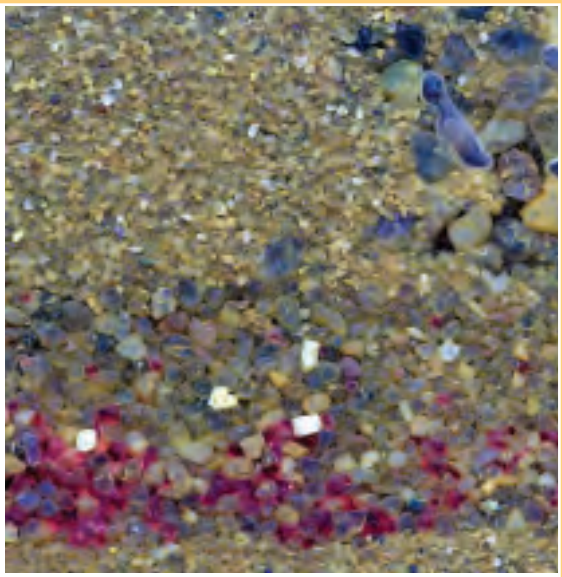




In this sample of tar from a former manufactured gas plant, the spaces between grains of sand are filled with water and a NAPL that is a complex mixture of chemicals. The chemicals in the tar of greatest environmental interest are polycyclic aromatic hydrocarbons (PAHs).

Scientists use red dye to highlight a single-chemical NAPL called tetrachloroethylene (PCE), which along with water and air fill the spaces between grains of sand. The blue spots are entrapped air.



But while they don't dissolve fully in water, they do dissolve sufficiently that they can taint drinking water or fish, so this is a major health concern. Our goal is to limit the population's exposure to these contaminants by removing them from the environment and disposing of them in a safe way."

For the past few years, the focus of Miller's research team has been on remediating chlorinated solvents that are made up of a simple, single-molecule chemical. Miller's group developed a complex method of injecting a dense brine (salt) solution into the ground. The brine accumulates on the bottom of the aquifer and forms a thin layer. Because the NAPLs are less dense than the brine, they pool on top of the brine layer, and can be removed with another solution.

"The team is now moving on to NAPLs that contain more complex mixtures of compounds," explains PhD candidate Pam Birak. "We're looking at former manufactured gas plants that were abandoned in the late 1950s and 60s, where the NAPLs are much more complex, with hundreds or even thousands of components to them." There are several of these sites in North Carolina, and many around the country.

Birak is working to understand the physical properties of tar, a byproduct from gas manufacturing that was often disposed of in pits at these sites. Large quantities of tar can actually move underground, so Birak is studying the tar's viscosity, density and other physical properties in order to predict the movement and behavior of these materials.

Meanwhile, doctoral student Scott Hauswirth is focused on the chemical nature of the tars. He is using gas chromatography to tease out and identify many components of these complex NAPLs. "Right now, I'm up to 290 compounds, plus some other classes of compounds that we haven't even been able to separate at this point."

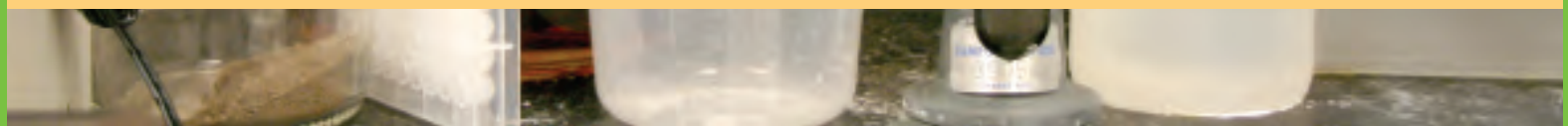
And Research Associate Joe Pedit, who runs the Miller group's laboratory, is working with Miller and another faculty member to test new modeling approaches to predict the movement of brines used in advanced remediation methods developed by the group. They are also trying to understand the process by which the brine solutions act, to determine how to most effectively use them as part of the remediation process for chlorinated solvents or tar-contaminated sites.

Going from one compound to more than 300 is a daunting task. Miller's group has done some preliminary experiments with brine on these complex mixtures, but they are mainly focused on trying to understand the variety of approaches that they could use to mobilize these contaminants.

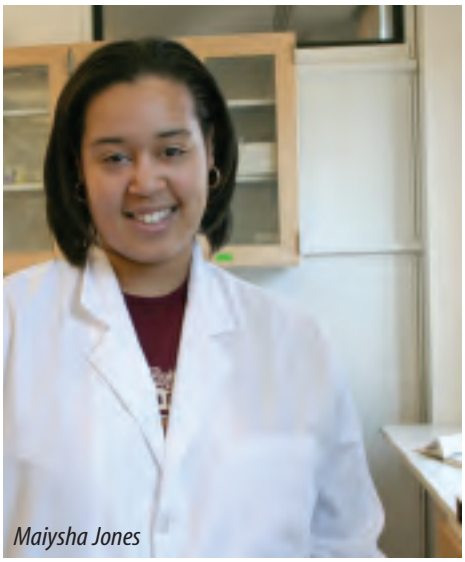
"When you look across the spectrum of problems in environmental sciences, this is among the most difficult to solve," Miller says. "The physiochemical processes and the complexity of the systems are on the high end of complicated environmental problems, so it's a real challenge to figure out how to do this."

A respected expert in the study and remediation of NAPLs, Miller is focused on developing improved mathematical models to describe what happens in these systems. For the last two decades, his group has been combining theoretical work and mathematical modeling with experiments to clearly describe what goes on in the environment. "Once we can simulate the system using mathematical models, it gives us a leg up on determining how to remediate it, and often provides a synergy along with the experiments that hastens the rate of discovery."

The SBRP is the chief support for Miller's research group. "That's been important," he notes, "because this funding allows for the continuity of effort over time that it takes to tackle some of these very complicated, large-scale problems. The SBRP gives us the ability to bring interdisciplinary groups together, and to approach these problems from a range of perspectives. That has proven very useful."



Speeding bioremediation by stimulating bacteria to eat more chemicals


Maiysha Jones

OVER TIME, BACTERIA THAT LIVE IN the soil at Superfund and other contaminated sites consume the polycyclic aromatic hydrocarbons (PAHs) that have leached into the soil. This process, called biodegradation, can be an effective way of remediating sites contaminated by PAHs, a group of more than 100 different organic – and sometimes cancer-causing – contaminants.

What if you could speed up the rate at which the bacteria ate the PAHs? Then you could get these hazardous chemicals out of the soil more quickly and reduce the environmental and health impacts of these sites.

Using contaminated soil samples from a former manufactured gas plant (MGP) in Salisbury, North Carolina, UNC doctoral students Maiysha Jones and Stephen Richardson are working in the laboratory of SBRP Investigator Michael Aitken to identify the bacteria responsible for biodegrading PAHs and to understand the process by which these bacteria consume PAHs. Their work could lay the foundation for new approaches to improving bioremediation, not only of PAHs but also other chemicals found at Superfund sites.

"Maiysha is a microbiologist, and I'm an environmental engineer," explains Richardson. "I've designed a series of stainless steel columns filled with contaminated MGP soil to examine different ways of stimulating PAH biodegradation. We're pumping oxygenated and nutrient-amended groundwater through these columns to simulate different remediation conditions, and we're collecting soil and water samples from different points in the columns to monitor changes in the microbial community and PAH concentration."

"I come at this problem from another angle," Jones says. "I use a technique called stable isotope probing (SIP). This technique relies on PAHs labeled with carbon molecules that are heavier than regular carbon. When bacteria living in the contaminated soil consume these PAHs, their cellular material, including their DNA, becomes labeled with these heavier carbons. Then, when we extract DNA from the soil bacteria, we can separate it based on density and identify which bacteria consumed the labeled PAHs. We can monitor these bacteria over time, and learn how different remediation treatments affect them, and what we can do to stimulate them to work more efficiently."


Stephen Richardson

Understanding how attacked DNA can mutate, cause human disease

SOME TOXIC CHEMICALS PRODUCE substances inside the body called reactive oxygen species (ROS), which can attack an exposed person's DNA and cause mutations that can lead to cancer, premature aging, degenerative diseases and other health problems.

But what, exactly, is happening to the DNA when it gets confronted by the ROS? That's what PhD candidate Wenjie Ye is trying to determine. Working with SBRP Chemistry and Analytical Core Director Louise M. Ball, Ye is studying the structural changes that occur in human DNA when it is attacked by these ROS, a process known as oxidative stress.

"Everyone is exposed to ROS in daily life," Ye explains, "through foods you eat or the oxygen you breathe. But exposure to chemicals at Superfund sites and elsewhere will increase the level of oxidative stress in the body, which can increase the damage to DNA and cause significant health problems."

But what, exactly, is happening to the DNA when it gets confronted by the ROS?

Ye is currently focusing on guanine, the most sensitive of the four nucleobases in DNA, to see what structural changes occur in the guanine when it is exposed to ROS in the laboratory. She exposes pure guanine and DNA to different forms of ROS and studies the structural changes to the DNA bases.

"Oxygenation of DNA has been researched for a very long time, and some

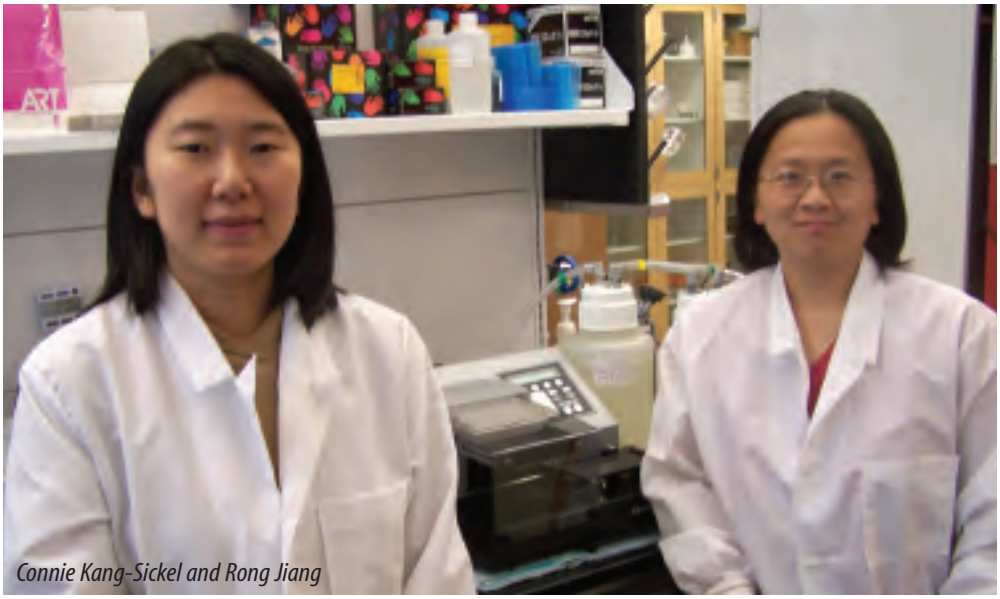
New techniques measure chemicals that get under your skin

IN THE SBRP LABORATORY OF Principal Investigator Leena Nylander-French, doctoral candidates Connie Kang-Sickel and Rong Jiang are building on the work of previous students to develop new approaches to measure what happens when auto and airplane mechanics get hazardous chemicals on their skin or inhale them from their work environment.

Other students had worked on a non-invasive method for measuring skin exposure to chemicals such as jet fuel by using special tape that is applied to the skin, then pulled off like a band-aid and analyzed chemically to determine levels of skin exposure.

Kang-Sickel is using that same tape-strip method to measure workers' dermal exposure to naphthalene, a common PAH often found in fuels, to develop a new detection method based on enzyme-linked immunosorbent assay (ELISA). This method is able to measure naphthalene metabolites that have attached themselves to keratin proteins, the most abundant proteins on the human skin, to help determine the levels of naphthalene exposure.

"The tape-stripping method can only measure how much exposure a person had to a chemical for that specific day," Kang-Sickel explains, "but with the ELISA technique, since the chemical gets metabolized and attaches to the keratin protein, it can stay in the skin for up to two or three weeks. By combining this new data with data from our previous studies, we can investigate the cumulative exposure over time. This may help us enhance the models for predicting the body's total burden of naphthalene exposure."



Connie Kang-Sickel and Rong Jiang

Jiang, meanwhile, is focusing on basic science research to test which genes play a role in exposure assessment of naphthalene. Using blood samples from the same workers who had the tape-strip samples taken, Jiang is looking at about 250,000 characteristics, or genetic variations, of genes in the human genome to identify potential genetic predictors of susceptibility or effect from a specific chemical exposure. This information will be incorporated into mathematical and statistical models along with dermal and inhalation exposure levels and data from ELISA studies to improve exposure and risk assessment.

of the structural changes have been identified, but many are still unknown because of analytical difficulties," she says. "Through this study, we hope to obtain a more complete picture of the DNA damage from different sorts of exposures, and relate these to disease outcomes. If we can identify the structural changes, we'll be one step closer to figuring out how to prevent or cure these diseases."

Wenjie Ye is Working with SBRP Chemistry and Analytical Core Director Louise M. Ball

Seminars at DENR open communication, lead to new collaborations

A SEMINAR SERIES THAT BRINGS UNC SBRP investigators to the N.C. Department of Environment and Natural Resources (NCDENR) to share their innovative research with NCDENR staff benefits both parties.

SBRP Investigator Marc Serre, an expert in geostatistical analysis, and his students have presented to staff in NCDENR's Superfund Section and Division of Water Quality. Serre's group uses space-time statistics to create maps of environmental pollutants and disease. Serre has shown agency staff how they can use geospatial analysis to map environmental contaminants in North Carolina, and the potential to map disease, such as clusters of renal cancer, so they can study whether links exist between contaminants and human health.

"Maps represent knowledge," says Serre, "and could be an excellent tool in the work NCDENR is doing."

NCDENR has collected a tremendous amount of public information about pollution in North Carolina, Serre notes. As a result of these seminars, he and fellow SBRP Investigator Ivan Rusyn have begun working with agency staff to determine how to put together an electronic database of environmental contaminants at sites throughout North Carolina. Then, they hope to compile a larger database of the thousands of samples collected from each site. This information could be used in future studies to explore potential links between contaminants and health effects – for instance, to map TCE levels at sites around the state and explore possible links to renal cancer – and would be helpful in making decisions about regulation and remediation.

"Doing these seminars has been extremely enjoyable and beneficial," says Serre. "It allows SBRP investigators to understand the unique types of problems the NCDENR staff is dealing with, and to see how the methods we have developed can be applied to help them."

SBRP Research Translation Core Co-Director Kathleen Gray says "By opening up communication between the agency and the university, we have created an environment in which we can work closely together to identify and address problems that affect North Carolinians."

Conference focuses on potential of bioavailability

IN FEBRUARY 2008, MORE than 100 environmental scientists, toxicologists, physicians, regulators and site remediators gathered in Tampa, Florida for a three-day SBRP conference, "Assessing Bioavailability as a Determinant of Pollutant Exposure: Building a Multidisciplinary Paradigm for the 21st Century and Beyond." The goal, explains Conference Chairman Frederic Pfaender, Research Translation Core Director for the UNC SBRP, was to establish common concepts and identify major systematic gaps in our knowledge of bioavailability and its implications, as well as define and prioritize research needs. Visit **www.uncsbrp.org/conference** for conference highlights.

More than 100 environmental scientists, toxicologists, physicians, regulators and site remediaters gathered in Tampa, Florida for a three-day SBRP conference.

The video medium spreads the message

UNC SBRP'S RESEARCH TRANSLATION CORE has begun testing video as a medium to reach broader audiences in both government agencies and communities.

In collaboration with The Exchange Project in the UNC School of Public Health, the SBRP has produced a 20-minute peer-to-peer training video for NCDENR and other groups to promote the value of effective community involvement in environmental health issues.

The SBRP also worked with classes at the UNC School of Journalism and Mass Communication on video projects aimed at educating the public about environmental health issues related to the Ward Transformer Superfund Site in Morrisville, which is being remediated due to PCB contamination. While waterways downstream are safe for recreation, there are advisories against eating fish which may be contaminated with PCBs. A 30-second public service TV announcement was created in both English and Spanish to inform the public not to eat fish caught in Lake Crabtree and adjacent waterways. Another class created a brief video documentary on the Ward Transformer site that will be shared with community groups to illustrate how exposure risk can vary by site and how they can learn about Superfund sites in their areas.

SUPERFUND SCOOP
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Programs for teachers help link environment, health

THROUGH TEACHER PROFESSIONAL development workshops, UNC SBRP's Research Translation Core (RTC) provides North Carolina educators with activities and resources to help students understand the connection between chemicals in the environment and human health. During these workshops, Dana Haine, a science educator for the RTC, discusses EPA's Superfund program, UNC SBRP research projects, and how to make Superfund relevant to students. She also emphasizes that RTC staff can help educators expose their students to these topics by identifying guest speakers or arranging lab tours.

For a second summer, RTC staff partnered with NCDENR's Office of Environmental Education (OEE) to co-sponsor a week-long professional development institute on water quality and health for North Carolina science educators. Through field trips, hands-on activities and guest speakers, participants gained in-depth knowledge and awareness of the environmental science, health and civic aspects of water quality issues in North Carolina. Additional summer workshops for middle and high school teachers and environmental educators were conducted in collaboration with Lake Crabtree County Park as well as for NCSU's The Science House through their collaboration with the NSF's Science and Technology Center for Environmentally Responsible Solvents and Processes.

In October, RTC staff will present "Making Superfund Relevant to Students" at a regional conference of the National Science Teacher Association in Charlotte.

Kelly Dennings, with NC's Division of Pollution Prevention and Environmental Assistance, pours "leachate" through a landfill model designed by workshop participants to test its effectiveness at preventing groundwater contamination.

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