UF UNIVERSITY of FLORIDA
IFAS
Soil and Water Science

A SOIL AND WATER SCIENCE DEPARTMENT PUBLICATION

Myakka

VOLUME 10
NUMBER 3

FALL 2010

contents

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Emerging Contaminants

From the Chair...

Globally, there is great concern on new contaminants entering our water bodies. The US Geological Survey (USGS) broadly defines these emerging contaminants as naturally occurring or synthetic chemicals or microorganisms that are not monitored in the environment. However, these contaminants can potentially affect the health of natural systems and human health. One of the key thrust areas of the Soil and Water Science Department (SWSD) is on remediation of contaminated soils, aquifers, and water as related to ecosystem soil and water quality and public health. Select faculty in Gainesville and those located at the Indian River Research and Education Center (IRREC) and Gulf Coast Research and Education Center conduct research on a range of organic contaminants and pathogens. State-of-the-art instrumentation is available both in Gainesville and IRREC for use in this research. The department is committed to strengthening the organic contaminants programs to address current and future needs of our clientele, while advancing the science in this area. In this newsletter we present a few examples of research conducted in our department on fate and transport of organic contaminants and pathogens in a range of ecosystems.

KRR

Seasons Greetings

"We wish you and your family a safe and happy holiday season"

From SWSD Faculty, Staff, and Students

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Emerging Contaminants of Concern

The public and scientific presses, the internet, and other forms of mass communication are awash with references to “emerging contaminants of concern” (ECCs). What are these contaminants, their sources, the sources of concern, and what is the Soil and Water Science Department doing about them?

Contaminants: The US Geological Survey (USGS) defines ECCs as “any synthetic or naturally occurring chemicals, or any microbe, that is not commonly monitored in the environment, but that has the potential to enter the environment and cause known or suspected adverse ecological and/or human effects.” Given this broad definition and modern analytical techniques, one can expect a wide diversity and huge number of substances to be labeled ECCs. Various lists of, and names for, ECCs exist and include substances such as pathogens, antibiotic resistant genes, prions, nanoparticles, pharmaceuticals and personal care products (PPCPs), endocrine disrupting chemicals (EDCs), flame retardants (e.g., polybrominated diphenyl ethers – PBDEs), hormones and anabolic steroids, perfluorinated chemicals (PFCs), etc. The chemicals are also referred to as microconstituents and trace organics. The potential list seems endless at times. Where have all of the substances come from, and is our civilization doomed to irreparable damage?

Sources: Few, if any, ECCs are actually new. Releases of ECCs are likely to have occurred for many years, but may not have been detected (nor their potential impact appreciated) until new detection (and impact assessment) methods were developed. Animal wastes, which can include numerous veterinary antibiotics, hormones, and various pathogens, have long been land applied. Human utilize an amazingly large array of personal care products (and pharmaceuticals) that have been marketed for many decades. Animal (including human) and plant hormone release to the environment is a natural part of life.

Most PPCPs and human hormones (e.g., microconstituents) are delivered to wastewater treatment plants and are effectively removed from influents by degradation and sorption to solids, or exit with effluent. A few chemicals are poorly removed, and some are actually produced (concentration increases in effluent from precursors). Properly treated effluent becomes “reclaimed water” for a variety of beneficial reuses (reducing freshwater demands). Digested solids from the plants often undergo additional treatment to become biosolids that are recognized as valuable soil amendments. Nature itself promotes antibiotic resistance among soil organisms as a survival mechanism against the numerous antibiotics produced by microbes as competition weapons (and that we “harvest” to ward off disease.)

All kinds of chemicals (inorganic and organic), microbes, and other “insults” have been added to the environment since time began. “Modern” civilizations add a dizzying array of new chemicals. Reclaimed water and biosolids, animal manures, numerous agricultural chemicals can contain EECs and pose risks to human and environmental health. History shows, however, that soils, aquatic systems, and humans are remarkably resilient, adaptive, and assimilative if the insults are managed. Minimize direct pollution of water bodies with “strong” (undiluted, or otherwise modified) wastes, apply wastes judiciously and appropriately (land application guidelines, best management practices) so as to not exceed system assimilative capacity, practice good personal hygiene (e.g., washing hands and food thoroughly), and use common sense (moderation in all things). For more information, contact George O’Connor at GAO@ufl.edu.

Mycoremediation of DDT-Contaminated Soil

The Organic Contaminant Analytical Research Laboratory (OCARL) currently has two toxic chemical degradation studies underway. The first one is the mycoremediation of DDT-contaminated soil from North Shore Restoration Area (NSRA) at Lake Apopka, near Orlando, FL. Natural attenuation rates of DDx (o,p'- and p,p'- isomers of DDT, DDE, and DDD) are slow in these soils. The chemical stability of these compounds may be a result of the low solubility combined with low activities of organisms capable of metabolizing the compounds, and low biological availabilities of the compounds. *In situ* bioremediation employing either indigenous or introduced microorganisms may provide an effective method at low cost for remediating this site. The general strategies to be investigated are mesocosms designed to stimulate aerobic pathways for DDx metabolism via: 1) biodegradation of contaminants by elimination of inhibiting factors to native fungal production of extracellular enzymes; and 2) application of mushroom agriculture waste or aqueous rinsates from non-native and native fungi, and 3) addition of substrates that enhance extracellular enzyme (e.g. laccase and peroxidase) production in the previously mentioned systems.

Aerobic mesocosm

Numerous wood-rot fungi are capable of degrading DDT, DDE, and DDD using non-specific extracellular lignin-degrading enzymes. A wood-rot fungi (*Nectria* sp.) isolated from NSRA muck soil has been shown to degrade DDT and its metabolites DDD and DDE. The use of filamentous fungi isolated from contaminated soil offers several advantages. In particular, the fungi are already adapted to the contaminant levels found in the soil and the fungi have already been shown to be competitive with the indigenous flora.

Fruiting bodies (~ 1 mm in size) of *Nectria* sp. fungus found in an aerobic mesocosm.

In addition to fungi from NSRA soil, other possibilities exist such as wood-rot fungi and their excreted enzymes obtained from commercial mushroom farms' waste material. One species of wood-rot fungi that is edible and produced commercially is *Pleurotus ostreatus*, commonly called the "oyster mushroom", which may be a candidate. *P. ostreatrus*, like the *Nectria* species, has been shown to biodegrade DDT. Another edible and commercially produced wood-rot species is *Agaricus bisporus*, commonly known as white button, Crimini, or Portobello mushroom. Although *A. bisporus* has not been reported as capable of degrading DDT, DDE or DDD, this species emits many of the same extracellular enzymes *as P. ostreatus*. The spent growing substrate is a waste material that contains these enzymes and spores from the mushroom. Land application of this waste material may lead to an inexpensive method of bioremediation.This project is being conducted by OCARL with guidance and funding from the St. Johns River Water Management District. For more information, contact John Thomas at Thomas@ufl.edu.

Congratulations!

Fall 2010 Graduates

BS

Scarlett Jacqueline Balboa
Juchan Choi
Jennifer Elizabeth Frey
Katlyn Beth Woodruff

MS

Miriam Githongo (Andy Ogram)
Jennifer Marriott (Amy Shober)
Jeff Van Treese (Yuncong Li & Kimberly Moore)
Stewart Whitney (Amy Shober)

PhD

Jaya Das (Samira Daroub & George O'Connor)
Jinghua Fan (Zhenli He & Lena Ma)
Yandi Fan (Rao Mylavarapu)
Ronald Gonzalez (Jerry Sartain)
Kim Haryun (Andy Ogram & Ramesh Reddy)

Welcome Incoming Students Spring 2011 !

PhD

Jeffery Van Treese (Yuncong Li)
Mriganka De (Gurpal Toor)

MS

Karen Balentine (Rex Ellis)
David Clark (Rex Ellis)
Bethzaida Colon (Gurpal Toor)
Benjamin Coppenger (John Thomas)
John Gum (Amy Shober)
Josefin Edeback (Gurpal Toor & Craig Stanley)
Shawn Jones (Gurpal Toor)
Sean Rochette (Rex Ellis)
Katlyn Woodruff (Mark Clark)

Potential Environmental Toxicity of Nanomaterials

Nanoparticles and nanomaterials have found broad application and are in common use in many products, although most of us probably don't realize it. Among the most common nanoparticles in use is nanosilver, used primarily for its anti-bacterial properties. A common use for nanosilver is incorporation into athletic clothing to suppress odors. The mode of action of nanosilver as an antibacterial agent is not completely clear, although it appears to destabilize cell membranes, resulting in cell death. Unintentional release of nanosilver from industrial sites into the environment might potentially disrupt a range of environmental processes mediated by resident soil bacteria, such that fundamental research is needed to investigate these potential impacts. Dr. Hee-Sung Bae of the Soil Microbial Ecology Lab has been investigating the potential impacts of nanosilver on anaerobic microbial communities in wetland soils, and has tentatively concluded that the potential for harm in these environments is low. Zimrisha Allah also worked with Dr. Bae on this project as part of her undergraduate capstone experience.

Nanosilver seems to be rapidly removed from contention by complexation with sulfide and perhaps other anions in wetland soils. Dr. Bae found no measureable effects of relatively high levels of nanosilver (up to 100 mg silver per gram of soil) on rates of methane or CO_2 emissions from soil. Dr. Bae also tested the impacts of nanosilver on methanogenic and fermentative bacteria in pure cultures, and again found no measureable response. We expected inhibition of growth rates with high concentrations of the toxic nanosilver, but found none. In addition, more subtle differences such as shifts in fermentation patterns in pure cultures of a fermentative bacterial strain were not detected. The lack of inhibition of bacterial activities in soils is not too surprising, although reassuring. The lack of inhibition of bacterial activities in pure cultures, however, is perplexing. Does this stuff not really work? Back to the lab. For more information, contact Andy Ogram at: aogram@ufl.edu

Carbonated Fumigant as Methyl Bromide Alternative

Tomato beds after fumigation and transplanting at UF Plant Science Education and Research Unit, Citra, FL

Methyl bromide is a pre-crop fumigant that destroys weeds, fungi, nematodes, and the ozone layer. It was to be phased out by 2005, except for critical use exemptions. Many alternatives have been put forth, but none are as economically effective. The UF Organic Chemical Analytical Research Laboratory (OCARL) will work in conjunction with University of California – Davis and USDA-ARS to demonstrate the viability of an alternative approach. Pressurized carbonated fumigant, with and without low permeability film, will be tested on different soil types in two states (FL and CA) with shallow rooting and/or deep rooting crops using either full field tarping or raised bed coverings. Multiple year field experiments are planned to quantify fumigant dispersion patterns and demonstrate efficacy of various treatments. These include using different types (virtually impermeable vs. new totally impermeable films) of plastic soil covers in combination with various application rates of Telone products applied with carbon dioxide or nitrogen. The UF OCARL group, along with the UF Entomology-Nematology Department and the USDA-ARS scientists, showed that a polar fumigant (Telone or Telone C35) is dispersed faster with a polar gas (carbon dioxide) than a non-polar gas (nitrogen). Carbonation in combination with low permeability films is expected to allow reduced application rates to be viable. Efficacy will be compared to control using a full rate of methyl bromide application. The expected outcome is an economically feasible alternative to methyl bromide that should reduce emissions, field buffer zones,

(Continued on page 5)

(Continued from page 4)
and the amount of fumigant needed per acre. The information generated will lead to training and adoption of new techniques for county extension agents, future scientists and educators, and other stakeholders such as growers.

This project is being conducted with funding from USDA-NIFA (formerly known as the USDA-CSREES Methyl Bromide Alternatives Program). For more information, contact John Thomas at Thomas@ufl.edu.

Of Chicks and Tomatoes: *Salmonella's* Coming of Age Short Story

Early this spring, one of the hens on my farm hatched a clutch of three adorable chicks. Lacking foul-naming imagination, I called the yellow fuzz balls Sal, Mona and Ella. The trio now has grown, developing into fairly unattractive birds with decidedly un-adorable habits. Sal, Mona and Ella wreak havoc in my yard by digging up mulch in flower beds, pecking at tomatoes in the vegetable garden and climbing into the fig bush to snack on the ripening fruit. As obnoxious as the three of them are, the damage they cause pales in comparison to the devastation to the Florida tomato industry caused by their name source: *Salmonella enterica* serovar St. Paul.

A multi-state outbreak of gastrointestinal illness a few years ago was initially blamed on tomatoes from Florida, bringing the industry to the brink of extinction. Consumers were advised not to buy tomatoes, whole-sale prices plummeted, farmers and processors were ridden by anxiety. The outbreak couldn't have happened at the worst time, as we were right in the middle of the busiest harvest time. Eventually, traceback investigations concluded that the source of the pathogen was imported hot peppers. Florida tomatoes were exonerated, just in time for producers to recoup some of their financial losses.

Unfortunately, the reports of gastroenteritis outbreaks linked to fruits and vegetables are becoming more and more common. Fresh fruits and vegetables, perhaps the most nutritious products at any supermarket, are now viewed with ever-growing suspicion. Scientists, producers and consumers need to find out what events lead to the produce-associated outbreaks of illness caused by *Salmonella* or pathogenic *E. coli*. With funding from Florida Tomato Committee, Center for Produce Safety and Florida Department of Agriculture and Consumer Services, our research group (in collaboration with researchers Drs. George Hochmuth, Jerry Bartz and Keith Schneider) contributes to figuring out what causes the outbreaks and finding the most sensible pro-active solutions to ensure microbiological safety of fresh fruits and vegetables.

So far it is clear that *Salmonella* and pathogenic *E. coli* can contaminate fruits and vegetables in the field, during harvest, after harvest and in retail. Improperly composted animal manure used as a fertilizer, animal intrusion, or contaminated irrigation water can all deposit pathogens in the field pre-harvest, and some eventually end up on produce. During harvest and immediately post-harvest, the contamination may become amplified, especially when workers' hygiene is not properly enforced. Supermarket surveys reveal that produce with visible signs of spoilage is most likely to also contain *Salmonella*, and these decaying fruits and vegetables can further contaminate nearby products. The results of these correlational studies are important because they allow producers and consumers to rapidly adjust practices for minimizing contamination, farm-to-fork. We are testing whether different fertilization and irrigation regimes can reduce the susceptibility of tomato fruits to contamination or transfer of the pathogens. We are also screening the existing commercial and heirloom cultivars to test if any is more or less "susceptible" to *Salmonella*. The results of these studies, we anticipate, will help develop comprehensive Best Agricultural Practices for reducing contamination of fresh produce with human pathogens. For more information, contact Max Teplitski at: maxtep@ufl.edu

Biosolids-borne Emerging Contaminants of Concern: Occurrence, Fate, and Impacts

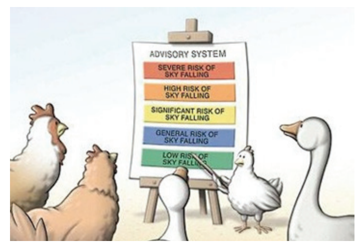
Modern science has produced innumerable products and medicines that improve our lives and provide many conveniences that we take for granted. Of the thousands of anthropogenic organic chemicals entering wastewater treatment plants every day, many (but not all) are effectively removed from waste influents (removal efficiencies vary from 10 to ~100%). Chemicals that are removed, but not degraded, accumulate in the solid phase (sewage sludge) at varying concentrations (μg/kg to high mg/kg values). About half of the 7 million dry tons of solids produced nationally are subsequently handled/processed to produce biosolids that are subsequently land-applied. To what extent should we worry about environmental and human exposure to biosolids-borne emerging contaminants of concern (ECCs)?

Numerous recent tabulations of ECC concentrations in biosolids, including the 2009 EPA Targeted National Sewage Sludge Survey, confirm wide variations in levels and frequencies of detection of compounds like pharmaceuticals, steroids, personal care products, and flame retardants even in domestic sewage sludges. Even more recent are troubling reports of perfluroinated chemicals accumulating in soils amended with biosolids (apparently, with significant industrial sources). Research interest in ECCs (aka. trace organics, microconstituents) is strong, given numerous reports of certain contaminants in various environmental components, as well as adverse effects on aquatic organisms (even at sub-part per billion concentrations) and soil organisms (plants, earthworms, micro-organisms), and possible unknown synergistic effects of the multiple ECCs introduced simultaneously .

Attitudes Towards Emerging Contaminants in Biosolids

It's all a bunch of hype!

- "pollutant du jour" syndrome
- WWTPs are very efficient and will degrade organics
- availability in biosolids is so low, and the concentration in biosolids-amended soil is so low, that there's nothing to worry about



The sky is falling!

- we're awash in evermore dangerous chemicals
- unknown toxicity, mutagenicity, carcinogenicity

Comparatively little research has focused the fate, transport, and potential impacts of ECCs, or groups of trace organics, in biosolids-amended soils. Often computer model predictions substitute for laboratory measurements or field confirmation of physical/chemical properties and estimates of human/environmental impacts (risk assessment). Few of the models, however, have been validated, especially for biosolids-borne trace organics applied to soils. Numerous data gaps exist that are pertinent and necessary for a scientifically sound risk assessment.

Our research program focuses on the risks of biosolids-borne ECCs, specifically, the antimicrobials triclosan (TCS) and triclocarban (TCC) that occur in toothpastes, soaps, shampoos and many other personal care products . We identify ECC occurrences, sources and typical concentrations in biosolids, possible fates of the compounds in biosolids-amended soils, and potential impacts of the chemicals on the environment and humans. Chemical principles learned through decades of research with pesticides and priority pollutants (e.g., PCBs, dioxins, PAHs) are likely applicable to trace organics. The research has shown that being biosolids-borne is likely to significantly alter (reduce) contaminant bioavailability to plants and micro-organisms, environmental lability and, ultimately, risk to the environment and humans. Much is known about biosolids-borne contaminants and extensive risk assessment has been conducted on many biosolids-borne contaminants, but there is much yet to be learned. Such knowledge will be critical to science-based regulations and to better inform attitudes toward risks to human and environmental health. For more information, contact George A. O'Connor at: gao@ufl.edu

Natural Organic Matter Sorption onto a Range of Laboratory-produced Biochars

An investigation was conducted to understand the nature and mechanism of interactions of natural organic matter with pyrogenic organic matter (biochar). The research goal was to understand how biochar soil amendments could increase soil quality, C sequestration and possible retention of organic contaminants. The study examined the interaction of catechol and humic acids with biochars pyrolyzed under a range of combustion conditions (250 to 650 ^{o}C) from hardwood, softwood and grass biomass types, using batch sorption equilibrium experiments with catechol (a natural OM monomer) and a humic acid mixture. The effects of biochar size (coarse vs. fine) and laboratory simulation of biochar aging on the sorption affinity of biochar were also investigated.

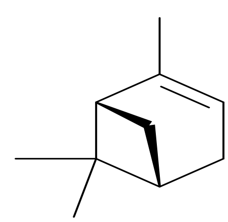
Time-course sorption experiments indicated that 14 days were sufficient to establish sorption pseudo-equilibrium and that among the three kinetics models tested, the diffusion model fit the data best. Maximum observed catechol sorption increased with biochar combustion temperature, from 250 to 400 to 650 $^{\circ}$C, and from oak to grass. The results of this study indicated strong correlation between catechol sorption affinity and micropore surface area and the dominance of a surface coverage adsorption process for catechol-biochar interaction. In contrast, humic acid sorption capacity was much lower and only within nanopores, indicating exclusion from the majority of biochar surfaces. The results suggest that biochar sorption is controlled by surface morphology, chemistry, and sorbent molecular size. In general, one can expect biochar added to soil to sequester large amounts of natural OM within its pore network. In addition, these results are of practical value to those considering biochar as a tool for soil remediation for trace organic contaminants. The research findings have been published in ES&T, 2010.

The research was conducted by Gabriel Kasozi (former SWSD PhD student) and now a post-doctoral research associate under Dr. Andrew Zimmerman (PI) from the Geological Sciences Dept., and other collaboration from Dr. Peter Nkedi-Kizza (SWSD) and Dr. Bin Gao (Agricultural and Biological Engineering Dept.). For more information, contact Kizza@ufl.edu.

Degradation Pathway of (-)-(α)-Pinene

TSQ Quantum Discovery Max LC-MS/MS

The second degradation study is on the degradation pathway of (-)-(α)-Pinene. The Organic Chemical Analytical Research Laboratory (OCARL) is providing liquid chromatagraph-tandem mass spectrometry (LC-MS/MS) technical training and support to Dr. Angela Lindner and Joonki Yoon of the UF Environmental Engineering Sciences. (-)-(α)-pinene was chosen as a typical model compound to study the biotransformation products of monoterpenes, which are volatile non-methane organic compounds generated by agricultural crops and forests. Globally, the biogenic production of these compounds exceeds the anthroprogenic sources. Monoterpenes inhibit ammonia monooxygenase , an important enzyme used in the nitrification process. Methane monooxygenase is very similar in structure to ammonia monooxygenase and suffers from many of the same inhibitors. Since methane monoxygenase plays an essential role in the activity of methanotrophs, an investigation into the binding of monoterpene and its oxidation products to the active sites of the enzyme was initiated. Elucidation of the oxidation mechanism of these ubiquitous monoterpenes will further our understanding of methanotroph's role in the global carbon cycle and in bioremediation efforts.



(-)-(α)-pinene

For more information, contact John Thomas at Thomas@ufl.edu.

Faculty, Staff, and Students

Congratulations to the following for their accomplishments

Scholarships

Ben Skulnick Fellowship - **Luke Gommermann** (Ellis)

Sam Polston Scholarship - **Davie Kadyampakeni** (Morgan & Kizza) & **Debolina Chakraborty** (Nair)

William Roberton Scholarhsip - **Lisa Gardner** (Reddy) & **Jason Lessl** (Ma)

UF GIS Day

Jongsung Kim (Grunwald)- First Place Poster

Soil Science Society of America

Jaya Das (Daroub & O'Connor) – Third Place Poster - S-10 Division

Xiong Xiong (Grunwald) - Third Place Poster Paper - S-5 Division

Alex Cheesman (Reddy & Turner) – First Place - S-10 Division

Society of Wetland Scientists

Lisa Gardner – Honorable mention for best poster

American Society Agronomy

Manmeet Waria (O'Connor & Toor) – First Place Poster Paper -A-5 Division

Gustavo Vasques - Nominated for Best Paper: Global Workshop on Digital Soil Mapping - Pedometrics, Rome, Italy, May 24-26, 2010

Brent Myers received newly established 'Quantitative Soil Science/Pedometrics Award" by the GIS Laboratory of the SWSD

SWSD Superior Accomplishment Award - **Michael Sisk**

Retirement – **Pete Straub** – 37 years of service ARL/ ESTL and Soil Chemistry program

Biodigestion, Sanitation, and Public Health in Developing Countries

Clean drinking water and proper sanitation techniques are vital to controlling the spread of disease. In developing countries, improper waste management is a common problem. Inadequate sanitation leads to the propagation of water borne diseases and promotes pathogen proliferation. These problems are exacerbated following natural disasters like the recent earthquake in Haiti or the flooding in Pakistan, with poor sanitary conditions in emergency/ refugee camps leading to increased risk of disease epidemics and death due to dehydration and diarrhea.

Anaerobic digestion technology offers a wastewater treatment solution that is inherently capable of significant pathogen reduction for a wide variety of organic wastes, including human waste and animal manure. The microbial ecology within an anaerobic digester effectively lowers pathogen levels. Competition with the established digester microflora leads to pathogen decimation.

Biodigester under construction in Pursat, Cambodia.

The Bioenergy and Sustainable Technology Laboratory is working on the design of a digesting toilet as a pre-fabricated kit that can be quickly deployed for use in natural disaster situations. Design parameters include easy deconstruction and reconstruction, and use of off-the-shelf materials and basic tools. This will be an important device not only for the victims of natural disasters, but also for first responders that find themselves lacking all basic services while trying to provide life saving attention to the victims.

In a related project with the UF Chapter of Engineers Without Borders, Ann Wilkie and students recently conducted an assessment trip to Cambodia. Rural Cambodia experiences many of the same problems that other remote and impoverished areas in the developing world face. The team worked with a locally-based NGO, Sustainable Cambodia, to evaluate the water, sanitation, and energy needs of their partner rural villages. They found that while many projects were being promoted for sanitation, clean water, and biogas, there was untapped potential for integrating sanitation with digestion technology. If an effective latrine system were designed and implemented, it would help reduce open defecation, which exposes water supplies to pathogens, and provide feedstock for anaerobic digestion. Human waste, mixed and treated in the digester with cattle and pig manure, could provide biogas for cooking and a safe organic biofertilizer to recycle valuable nutrients back to rice fields. Also, if clean water can be stored in the wet season, families that cannot afford deep wells will not have to rely on distant, polluted water sources during the dry season for drinking, cooking, and irrigation of small family gardens. The team is continuing to develop sustainable solutions to address these problems and help to improve the quality of life in rural Cambodia. For more information, visit Biodigesters for Developing Countries or contact Ann Wilkie at acwilkie@ufl.edu.