MIT CEHS Center for Environmental Health Sciences

NEWSLETTER

Supported by NIH NIEHS Core Center Grant P30-ES002109

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Fall/Winter 2014/2015

Characterizing the Composition and Variability of Particulate Emissions from Cookstoves, in Real-time

Article by Dr. Eben Cross of the Kroll Lab

This past summer, an inter-disciplinary team of researchers from MIT and Lawrence Berkeley National Laboratory combined forces to complete one of the most comprehensive, chemically detailed, real-time characterization studies of particulate emissions from biomass cookstoves, to date. The team, led by Dr. Eben Cross (a research scientist in Professor Jesse Kroll's group in Civil and Environmental Engineering) and Dr. Dan Sweeney (a research scientist with the MIT D-Lab) combined expertise in experimental atmospheric chemistry, alternative biofuel production, and improved cookstove design to improve our understanding of the amounts, chemistry, and variability of cookstove emissions.

Solid fuel combustion represents a major public health risk globally: more than three billion people rely on biofuels (wood, agricultural residue, charcoal, and dung) to heat their homes and cook their food, exposing families (especially women and children) to extremely high concentrations of indoor toxics. These include both particulate matter (smoke) and gas phase pollutants (e.g. carbon monoxide), whose indoor concentrations throughout the developing world often exceed health standards by an order of magnitude or more. The resultant global health burden associated with cooking emissions is estimated at 3.5 million premature deaths each year, making it the third-largest risk factor for premature death globally. However, the detailed health effects remain highly uncertain, largely because cookstove emissions (amounts, chemical composition, and variability) remain poorly characterized. An improved understanding of such emissions is especially critical for assessing the benefits of various "interventions", such as improved cookstoves and adoption of alternative fuels.

This CEHS pilot study took place in Professor Ashok Gagil's state-of-the-art cookstove testing laboratory within LBNL's Environmental Energy Technologies Division. Highly time-resolved measurements (every ~30s) of particle chemistry (made with a Soot-Particle Aerosol Mass Spectrometer (SP-AMS) from Aerodyne Research, Inc.) and size were captured across a range of controlled laboratory conditions systematically varying key combustion parameters including fuel type, cookstove design, and ignition source. Results from a sample burn are shown in Figure 2. This experiment involved the combustion of Ugandan charcoal produced from agricultural crop residues and char-dust collected in the charcoal markets. The burn consisted of a 'cold start' phase bringing an initial pot of water to boil followed by agitation of the hot

Figure 1. Photo of a traditional three stone fire. During each wood-burning experiment, wood is continually added to the fire to heat 2kg of water from room temperature to boil. The orange hue of the flame front is indicative of the production of black carbon (or soot) particulates emitted in the ultra-fine particle size mode (<100nm in diameter).

coals and then completed with a hot-start, bringing a fresh pot of water to boil. In this way, the experiment was designed to mimic basic in-use patterns for families that cook with charcoal fuels. The concentration and chemistry of par-

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Funding Opportunities

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J-WAFS Request for Proposals due March 18, 2015

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CEHS Pilot Project Call to be issued in February 2015

Upcoming Events

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David Schauer Lecture to be held on **March 19, 2015**

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Gerald Wogan Lecture to be held on **April 2, 2015**

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CEHS Poster Session to be held on **May 6, 2015**

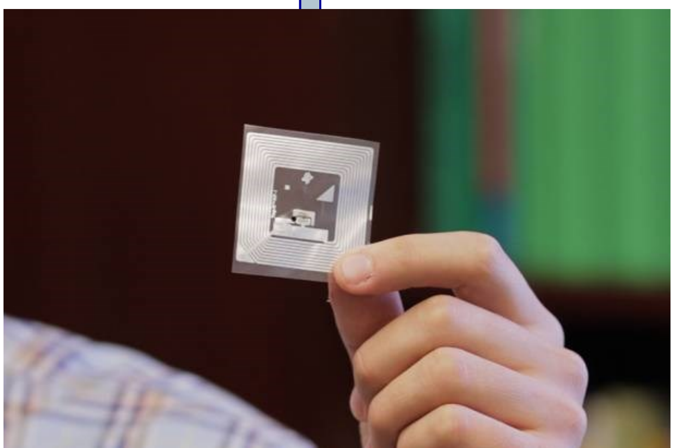
Detecting Gases Wirelessly and Cheaply

New senor can transmit information on hazardous chemicals or food spoilage to a smartphone

Article by MIT News Office, Ms. Anne Trafton

MIT chemists have devised a new way to wirelessly detect hazardous gases and environmental pollutants, using a simple sensor that can be read by a smartphone.

These inexpensive sensors could be widely deployed, making it easier to monitor public spaces or detect food spoilage in warehouses. Using this system, the researchers have demonstrated that they can detect gaseous ammonia, hydrogen peroxide, and cyclohexanone, among other gases.



The MIT researchers' wireless chemical sensor.

Photo: Melanie Gonick

"The beauty of these sensors is that they are really cheap. You put them up, they sit there, and then you come around and read them. There's no wiring involved. There's no power," says Timothy Swager, the John D. MacArthur Professor of Chemistry at MIT. "You can get quite imaginative as to what you might want to do with a technology like this."

Swager is the senior author of a paper describing the new sensors in the *Proceedings of the National Academy of Sciences* the week of Dec. 8. Chemistry graduate student Joseph Azzarelli is the paper's lead author; other authors are postdoc Katherine Mirica and former MIT postdoc Jens Ravnsbaek.

Versatile gas detection

For several years, Swager's lab has been developing gas-detecting sensors based on devices known as chemiresistors, which consist of simple electrical circuits modified so that their resistance changes when exposed to a particular chemical. Measuring that change in resistance reveals whether the target gas is present.

Unlike commercially available chemiresistors, the sensors developed in Swager's lab require almost no energy and can function at ambient temperatures. "This would allow us to put sensors in many different environments or in many different devices," Swager says.

The new sensors are made from modified near-field communication (NFC) tags. These tags, which receive the little power they need from the device reading them, function as wirelessly addressable barcodes and are mainly used for tracking products such as cars or pharmaceuticals as they move through a supply chain, such as in a manufacturing plant or warehouse.

NFC tags can be read by any smartphone that has near-field communication capability, which is included in many newer smartphone models. These phones can send out short pulses of magnetic fields at radio frequency (13.56 megahertz), inducing an electric current in the circuit on the tag, which relays information to the phone.

To adapt these tags for their own purposes, the MIT team first disrupted the electronic circuit by punching a hole in it. Then, they reconnected the circuit with a linker made of carbon nanotubes that are specialized to detect a particular gas. In this case, the researchers added the carbon nanotubes by "drawing" them onto the tag with a mechanical pencil they first created in 2012, in which the usual pencil lead is replaced with a

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compressed powder of carbon nanotubes. The team refers to the modified tags as CARDs: chemically actuated resonant devices.

When carbon nanotubes bind to the target gas, their ability to conduct electricity changes, which shifts the radio frequencies at which power can be transferred to the device. When a smartphone pings the CARD, the CARD responds only if it can receive sufficient power at the smartphone-transmitted radio frequencies, allowing the phone to determine whether the circuit has been altered and the gas is present.

See the new sensor in action, as it is wirelessly transmits data on chemicals to a smartphone. To view the video, please click here: http://youtu.be/n_-Gxtiqf7E

Video: Melanie Gonick

Current versions of the CARDs can each detect only one type of gas, but a phone can read multiple CARDs to get input on many different gases, down to concentrations of parts per million. With the current version of the technology, the phone must be within 5 centimeters of the CARD to get a reading, but Azzarelli is currently working with Bluetooth technology to expand the range.

Widespread deployment

The researchers have filed for a patent on the sensing technology and are now looking into possible applications. Because these devices are so inexpensive and can be read by smartphones, they could be deployed nearly anywhere: indoors to detect explosives and other harmful gases, or outdoors to monitor environmental pollutants.

Once an individual phone gathers data, the information could be uploaded to wireless networks and combined with sensor data from other phones, allowing coverage of very large areas, Swager says.

The researchers are also pursuing the possibility of integrating the CARDs into "smart packaging" that would allow people to detect possible food spoilage or contamination of products. Swager's lab has previously developed sensors that can detect ethylene, a gas that signals ripeness in fruit.

"Avoiding food waste currently is a very hot topic; however, it requires cheap, easy-to-use, and reliable sensors for chemicals, e.g., metabolites such as ammonia that could indicate the quality of raw food or the status of prepared meals," says Wolfgang Knoll, a managing director of the Austrian Institute of Technology, who was not part of the research team. "The concept presented in this paper could lead to a solution for a long-lasting need in food quality control."

The CARDs could also be incorporated into dosimeters to help monitor worker safety in manufacturing plants by measuring how much gas the workers are exposed to. "Since it's low-cost, disposable, and can easily interface with a phone, we think it could be the type of device that someone could wear as a badge, and they could ping it when they check in in the morning and then ping it again when they check out at night," Azzarelli says.

The article can be found here: http://newsoffice.mit.edu/2014/wireless-chemical-sensor-for-smartphone-1208

The video can be viewed here: http://youtu.be/n_-Gxtiqf7E

MIT CEHS

Study Details a Link between Inflammation and Cancer

Timing of inflammation determines whether potentially cancerous mutations may arise.

Article by MIT News Office, Ms. Anne Trafton

A new study from MIT reveals one reason why people who suffer from chronic inflammatory diseases such as colitis have a higher risk of mutations that cause cancer. The researchers also found that exposure to DNA-damaging chemicals after a bout of inflammation boosts these mutations even more, further increasing cancer risk.

The findings confirm a longstanding theory about why inflammation and cancer are linked, and offer possible ways to help prevent and treat cancer, says Bevin Engelward, an MIT professor of biological engineering and senior author of a Jan. 15 *PLoS Genetics* paper describing the findings.

"Chronic inflammation drives a lot of cancers, including pancreatic, esophageal, liver, and colon cancers," says Engelward, who is also deputy director of the MIT Center for Environmental Health Sciences. "There are things that people with chronic inflammation could do to avoid exposures that would be problematic for them. For example, certain foods lead to DNA damage and could be avoided."

The paper's lead author is former MIT postdoc Orsolya Kiraly. Other authors are postdoc Guanyu Gong, former postdoc Werner Olipitz, and Sureshkumar Muthupalani, chief of comparative biology in MIT's Division of Comparative Medicine.

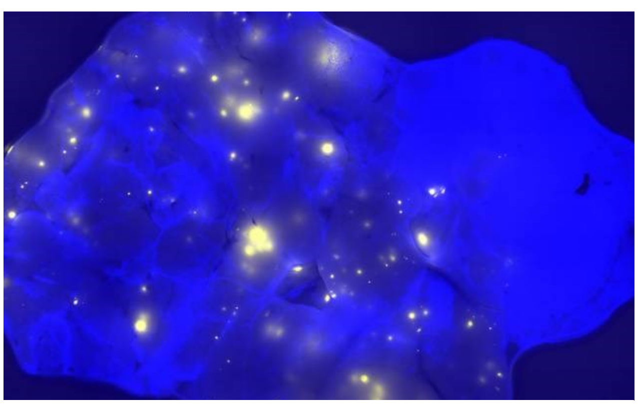

Figure 1. In this pancreatic tissue sample, bright spots represent cells that have undergone a specific genetic alteration.

Image: Orsolya Kiraly

Timing is everything

Inflammatory diseases such as colitis, pancreatitis, and hepatitis have been linked to greater risk for cancer of the colon, pancreas, and liver. In these chronic inflammatory diseases, immune cells produce highly reactive molecules containing oxygen and nitrogen, which can damage DNA. Inflammation also stimulates cells to divide.

Biologists had theorized that simultaneous DNA damage and cell division during inflammation could lead to cancer because dividing cells are more vulnerable to mutations caused by DNA damage. However, until recently it was difficult to test this hypothesis in animals under physiologically relevant conditions.

"You have to have the right set of tools, and they just weren't available before," says Engelward, who is also a member of the Singapore-MIT Alliance for Research and Technology (SMART). "You need to control inflammation onset, you have to have markers for DNA damage that you can see in the tissue, and you need a readout for mutation that you can see in the tissue."

Before this study began, Engelward and her students engineered a mouse that allows them to track DNA mutations. Whenever a certain class of mutations occurs in the pancreas, the cell with the mutation fluoresces, allowing it to be seen with a standard microscope. Using this model for mutation detection, researchers induced inflammation in the pancreas and found that the amount of mutation depends on the timing of bouts of inflammation.

When the inflammation occurred in short bursts a week or more apart, the researchers did not see any evidence of increased mutations. However, when the bouts occurred within a few days of each other, there was a significant increase in mutations.

Further studies in the pancreas revealed that inflammation-provoked cell division does not start happening until several days after inflammation begins, while most of the DNA damage occurs right away. This DNA damage is repaired fairly easily without causing potentially cancerous mutations. However, if another bout of inflammation induces DNA damage at a time when

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cells are dividing due to the previous bout of inflammation, many mutations appear.

This delay between DNA damage and cell division likely serves as a defense mechanism against mutations from acute bouts of inflammation. However, this defense breaks down when the inflammation occurs soon after the original flare-up or is sustained for a long time.

"That means the model that's been around for a long time is accurate, because you do get synergy between cell division and inflammation-induced DNA damage, but in these studies there was only a mutation risk if there is chronic or repeated inflammatory responses," Engelward says.

The effect in humans could be even more dramatic because many people suffer from chronic inflammation that goes on for years, she says.

Too much DNA damage

In a second set of experiments, the researchers studied the effects of exposure to an alkylating agent similar to those found in food, cosmetics, environmental pollutants, and certain cancer chemotherapy drugs.

Alkylating agents cause damage to DNA, which cells are usually able to repair. However, if too much occurs, alkylated DNA bases lead to mutations that can cause a cell to become cancerous. Engelward and Kiraly suspected that alkylation-induced mutations would accumulate at a much faster rate in inflamed tissue, where cells are dividing rapidly, than in healthy tissue. This turned out to be exactly what happened.

"These findings suggest that chronic inflammation potentially results in increased DNA damage and proliferation that together can conspire to increase the chance of cancer formation," says Peter McKinnon, a professor of genetics and tumor cell biology at St. Jude Children's Research Hospital who was not part of the research team.

This discovery suggests that people with chronic inflammatory diseases, which are common, may be more sensitive to carcinogens in the air, food and water. Also, developing fetuses and very young children may also be more sensitive to these agents because their cells are dividing more rapidly, Engelward says. Another new study from the Engelward laboratory, published in the journal *Carcinogenesis*, shows that animals treated with a growth-inducing hormone are more susceptible to damage-induced mutations.

"A lot of what we do for safety evaluation is based on adults, and not … during development. The conditions are really very different. Our findings are consistent with studies done in the MIT laboratories of John Essigmann and Gerald Wogan showing that there is a critical 'window of susceptibility' to DNA damage-induced mutations during development. I'm hoping that studies like these will help to call attention to the importance of analyzing mutation susceptibility during development," Engelward says.

The findings could also have implications for cancer treatment, because many chemotherapy drugs work by damaging DNA. Cancer cells divide frequently, making them more susceptible to mutations, which can help them to survive chemotherapy because some of those mutations confer drug resistance. The new results offer support to the idea that increasing the toxicity of DNA-damaging chemotherapy by novel drug combinations can make cancer chemotherapy more effective by suppressing evolution of the tumor, Engelward says.

While this study focused on the pancreas, Engelward's lab now investigates mutations in the colon and the lung using a new version of the engineered mice described in another recent paper in *PLoS Genetics*. Using the newly developed mice it is now possible to study mutations in virtually any tissue and to learn about how infectious diseases impact mutations. "Our fundamental advances in our understanding of inflammation and mutations form the basis for our ongoing studies of inflammation of the lung caused by infections, such as influenza and S. pneumoniae," says Engelward.

These studies were supported by the National Institute of Environmental Health Sciences with additional support from the Singapore-MIT Alliance for Research and Technology and the Austrian Academy of Sciences.

The article can be found here: http://newsoffice.mit.edu/2015/link-between-inflammation-and-cancer-0115

MIT CEHS COE^{2}C Aids Communities in Gaining Public Access to the Malden River by Working to Improve Water Quality

By Dr. Kathleen Vandiver, CEHS COE^{2}C Director

The Malden River, a tributary of the Mystic River that runs through Boston, is bordered by three towns: Medford, Malden, and Everett. All three towns considered creating a public boating area for family use but no town has undertaken this project, fearing that they might be liable should a health risk be present. Thus, a human health risk assessment for the Malden River seems necessary before progress can be made. Additionally, there is only one short strip of land along the river that is zoned for public access. Clearly, greater public access to the waterway is warranted. The MIT CEHS COE^{2}C Director, Dr. Kathy Vandiver, has been an active member of the Friends of the Malden River (FoMR) for more than a year. The parent organization for FoMR is the Mystic River Watershed Association (MyRWA) and it was established in 1972 to protect and restore the Mystic River, one of three large rivers that empty into the Boston Harbor. The Mystic River watershed includes three superfund sites and several environmental justice communities. Thus the Friends of the Malden River have to contend with the century-old chemical industry contamination sites and aging wastewater systems.

Learning firsthand about the conditions of the Malden River for boating, COE^{2}C Director Kathy Vandiver paddles the length of the river on August 31, 2014. Paved industrial parking lots just behind the trees in the photo contribute to contaminant run-off issues.

In February 2014, two organizations asked MIT CEHS for help, the Friends of the Malden River (FoMR) and the Tri-City Community Action Plan (Tri-Cap) a community assistance organization for immigrants and low income families. Therefore, the CEHS COE^{2}C recruited CEHS toxicologists to advise and select the most cost effective proposal from several environmental firms that were solicited for a health risk study of the Malden River. We also attended the initial meetings with the chosen environmental firm. Then when the prerequisite funding for the project wasn't available, COE^{2}C proposed a candidate project for a team of MIT students. They would conduct the preliminary research that would help to determine whether the river's contaminates posed a significant health risk for recreational boating on the Malden River. Three MIT graduate environmental engineering students and two undergrads are currently working on this team project, guided by Professor Harold Hemond from CEHS and Dr. David Langseth, and by Dr. Vandiver in matters related to the community relations.

Three MIT students from the Civil and Environmental Engineering Department's Masters in Engineering program present their preliminary proposals for the team project on Malden River, October 17, 2014

To help the students connect with the residents in Medford, Malden, and Everett, COE^{2}C director Dr. Vandiver offered transportation to evening FoMR meetings, and she introduced the team to numerous locals, including townspeople, town mayors, local watershed associations' staffers, Malden River Development Corporation presenters, as well as Army Corps of Engineers personnel and involved in river restoration. In November 2014, Dr. Vandiver also arranged for guided tours of Malden River backwaters with the long-time river aficionado, patrolman Patrick Johnston from the Everett Police Force to provide a historical perspective on the community. The students' research proposals were finalized in December 2014 and their work will be completed by May 2015. Additionally, the MIT's Department of Civil and Environmental Engineering Master's Program offered that the department would be interested in annually continuing this partnership with CEHS.

The COE^{2}C is pleased to learn of the increased interest of MIT environmental engineering faculty, since we know that public access to the Malden River is an example of environmental justice issue that will take some time to rectify. Brownfield areas near the riverbanks have remained fenced for years. Providing open spaces for public use and natural habitats for wildlife will invite families to exercise and recreate together, thus inspiring people to lead healthier lives. This is especially true of people living in communities with environmental justice issues who already are burdened with many challenges, economic and social. COE^{2}C agrees with the World Health Organization. Good health is much more than the absence of disease.

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ticulate matter (PM) in the emissions is shown in the middle panel of the figure (for comparison, the average $PM_{2.5}$ concentrations in Cambridge are < 10 μg/m^3, whereas the organic PM emissions during the cold start from this single burn are 1000 μg/m^3); the particles are mostly organic, though inorganic species (chloride as well as sulfate) are also important.

Black carbon ("soot") is a relatively small (but non-negligible) fraction of the total PM from charcoal combustion. The combination of these real-time mass concentration measurements with the fuel consumption rate (charcoal mass (displayed in the top panel) provides the data necessary to calculate time-dependent emission factors for each chemical component (mg of PM emitted per mass of fuel combusted). The high time resolution of the measurements reveal important features of the emission profile of the burn. These include the relatively invariant ratio of organics and black carbon (BC) throughout, other than the initial spike in BC upon ignition; the large spikes in PM (especially inorganics) with addition/agitation of the hot coals; and the wide variability of the fuel consumption rate (spanning factors of ~2) and particulate emissions (100-fold increases at different stages of the burn), even in the absence of changes to the stove or fuel.

The burn test shown in Figure 2 is only a single burn, out of a total of 55 performed: experiments included 15 burns with wood fuel (3 different stoves, 5 trials each), 15 with charcoal fuel (3 different charcoal types, 5 trials each), 20 with different ignition sources, and 5 with different wood types (smoldering only). Thus an extremely large dataset was collected, and analysis is still underway. Some key results from comparing different burn conditions include: improved cookstoves do indeed emit lower levels of PM than traditional ones (especially after the initial ignition), but the use of charcoal fuel decreases emissions by a still larger factor; wood fuel emits much higher levels of BC (in both an absolute and a relative sense) than charcoal fuel; the majority of PM emissions for improved cookstoves and charcoal fuel arises from not only ignition but also agitation/addition of fuel; and a large fraction of PM mass is present as ultrafine particles, which most conventional PM instruments do not detect (implying that most estimates of PM exposure from cookstove use are likely to be biased low).

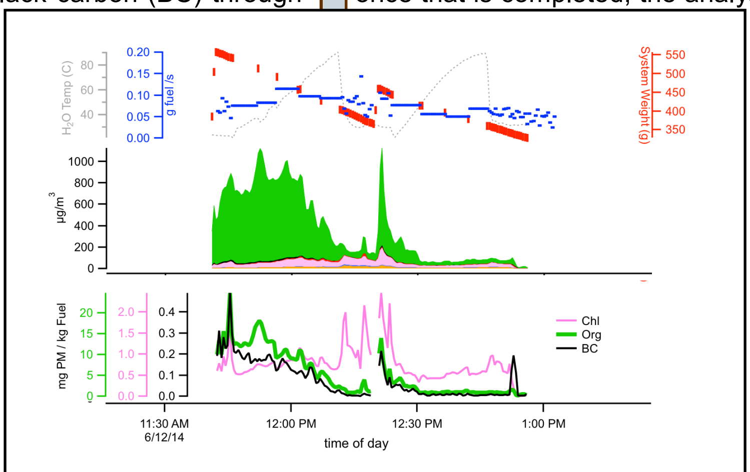

Figure 2. Sample PM emissions data from a charcoal burn. Top Panel: Combustion parameters - H2O temp, fuel mass, fuel combustion rate. Middle Panel: Absolute mass concentration of key PM species - **organics, black carbon**, **chloride**. Lower Panel: Real-time emission indices (mg pollution emitted/kg fuel burned) for different chemical constituents of the PM.

It should be noted the data collected includes a substantial amount of chemical information not illustrated in Figure 2; a high-resolution mass spectrum was collected by the SP-AMS at least every minute, providing detailed information on the chemical composition of the organic fraction of the PM. Most important is the evolving concentrations and identities of major polycyclic aromatic hydrocarbons (PAHs, known mutagens and carcinogens) in the PM; other parameters include the relative contributions of oxygenates vs. hydrocarbons and aliphatic vs. aromatic species. Extracting such chemical information from the mass spectra is currently the focus of our data analysis; once that is completed, the analysis will shift to quantifying variability (within a single burn and among identical burns) in all the parameters measured: rate of PM emissions, chemical composition of the emissions, and effects of external activities (method of ignition, addition of fuel, agitation of the fuel or cooking vessel, etc.).

The dataset collected as part of this project is unique, in terms of the high time resolution of the measurements made, the chemical information collected, and the number of combustion parameters varied. To our knowledge, emission factors have not been previously measured with this sort of time resolution, nor with any chemical information (let alone both). Further, variability of emissions (within and among burns) has never been quantified. We thus anticipate such measurements will be of great value for improving estimates of exposures to toxics emitted from cookstoves, as well as for devising effective mitigation strategies.